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Light scattering and microcalorimetry studies on aqueous solutions of thermo-responsive PVCL-*g*-PEO copolymers

Sam Verbrugghe[a], Antti Laukkanen[b], Vladimir Aseyev[b,1], Heikki Tenhu[b], Françoise M. Winnik[c], Filip E. Du Prez[a,*]

[a]*Department of Organic Chemistry, Polymer Chemistry Division, Ghent University, Krijgslaan 281, S4-bis, B-9000 Gent, Belgium*
[b]*Laboratory of Polymer Chemistry, University of Helsinki, PB 55, FIN-00014 HY, Helsinki, Finland*
[c]*Department of Chemistry and Faculty of Pharmacy, Université de Montréal, CP 6128 Succursale Centre-ville, Montréal, QC, Canada H3C 3J7*

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Abstract

Dilute aqueous solutions of thermo-responsive poly(*N*-vinyl caprolactam)-*graft*-polyethylene oxide (PVCL-*g*-PEO) copolymers were studied by light scattering and high sensitivity differential scanning microcalorimetry. These copolymers are double hydrophilic at low temperatures, but become amphiphilic upon heating the solutions above the cloud point temperature of the PVCL segments (T_{CP}). The self-assembly properties of the copolymers are investigated by dynamic light scattering as a function of the temperature, degree of grafting and concentration. It was found that a certain critical polymer concentration is needed for the polymers to form stable aggregates. These structures are expected to consist of a hydrophobic PVCL core, stabilized by a hydrophilic PEO shell. The size of these aggregates increases with the degree of grafting. Microcalorimetry results revealed that the grafting of PVCL with hydrophilic PEO does not influence the phase transition enthalpy of PVCL.

Keywords: Poly(*N*-vinyl caprolactam); Light scattering; Microcalorimetry

1. Introduction

The self-assembling of amphiphilic copolymers in aqueous solutions has recently attracted considerable attention from both academy and industry [1–3]. These copolymers, consisting of hydrophilic and hydrophobic parts, are known as macro-surfactants. Both amphiphilic block and graft copolymers have shown interesting solution properties. In several cases, poly(ethylene oxide) (PEO) was chosen as a hydrophilic segment because of its biocompatibility [4,5]. For example, PEO containing macro-surfactants have been explored as vehicles in drug delivery systems [6].

In particular, the thermo-responsive micellization of copolymers has gained keen attention [7]. Thus, thermo-responsive polymers showing a lower critical solution temperature (LCST) in water have been combined with a hydrophilic segment in order to trigger the self-assembly as a function of temperature. Below the critical temperature, often referred to as the cloud point temperature (T_{CP}), the thermo-responsive segment behaves as a hydrophilic polymer and the overall copolymer is double hydrophilic. Upon heating above T_{CP}, the thermo-responsive polymer segment undergoes dehydration, the polymer coil shrinks and tends to precipitate. Under these conditions, the copolymer becomes amphiphilic, with the hydrophobic units forming a core, stabilized by a hydrophilic corona [8,9].

Temperature controlled micellization behavior has been reported for block and graft copolymers of poly(*N*-isopropylacrylamide) (PNIPAAm) and PEO. Qiu et al. investigated the formation of a core-shell structure of aggregates and of single chains having a thermo-responsive PNIPAAm core shielded by a PEO shell [8]. Recently, Virtanen et al. reported studies on the influence of the number of PEO grafts on the aggregation of PNIPAAm-*g*-PEO [10,11].

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[*] Corresponding author. Tel.: +32-9-264-45-03; fax: +32-9-264-49-72. *E-mail address:* filip.duprez@ugent.be (F.E. Du Prez).

[1] Permanent address: Institute of Macromolecular Compounds, Russian Academy of Science, Bolshoi Prospect 31, 199004, St Petersburg, Russia.

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In the present study, poly(*N*-vinyl caprolactam) (PVCL) was used as a thermo-responsive polymer with a LCST behavior around the physiological temperature [12]. It is also known for its biocompatibility and, as a result, for its promising bio-medical applications [13].

Solution properties of LCST polymers can be monitored with several methods. FTIR [14,22] as well as NMR spectroscopy [15,16] has been utilised to study temperature-dependent hydration of water-soluble polymers. However, these methods deal with rather concentrated solutions. High sensitivity differential scanning calorimetry (HSDSC) brings new knowledge of the dehydration of the polymer chain during the phase transition in very dilute solutions. Combination of the HSDSC method with light scattering (LS), working in the same range of polymer concentrations, gives deeper insight on the solution properties of the polymers under investigation. Studying the same concentration range is especially important for PVCL, while its cloud point is highly dependent on polymer concentration [17]. Combination of HSDSC and LS also allows one to verify the causal connection between the dehydration and the aggregation of the polymer chains.

Elsewhere, we described the synthesis and emulsifying properties of graft copolymers based on PVCL [18]. The copolymers have been constructed from a PVCL backbone and either hydrophilic PEO or hydrophobic PTHF side chains. The thermal properties of their aqueous solutions were studied by turbidimetry measurements and compared to the corresponding ternary solutions and segmented polymer networks. It was shown that the phase behavior of PVCL is strongly affected by the nature of the grafts and especially by the degree of grafting.

The aim of this study is to investigate the solution properties and self-assembly of PVCL-*g*-PEO copolymers by LS and HSDSC. The influence of the degree of grafting on the particle size of the aggregates will be described as a function of temperature.

2. Experimental

2.1. Polymer synthesis

The PVCL-*g*-PEO copolymers have been synthesized using a grafting onto method. The detailed procedure is described elsewhere and therefore only briefly summarized here [18]. A PVCL backbone with reactive functional groups (PVCL-*co*-NASI) was prepared by the radical copolymerization of VCL and a small amount of *N*-acryloylsuccinimide (NASI). These succinimide groups react easily with a primary amine, such as amino terminated PEO ($M_w = 5000$). Different amounts of PEO were connected to the backbone in order to prepare a wide variety of graft copolymers. The chemical compositions and the molecular characteristics of these polymers are presented in Table 1.

Table 1
Compositions and molecular weights of PVCL-*g*-PEO [15]

Sample name[a]	PEO (wt.%)[b]	PEO grafts[c]	M_w (g/mol)
PVCL-*co*-NASI	–	–	45,000[d]
GPEO7.3	7.3	1	50,000[e]
GPEO15.9	15.9	2	55,000[e]
GPEO20	20	2.5	57,500[e]
GPEO35.2	35.2	5	70,000[e]
GPEO38.7	38.7	6	75,000[e]
GPEO50.6	50.6	8	85,000[e]

[a] GPEO*x* in which *x* represents the amount (wt.%) of PEO in the graft copolymer.
[b] Calculated from ^{1}H NMR.
[c] Calculated from the amount of PEO and the number of NASI groups per backbone chain.
[d] Measured by SLS in ethanol solutions.
[e] Calculated from: $M_w = M_w(\text{backbone}) + (\text{amount of grafts} \times M_w(\text{PEO}))$.

2.2. Instrumentation

High sensitivity differential scanning microcalorimetry (HSDSC). HSDSC measurements were conducted with a VP-DSC by Microcal (Northampton, MA). The samples were scanned at constant heating rates of either 45 or 20 °C/h. Concentrations of the samples were 1.0 mg/ml. The samples were equilibrated at 10 °C for 15 min before each subsequent scan.

Light scattering (LS). LS measurements were conducted with a Brookhaven light scattering equipment: a BI-200 SM goniometer and a BI-9000AT digital correlator. The light source was a LEXEL Inc. 85 argon laser, operating at 514.5 nm in the power range of 15–50 mW. Aqueous solutions were prepared from dry samples in de-ionized bi-distilled water. Water was de-ionized with an ELGASTAT UHQ-PS device. The polymers were first dissolved in water during three days at 5 °C. Stock solutions were diluted to get solutions with various polymer concentrations. The range of graft copolymer concentrations was 0.02–6.50 mg/ml. The solutions were kept at room temperature for 24 h to reach equilibrium. The solutions were purified of dust using filter units of 0.45 μm pore size (Millex, PVDF filter). Experiments were carried out in a temperature range from 10.0 to 60.0 ± 0.1 °C, at a scattering angle of 90°. At each temperature, the samples were equilibrated from 20 to 120 min, to stabilize the intensity of the scattered light.

Dynamic light scattering (DLS) was applied to determine the hydrodynamic radius (R_h) and the hydrodynamic size distribution of the copolymers synthesized. In DLS experiments, time autocorrelation functions of the scattered light intensity were collected in the self-beating mode [19]. Time correlation functions were analysed with a Laplace inversion program CONTIN. Correlation functions were measured at least three times for each sample. The mean peak hydrodynamic radius was used to trace changes in R_h. Static light scattering (SLS) was applied for the determination of the molar mass (M_w). Calibration was done according to the standard procedure using toluene as a calibration standard [20]. Intensities of scattered light were analysed using Zimm's double extrapolation method. A WYATT/OPTILAB 903 interferometer was employed to measure the dn/dc at $\lambda = 514.5$ nm. SLS measurements were performed at 20.0 ± 0.1 °C.

2.3. Light scattering methods

In static light scattering experiments, the time-averaged intensity of scattered light was collected as a function of sample concentration (c) and scattering angle (θ). When extrapolated to zero scattering angle and zero concentration, such measurements yield the weight-averaged molar mass M_w.

In dynamic light scattering experiments, an autocorrelation function of scattered light intensity $G_2(t) = \langle I(0)I(t)\rangle$ was collected and then converted into an autocorrelation function of scattered electric field $g_1(t)$ using the Siegert's relationship

$$|g_1(t)| = \beta^{1/2}\sqrt{\frac{G_2(t) - G_2(\infty)}{G_2(\infty)}}, \tag{1}$$

where $G_2(\propto)$ is the experimentally determined baseline, and β is the coherence factor determined by the geometry of the detection (typically $0.5 \le \beta \le 0.8$). Characteristic decay times of a field correlation function τ_i and their relative amplitudes $A_i(\tau_i)$ were evaluated via moments of a corresponding distribution function of decay times $A(\tau)$ obtained using an inverse Laplace transform programs CONTIN as

$$g_1(t) = \int_0^\infty A(\tau)\mathrm{e}^{-1/\tau}\mathrm{d}\tau, \tag{2}$$

Corresponding hydrodynamic radii R_{hi} were obtained from relaxation times τ_i via the Stokes–Einstein equation

$$R_{hi} = \frac{kT}{6\pi\eta_0}\tau_i q^2, \tag{3}$$

where k is the Boltzmann constant, T is the absolute temperature, η_0 is the solvent viscosity, q is the scattering vector determined as $q = \frac{4\pi n_0}{\lambda_0}\sin\frac{\theta}{2}$, λ_0 is the wavelength of the incident laser light source; n_0 is the refractive index of the solvent. Mean peak values of hydrodynamic size distributions were used as an average hydrodynamic radius Rh.

3. Results and discussion

3.1. Investigation of PVCL-g-PEO by dynamic light scattering

The aggregation behaviour of the PVCL-*g*-PEO polymers was investigated in water as a function of temperature using dynamic light scattering (DLS). As expected from the thermo-responsiveness of PVCL, the solution behavior of PVCL-*g*-PEO polymers is different below and above LCST and discussed separately.

Below T_{CP}. In the temperature range between 10 and 33–35 °C, DLS experiments on the PVCL-*co*-NASI prepolymer revealed two peaks in the distribution of hydrodynamic radius with R_h about 7 and 60 nm, respectively. The peak corresponding to small particles obviously represents single PVCL-*co*-NASI molecules, while the presence of large aggregates indicates the tendency of the polymer to associate in water. For well purified samples, the number of the large particles is low relative to the number of single molecules, namely in the order of 1:500.

The distributions of hydrodynamic radii of the PVCL-*g*-PEO graft copolymers are also bimodal below T_{CP}. The hydrodynamic radius of the single macromolecules was about 7 nm. The amplitude of the second signal decreases with increasing degree of grafting and vanishes for GPEO50. This could be attributed to the fact that the relative intensity of the light scattered from individual macromolecules becomes more important with higher degrees of grafting, as a result of increasing molar masses and varying densities, and thus hiding the contribution of the second signal. Moreover, the PEO grafts are increasing the solubility of the graft copolymers and thus diminishing the formation of aggregates with increasing degree of grafting.

Above T_{CP}. The hydrodynamic size distributions change drastically above T_{CP}. Whereas PVCL-*co*-NASI strongly aggregates and precipitates above LCST, no macroscopic phase separation and precipitation was observed for any of the grafted copolymers studied. Both peaks observed below T_{CP} vanish and a new, rather narrow peak is formed. Its position and shape will be discussed as a function of the degree of grafting, polymer concentration and temperature.

The aggregates, formed above T_{CP}, were studied in more detail for GPEO20, GPEO35.2 and GPEO50.6, representing graft copolymers with, respectively, 2.5, 5 and 8 PEO chains per PVCL chain (Table 1). The temperature dependencies of the hydrodynamic radius and the general aggregation behavior of all PEO graft copolymers were similar. The scattered light intensity increases upon heating, shows a maximum, and then monotonically decreases again. The temperature dependence of R_h follows a trend similar to that of intensity, as may be seen in Fig. 1.

At the cloud point, a strong increase in R_h is observed, due to the formation of interchain aggregates. The formation of aggregates is a kinetically controlled process and also depends on copolymer composition and concentration. Furthermore, in the vicinity of the phase separation boundary, strong concentration fluctuations take place leading to large experimental errors. For this reason, the values obtained just above the T_{CP} cannot be taken as absolute values.

Heating of the solutions above 40 °C leads to the formation of stable aggregates. Apparently, the copolymers

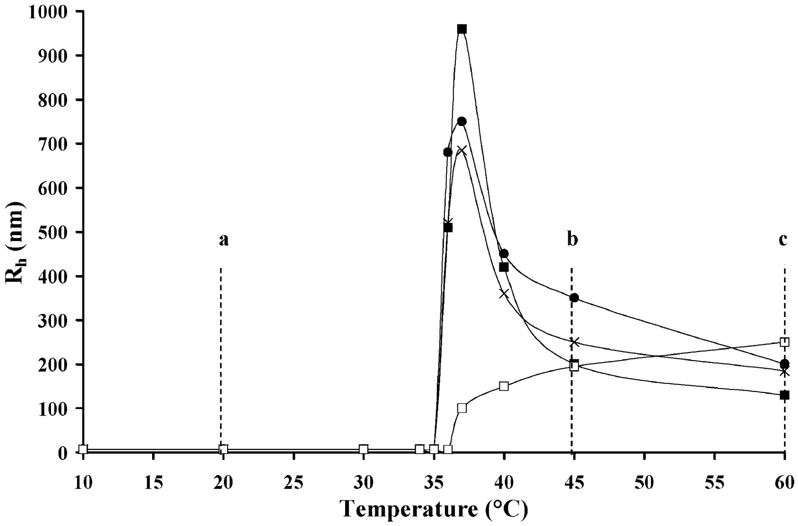

Fig. 1. Dependence of the hydrodynamic radius (R_h) on temperature measured for copolymers with different degree of grafting at a copolymer concentration of 0.65 mg/ml: GPEO20 (■), GPEO35.2 (×) and GPEO50.6 (●), and at a copolymer concentration of 0.065 mg/ml for GPEO20 (☐). Letters (a), (b) and (c) correspond to those in Fig. 2.

form stable particles above T_{CP}, indicating that hydrophilic PEO, grafted onto the PVCL chain, stabilises PVCL, which leads to the formation of PVCL-*g*-PEO polymeric structures. These structures are thought to consist of a hydrophobic PVCL core and a hydrophilic PEO shell (see Fig. 2). A core-shell structure has recently been reported for PNIPAAm-*g*-PEO [10,11] and is expected to be similar for PVCL-*g*-PEO. Though, detailed investigations on the internal structure of the aggregates formed by PVCL-*g*-PEO are needed and will be reported separately.

Summarized, this means that at 20 °C (Fig. 2a), the copolymers are distributed in the solutions as single molecules, which aggregate above T_{CP} (45 °C) with the formation of stable aggregates (Fig. 2b). Further heating (60 °C) leads to a shrinking process of the aggregates (Fig. 2c). A similar phenomenon has recently been observed for PNIPAAm-*g*-PEO polymers by Virtanen et al. and ascribed to the shrinking of the thermo-responsive core upon heating [10]. This indicates that the collapsed macromolecules are still surrounded by water molecules, which can only be removed upon further heating.

From Fig. 1, it can be seen that an increasing degree of grafting leads to larger aggregates. This is obviously caused by a larger PEO corona and by a looser PVCL core for the samples with higher degree of grafting. It is highly probable that some PEO chains are incorporated in the PVCL core. Such intermixing phenomena in micelles have also been observed recently on the basis of neutron reflection experiments on PEO-PPO triblock copolymers [21].

The concentration dependence of the size of the aggregates has also been studied. It has been observed that a certain polymer concentration is needed to form stable polymer aggregates at elevated temperatures. This is shown for GPEO20 in Fig. 3. At low polymer concentration, there is not enough polymer material around the centres of aggregation. Obviously, at infinite dilution, there is only one polymer molecule around a centre of aggregation. With increasing polymer concentration, larger aggregates are formed. In the intermediate region, the aggregates are not uniform in size and size distributions are broad. This results in large values of the mean R_h, owing to higher scattering from larger aggregates. At high polymer concentrations, stable globules start to build up. This results again in narrow size distributions and in a decrease of the mean R_h. As is seen in Fig. 3, for GPEO20 with a concentration around 0.5 mg/ml, R_h drops to its minimum value. This value is temperature dependent, because the aggregates shrink upon heating. The R_h of the aggregates is 185 nm at 45 °C and decreases to 120 nm upon heating up to 60 °C. At a fixed temperature, larger polymeric aggregates may form at

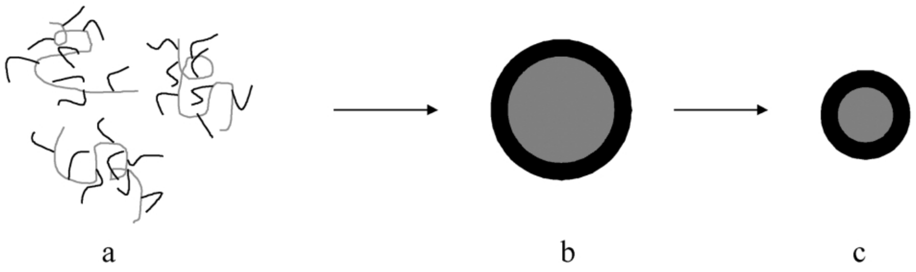

Fig. 2. Model describing the formation of aggregates and their shrinkage upon heating: (a) 20 °C, (b) 45 °C, and (c) 60 °C.

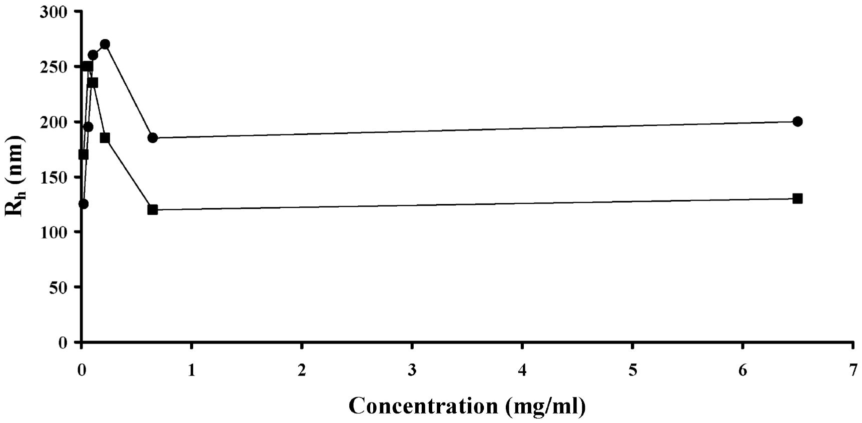

Fig. 3. Concentration dependence of GPEO20 aggregates at 45 °C (●) and 60 °C (■).

higher polymer concentrations, which results in a minor increase in R_h in the concentration region of 1–7 mg/ml.

The position of the R_h maximum in Fig. 3 slightly depends on temperature. The maximum of R_h at 60 °C corresponds to a lower concentration in comparison to that at 45 °C. This can be understood by the increasing stability of the particles with increasing temperature, as a result of a greater discrimination between the PEO and PVCL components. Therefore, less material is needed to form stable structures.

From the data above, it can be concluded that there exists a critical concentration at which stable aggregates, uniform in size, are formed. This may be due to the relatively low molecular weight of the PVCL-*g*-PEO polymers.

The existence of the critical concentration was confirmed using solutions of GPEO20 with two concentrations: one above the critical concentration (0.65 mg/ml) and another below (0.065 mg/ml). The temperature dependence of R_h is presented in Fig. 1 for both concentrations. From the comparison, it is clear that the two samples behave in a distinctively different manner. In a dilute solution, particles build up and continue to grow with increasing temperature. Above the critical concentration, particles are formed which collapse upon heating.

Although it was found earlier that the degree of grafting influences the size of aggregates, no effect is observed on the shape of the size distribution at a particular concentration. Above the minimum concentration at which uniform particles are formed, the profile of the size distributions does not vary significantly with temperature. Fig. 4 shows the size distributions of GPEO20 for two concentrations, both above the critical concentration. It can be seen that the size distribution is narrower at higher concentrations. Moreover, the aggregates become larger with increasing concentration, as was already observed in Fig. 3. This was found to be the case with all the graft copolymers studied.

In the range of moderate polymer concentrations, above the T_{CP}, the thermodynamic quality of the solvent is poor and the distributions of hydrodynamic size are narrow. Apparently, the stability of the PVCL-*g*-PEO aggregates is not only determined by the hydrophilicity of the outer surface of the aggregates (i.e. shell), but also by their surface to molar mass ratio. It may be suggested that stable aggregates of optimum size are formed when attraction between PVCL chains is compensated by the translational entropy of the system. Obviously, the heating rate and kinetics of the aggregation may also affect the width of the size distribution.

In concentrated polymer solutions, the mean R_h may increase due to strong intermolecular association. However, the observed increase in R_h with polymer concentration can also be apparent. In DLS experiments, the diffusion coefficient is measured rather than R_h and an increase in R_h can be associated with a decreasing diffusion coefficient with increasing polymer concentration, due to strong interactions between the polymer aggregates in a thermodynamically poor solvent.

3.2. Investigation of PVCL-g-PEO by scanning microcalorimetry

The thermal behavior of aqueous solutions of PVCL-*g*-PEO was studied by microcalorimetry (Figs. 5 and 6). As expected, all polymers undergo a phase transition starting at temperatures close to the T_{CP} of PVCL [17], accompanied by a clear endothermic heat effect. Varying the heating rate does not cause any systematic change in the thermograms, at least not in the studied range (20–45 °C/h). The transition is completely reproducible, proven by the second and subsequent scans with identical run parameters. The endothermic transition occurs within a rather broad temperature range starting at temperatures that are very close to those measured with LS. This transition is caused by the sequential dehydration of the polymer chain and therefore the onset temperature is closely related to the starting point of the aggregation process, i.e. T_{CP}. The width of the DSC peaks for PVCL polymers is due to the strong concentration dependence of the demixing temperature [17,22].

All thermograms, shown in Fig. 5, have a similar shape: at the critical temperature, there is a sharp increase in the

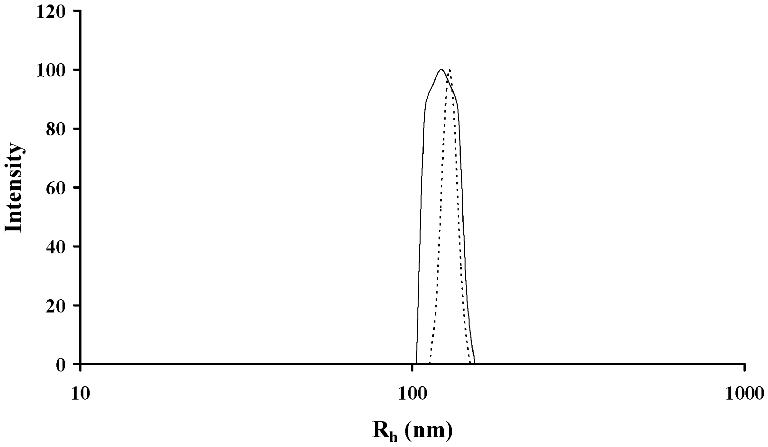

Fig. 4. Size distributions of the GPEO20 aggregates at 60 °C obtained from solutions of two copolymer concentrations: 6.5 (broken line) and 0.65 (continuous line) mg/ml.

heat capacity (C_p) followed by a relatively slow continuous decrease of C_p after the maximum. The heat capacity continues to decrease, even at very high temperatures, reaching lower values than before the T_{CP}. In Fig. 5, it can be observed that the heat capacity of the graft copolymers reaches a constant value above 70 °C and the total negative change in C_p is approximately 0.5 J g^{-1} K^{-1}.

For poly(*N*-isopropyl acrylamide) (PNIPAAm), a similar negative change in C_p has been observed [23], although in this case a sharp endothermic peak of the heat capacity is followed by a well-defined plateau. This negative heat capacity change was explained by the dehydration of NIPAAm units during the coil-to-globule transition. A similar lowering of the heat capacity can also be detected for low molar mass surfactants during micelle formation [24] and for protein refolding [25], as well as for phase transitions of various pluronic-type block copolymers [26]. Usually, such a negative heat capacity change during phase transition is understood as an indication of diminished interaction between water molecules and polymer chains.

The influence of the degree of grafting with PEO on the T_{CP} has been reported earlier [18]. It was found that the T_{CP} of PVCL decreases if PEO is grafted onto the PVCL backbone. A similar decrease had been found for ternary aqueous solutions of linear PVCL and PEO and for the corresponding segmented polymer networks [27]. This behavior was ascribed to a certain competition between PVCL and PEO to interact with water, which diminishes with increasing branching or crosslinking. However, in Fig. 5, the onset values for the PVCL-*g*-PEO copolymers are scattered randomly over a very narrow temperature range (34.5–36 °C) and there is not any clear dependence between the onset temperatures and PEO grafting degree. Most likely, the dependence is not detectable when the polymer

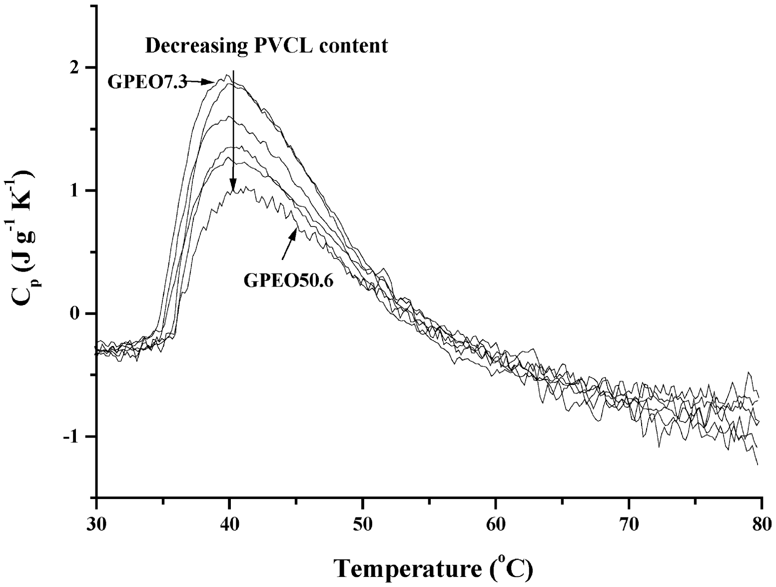

Fig. 5. Temperature dependence of the heat capacity of PVCL-*g*-PEO copolymers with varying PVCL content. C_p is expressed per gram of dry polymer. The polymer concentration is in all cases 1.0 mg/ml and the heating rate is 45 °C/h.

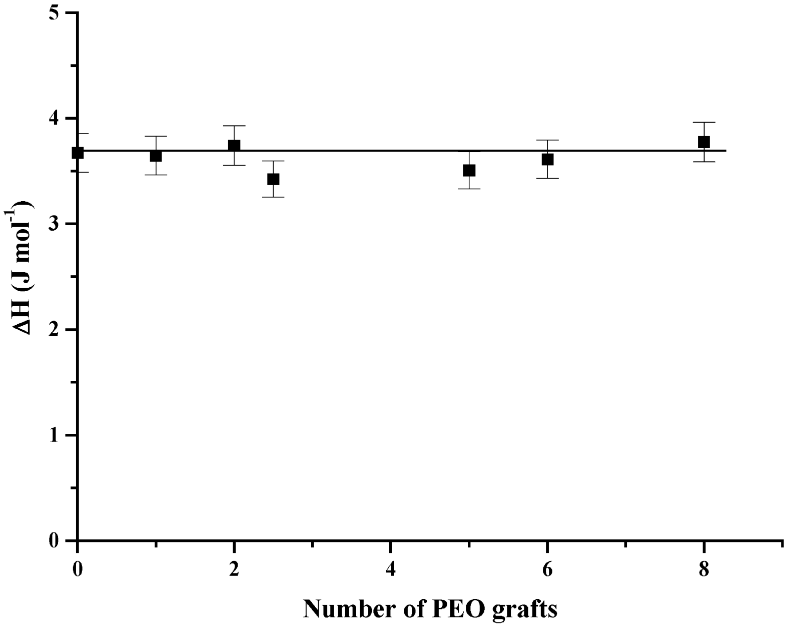

Fig. 6. Dependence of the heat of transition on the mass fraction of PEO in PVCL-*g*-PEO. Enthalpy is given in kilojoules per mol VCL repeating units.

concentration is very low, as in the microcalorimetry measurements.

In Fig. 6, the heats of transition of PVCL-*g*-PEOs, obtained from the thermograms in Fig. 5, are shown as a function of the mass fraction of PEO. ΔH is expressed as kilojoules per mole of repeating units of *N*-vinyl caprolactam. From this, it becomes clear that the heat of transition results from the PVCL fragments as the enthalpy change is constant regardless of the degree of grafting. The average ΔH (3.6 kJ/mol) in Fig. 6 is somewhat higher than those reported for homopolymer PVCL in earlier studies. Mikheeva et al. obtained 1.8 kJ/mol [28] and Maeda et al. approximately 2.2 kJ/mol [29].

Grafted PVCL copolymers have a high tendency to form stable aggregates when heated, because of the PEO grafts tending to solvate the contracted PVCL backbone. However, according to the light scattering measurements discussed above, the particle size is not constant upon heating above $T > 45$ °C. The size of aggregates decreases in a rather broad temperature range (Fig. 1). Therefore, the interaction between water molecules and PVCL might, to some extent, still exist even at relatively high temperatures. PVCL slowly dehydrates upon heating and the aggregates shrink. Just above the onset temperature of the thermograms, the aggregation of the polymer chains is very intense while the polymer starts to dehydrate and the heat capacity function undergoes an abrupt change. Most of the enthalpy change is related to this very first stage of the phase transition. However, further heating from 45 to 60 °C induces a notable enthalpy change as well, while the aggregates shrink. Above 60 °C, the heat capacity function levels off. This trend is similar to that seen in Fig. 1. The size of the aggregates is not expected to change significantly with heating above 60 °C.

4. Conclusions

The solution properties of aqueous PVCL-*g*-PEO copolymers have been investigated using light scattering and microcalorimetry. Interpolymer aggregates, stable in water above the LCST of PVCL, have been studied as a function of temperature and copolymer concentration. A certain critical concentration is needed, at which uniform aggregates of PVCL-*g*-PEO can be formed. PEO grafts form a hydrophilic shell stabilising the hydrophobic PVCL core. According to the light scattering measurements, after PVCL-*g*-PEO aggregates are formed above the T_{CP}, the size of the aggregates decreases upon further heating. This observation is in accordance with the microcalorimetry results, which suggest that PVCL dehydrates upon heating in the broad range of temperature. It was also found that the particle size of the aggregates increases with the degree of grafting.

Microcalorimetry measurements revealed that the grafting of PVCL with the hydrophilic PEO chains does not influence the enthalpy change of PVCL during the phase transition, i.e. ΔH is directly proportional to the mole fraction of VCL in the copolymers. Also, the transition range is remarkably broad, which implies that the dehydration continues after the first stage of the phase transition. This finding is in accordance with the light scattering results.

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