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ORIGINAL PAPER

# Formation of mesoglobules in aqueous media from thermo-sensitive poly(ethoxytriethyleneglycol acrylate)

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**Abstract** A series of six poly(ethoxytriethyleneglycol acrylate) (PETEGA) homopolymers were synthesized by atom transfer radical polymerization, reversible addition-fragmentation transfer polymerization, and anionic polymerization in order to cover a molecular weight range from 7,000 to 40,000 Da. The polymers exhibited a lower critical solution temperature (LCST) behavior in water, which was observed by the occurrence of a cloud point (CP) at around 35 °C. The transmittance of visible light versus temperature dependence overlapped during the cooling and the heating cycles, showing almost a complete lack of hysteresis. Moreover, instead of the occurrence of an uncontrolled macroscopic phase separation, stable colloidal aggregates (mesoglobules) of narrow distribution in particle size were formed in water at temperatures above the LCST of PETEGA at 1 g $L^{-1}$ solutions. The dimensions of the mesoglobules ranged from 91 to 235 nm, and particle size was not influenced by the molecular weight of PETEGA. Temperature changes caused considerable variations of the mesoglobules dimensions, which were smaller at higher temperatures. The addition of an anionic surfactant simultaneously increased the CP values by 4–6 °C and lowered the dimensions of the mesoglobules.

**Keywords** Thermo-responsive polymers · LCST · Mesoglobules

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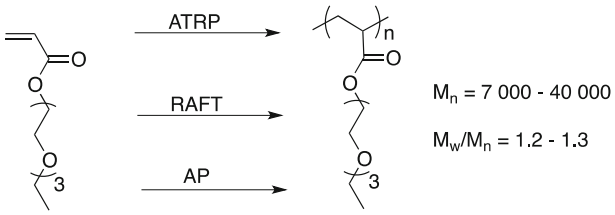
## Introduction

The thermodynamic quality of water as a solvent gradually becomes poorer upon heating of an aqueous solution of a thermo-sensitive polymer and at the lower critical solution temperature (LCST), the individual polymer chains undergo a coil-to-globule transition collapse resulting from dehydration. The formed globules are also referred to as "mesoglobules" [1] and they associate quickly, which is manifested by a macroscopic phase separation. In the ideal case that occurs below the overlapping concentration of the most studied LCST polymer, poly(*N*-isopropylacrylamide) (PNIPAm), and also other LCST polymers [1–3], colloidal mesoglobules of spherical shape are formed. Even at higher polymer concentrations than the overlapping, it is still possible to form mesoglobules of low size dispersity and dimensions ranging from 50 to 200 nm. The size of mesoglobules could be controlled by the polymer concentration and the rate of heating. In general, the lower the concentration and/or the faster the heating rate, the smaller the formed aggregates [2, 3]. The presence of surfactants decreases the size of mesoglobules [4].

Mesoglobules from LCST polymers are attractive as templates for the formation of nano-capsules as we have recently reported [5]. For this purpose, mesoglobules from PNIPAm with dimensions controlled by the presence of a surfactant were prepared. Then the PNIPAm mesoglobules were used as nucleating agents for the seeded radical copolymerization of 2-hydroxyethylmethacrylate and the cross-linker poly(ethylene glycol) dimethacrylate to form core–shell type of particles. The PNIPAm core was partially dissolved at temperatures below LCST to give empty nano-capsules. The latter were prepared by mild methods and are attractive for the encapsulation of biomacromolecules [6]. Furthermore, PNIPAm has been used by Yokoyama et al. [7, 8] to entrap DNA at temperatures above the LCST of PNIPAm (32 °C). Above the LCST, the complex between PNIPAm and DNA is tight due to dense packing, which facilitates the cellular uptake and helps evasion the enzymatic degradation of DNA. Upon decreasing temperature below the LCST the complex loosens and even completely dissociates, thus, the transcription of the released DNA is favored. However, temperatures below the physiological temperature are disadvantageous for transfection since cell activity is reduced at such conditions, which stresses the need for optimization the temperature response for DNA association and release by using other (co)polymers with appropriate phase transition temperatures.

Poly(ethoxytriethyleneglycol acrylate) (PETEGA) is an interesting and promising alternative of PNIPAm as a thermo-sensitive polymer. PETEGA of $M_n = 14{,}500$ has been reported recently by Zhao et al. [9] to have a cloud point value of 35 °C in water, and moreover, there was almost no hysteresis after a heating/cooling cycle. Surprisingly no further research has been performed in order to investigate in detail the aqueous solution properties of this LCST polymer. PETEGA resembles the most used thermo-sensitive polymer PNIPAm, but its phase transition temperature is actually closer to the body temperature. Therefore, PETEGA could be a polymer of choice for the preparation of defined mesoglobules for bio-applications.




**Scheme 1** Synthesis of PETEGA homopolymers by different polymerization techniques

In this study, a series of homopolymers of ethoxytriethyleneglycol acrylate (ETEGA) were prepared by atom transfer radical polymerization (ATRP), reversible addition-fragmentation transfer polymerization (RAFT), and ligated anionic polymerization in order to cover a relatively wide molecular weight range from 7,000 to 40,000 (Scheme 1). The aqueous solution properties in response to temperature changes were studied in detail by turbidimetry. The formation of PETEGA mesoglobules was followed by dynamic light scattering at different temperatures above the LCST with or without of fixed amounts of surfactant.

## Experimental section

### Materials

Tri(ethylene glycol) monoethyl ether (TEGME) (95%, Aldrich), triethylamine (99%, Aldrich), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) (99%, Aldrich), ethyl 2-bromopropionate (EBP) (99%, Aldrich) were distilled before using and characterized additionally by gas chromatography. Acryloyl chloride (98%), CuBr (99.99%), sodium dodecyl sulfate (99%), and LiCl (99.9%) were purchased from Aldrich and used as received. 2-cyano-2-butyl dithiobenzoate was prepared as described elsewhere [10] for related compounds. Lithium diisopropylamide was prepared in situ from diisopropylamine (99%, Aldrich) and *n*-butyllithium (2 M in cyclohexane, Aldrich). Azobisisobutyronitrile (98%) was purchased from Fluka. Anisole and hexane were purified by distillation before using. Tetrahydrofuran (THF) was first refluxed over $CaH_2$ for 24 h and then distilled under $N_2$ into a flask containing Na/K alloy from which was further refluxed and distilled before use. ETEGA was synthesized as described elsewhere [9].

### Synthesis of PETEGA by ATRP

Similarly to Ref. [8], into a two-necked flask desired amounts of ETEGA in anisole, CuBr, and PMDETA were added. The mixture was stirred under Ar atmosphere and degassed by three freeze-pump-thaw cycles. Then the initiator EBP was added. The molar ratios [ETEGA]:[CuBr]:[PMDTA]:[EBP] were DP:1:1:1 where DP is the targeted degree of polymerization. The mixture was stirred at room temperature until CuBr formed a dark green complex with PMDETA. Then the polymerization

reactor was immersed in an oil bath at 90 °C for different time intervals. The polymerization was terminated by exposing the mixture to air. To remove the catalyst complex, the terminated polymerization mixture was diluted with THF and passed through a neutral $Al_2O_3$ column. The solution collected from the column was concentrated and precipitated three times in hexane. Traces of anisole were removed by lyophilization.

### Synthesis of PETEGA by RAFT

Stock solutions of azobisisobutyronitrile (13.4 mg, 0.082 mmol) in benzene (50 mL) and 2-cyano-2-butyl dithiobenzoate (9.62 mg, 0.049 mmol) in benzene (10 mL) were prepared. 2 mL of the former and 4 mL of the latter solution were transferred into a two-necked flask containing 4 mL of ETEGA. The molar ratio [ETEGA]:[2-cyano-2-butyl dithiobenzoate]:[azobisisobutironitrile] was 0.17:0.016:0.0032 [10]. The flask was degassed, sealed, and heated at 70 °C for 90 min. The system was opened to the air and cooled down to stop the polymerization. The polymer solution thus obtained was concentrated and precipitated three times in hexane.

### Synthesis of PETEGA by anionic polymerization

The anionic polymerization of ETEGA was performed in THF at −78 °C under a high purity argon atmosphere using lithium diisopropylamide as an initiator in the presence of LiCl (fivefold molar excess with respect to the initiator) as described elsewhere [11, 12]. In a typical reaction LiCl (0.064 g, 1.5 mmol) was dissolved in 45 mL of THF followed by the addition of diisopropylamine (0.03 g, 0.3 mmol). The temperature was decreased to −78 °C and *n*-butyllithium solution was added (0.15 mL, 0.3 mmol). After stirring the initiator solution for 30 min, ETEGA (1.5 mL, 6.5 mmol) was added drop-wise via a Hamilton air tight syringe. The polymerization was quenched after 90 min with degassed methanol. The reaction mixture was concentrated, and the polymer was precipitated in hexane.

### Mesoglobule preparation

Mesoglobules were prepared simply by heating the aqueous solution of PETEGA (1 g $L^{-1}$ in deionized water) without or in the presence of SDS.

### Methods

#### *Nuclear magnetic resonance (NMR)*

$^1H$ NMR spectra were recorded at room temperature in $CDCl_3$ on a Bruker Avance 600 spectrometer operating at 600 MHz.

*Size exclusion chromatography (SEC)*

The molecular weights and dispersities were determined by SEC using a multiangle light scattering detector ($\lambda = 658$ nm) DAWN HELEOS of Wyatt Technology and a refractive index detector Δn-1000 RI from WGE DR Bures. SEC measurements were performed at 45 °C in THF at a nominal flow rate of 1 mL $min^{-1}$. Three columns PSS GRAM, 30, 102, and 103 Å (Polymer Standards Services) were used. Results were evaluated using the ASTRA 4.73 software from Wyatt Technologies and WINGPC 6.0 software from PSS.

*Differential scanning calorimetry (DSC)*

Differential scanning calorimetry was performed on a TA Instrument DSC Q100 V9.0 Build 275 in the −90 to 150 °C temperature range, at a heating rate of 20 °C $min^{-1}$ under a nitrogen flow (50 mL $min^{-1}$). Samples (6.0 ± 0.1 mg) were heated up to 150 °C at a rate of 20 °C $min^{-1}$ (first scan) and then quenched to −90 °C at a rate of 100 °C $min^{-1}$ in order to erase the thermal history. They were again heated up to 250 °C (second scan) at a rate of 20 °C $min^{-1}$. The glass transition temperature ($T_g$) was taken as the inflection point of the second heating run.

*Thermal gravimetric analysis (TGA)*

Thermal gravimetric analysis was performed on a TA Instrument Q500 V6.3 Build 189 in the 0–600 °C temperature range under a nitrogen flow of 40 mL $min^{-1}$. The heating rate was 20 °C $min^{-1}$. The ±1 °C accuracy on the degradation temperatures determined from the derivatives of the weight losses versus temperature curves was established.

*Dynamic light scattering (DLS)*

Dynamic light scattering measurements were performed on a Brookhaven BI-200 goniometer with vertically polarized incident light of wavelength $\lambda = 632.8$ nm supplied by a helium–neon laser operated at 75 mW and a Brookhaven BI-9000 AT digital autocorrelator. Measurements of scattered light from the polymer aqueous solutions ($c = 1$ g $L^{-1}$) were made at an angle of 90° to the incident beam in the temperature range from 25 to 70 °C. The autocorrelation functions were analyzed by the constrained regularized CONTIN method to obtain the apparent hydrodynamic diameters, $D_h$ [13].

*Turbidimetry*

Cloud points of 0.5 and 1.0 g $L^{-1}$ aqueous polymer solutions were determined on a JASCO V-530 UV–Vis spectrophotometer switched to transmittance regime at constant wavelength of 500 nm. The cuvette compartment was thermostated by

Medson MTC-P1 thermo controller with a stability of ≤0.05 °C. The temperature range was from 20 to 70 °C and heating/cooling rates were 1 °C $min^{-1}$.

## Results and discussion

### Synthesis and bulk properties of PETEGA

A series of six homopolymers of ETEGA were prepared by ATRP, RAFT, and anionic polymerization in order to cover a relatively broad molecular weight range (Scheme 1). The polymers were purified by repetitive precipitations in hexane and characterized by SEC and $^1$H NMR (Fig. 1). The characterization data is collected in Table 1.

The molecular weights of the polymers prepared by ATRP were in line with the conversions and the molecular weight distributions were narrow (1.2–1.3) if anisole was used as a solvent. Yields were intentionally kept low to avoid radical coupling and recombination reactions. For the acetone system in which higher yield was obtained (entry # 2, Table 1) higher dispersity of 2.3 was observed [6] most likely due to the above mentioned side reactions.

In the case of RAFT and anionic polymerizations, very low initiator efficiencies were observed and the obtained polymers were in the higher molecular weight region but still the polymers had acceptably low dispersities.

Unlike PNIPAm, PETEGA as a polyacrylate is a more flexible polymer of low $T_g$. The measured $T_g$s for entries # 1, 5, and 6 (Table 1) were between −58 and −55 °C (Fig. 2a; Table 2). Thermo-gravimetrical measurements revealed that PETEGAs is stable at temperatures up to around 320 °C (Fig. 2b; Table 2).

### Aqueous solution properties of PETEGA

#### *Cloud point measurements*

Variations of the incident light intensity transmitted through 1 g $L^{-1}$ PETEGA aqueous solutions with temperature were monitored for all of the studied homopolymers. A representative transmittance versus temperature heating–cooling cycle is shown in Fig. 3. A typical clouding process upon heating is represented by a sharp sigmoidal curve. Upon cooling an abrupt phase transition, which could also be visually monitored as a cloudy-to-transparent transition of the solution, was observed. At temperature ramps of 1 °C $min^{-1}$, the heating and cooling curves fully overlapped, that is, there was no hysteresis in the cycles as observed previously for PETEGA of $M_n = 14{,}500$ [10].

In good agreement with previously reported values [6, 10], cloud points (CPs) of 35–39 °C were determined from the experimental curves (Table 3). Importantly, the molecular weight does not affect substantially the CP values, and therefore, PETEGA, like PNIPAm, is a Type II LCST polymer [14]. It should be also mentioned here that the poly(oligoethyleneglycol methacrylate)s investigated by Lutz et al. [15, 16] behaved also as Type II LCST polymers.

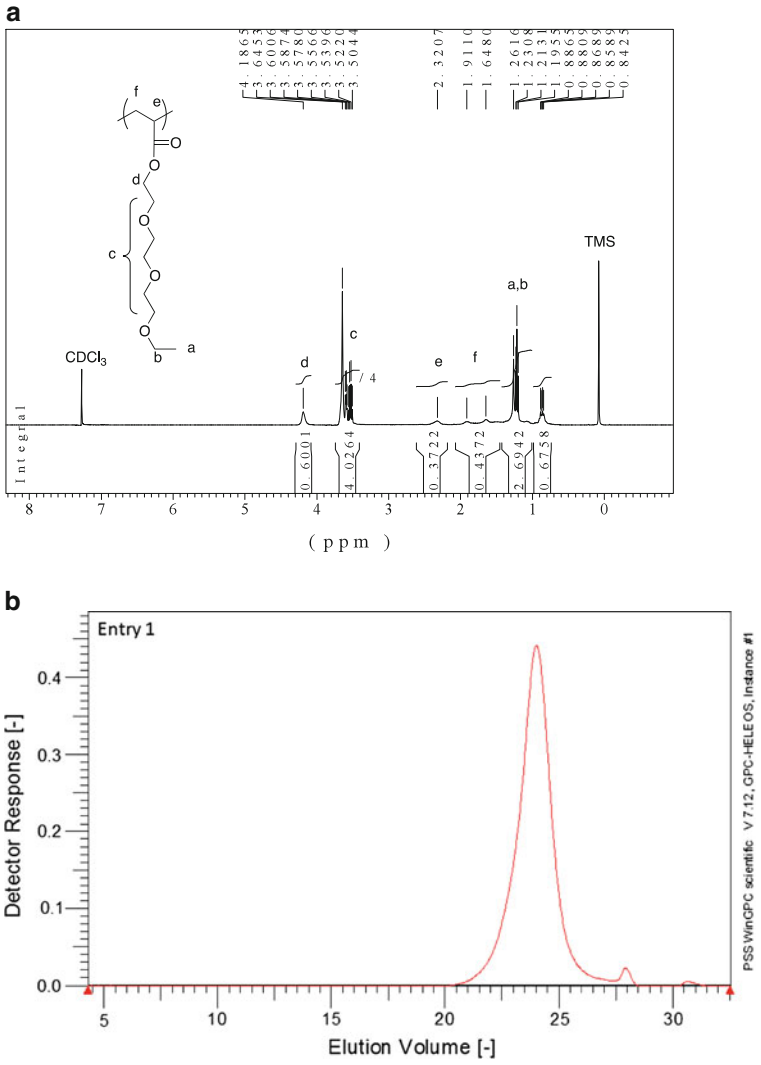



**Fig. 1** **a** $^1$H NMR spectrum in $CDCl_3$ of PETEGA (entry 3, Table 1). **b** SEC curve of PETEGA (entry 1, Table 1)

In general, it is largely accepted that certain additives are able not only to influence the CP values of LCST polymers, but also to substantially alter their chemical potential so that the driving force for association is altered [2, 3]. For example, the addition of fixed amounts of an anionic surfactant, sodium dodecyl sulfate (SDS) to aqueous PETEGA solution was found to gradually shift the clouding curves to higher temperatures as shown in Fig. 3b for PETEGA of molecular weight of 8,000 (entry 2). Importantly, the presence of surfactant molecules did not compromise the intrinsic reversibility of the thermo-responsive systems: the heating and cooling curves overlapped and hysteresis did not occur

**Table 1** Polymerization data for PETEGA homopolymers prepared via different polymerization techniques

| Entry # | Polymerization technique | Yield (%)[a] | $M_n$ (calc.) | $M_n$ (SEC) | $M_w/M_n$ (SEC) |
|---|---|---|---|---|---|
| 1 | ATRP | 50 | 10,000 | 7,000 | 1.2 |
| 2[b] | ATRP | 72 | 7,200 | 8,000 | 2.3 |
| 3 | ATRP | 50 | 25,000 | 20,000 | 1.3 |
| 4 | RAFT | 50 | 1,150 | 24,000 | 1.2 |
| 5 | AP | 50 | 2,500 | 36,000 | 1.3 |
| 6 | RAFT | 55 | 1,265 | 40,000 | 1.3 |

[a] Yield was determined gravimetrically

[b] ATRP was performed in acetone, data taken from Ref. [6]

(Fig. 3b). Most likely, the presence of SDS facilitated just the stronger repulsion between the collapsed PETEGA aggregates, which resulted in lower tendency for inter-particle association. At all surfactant to PETEGA ratios studied ranging from 1:0.5 to 1:2 the CP values were found to increase by 4–6 °C. Obviously, simply by adding a surfactant we are able to control the phase transition temperature and, as shown later, the dimensions of PETEGA mesoglobules.

*Dynamic light scattering measurements*

The process of clouding upon heating above the LCST is associated with formation of aggregates due to hydrophobic interactions. Similarly to PNIPAM, in dilute aqueous solution and in wide temperature intervals above the LCST, PETEGA homopolymers are also expected to form stable nano-sized mesoglobules. The literature, however, contains only scarce data about the dimensions of aggregates (mainly micelles) formed by copolymers of methacrylates possessing short oligo(ethylene glycol) side chains, cross-linked microgels based on such copolymers as well as their thermal and, in general, stimuli-responsive properties [10, 17]. The information about mesoglobules prepared from PETEGA homopolymers is even more limited [6]. In this study, PETEGA mesoglobules were parameterized by DLS. Figure 4a shows size distributions of PETEGA mesoglobules (entry 2) at different temperatures. The size distribution of PETEGA mesoglobules was broad at 40 °C. This is not surprising, as at temperatures just above LCST the globules are not densely packed. With increasing temperature the dimensions gradually got smaller and the mesoglobules became better defined in terms of size distribution; they were stable at temperatures as high as 70 °C.

The effect of PETEGA molecular weight was not obvious as no clear trend of mesoglobule size variation was observed. The diameters of mesoglobules ranged from 177 to 235 nm at 40 °C, from 132 to 178 nm at 50 °C, and from 91 to 151 nm at 70 °C (Fig. 5a). Unlike molecular weight, the effect of temperature on mesoglobule dimensions was more noticeable. The decrease of mesoglobules dimensions is well demonstrated in Figs. 4a and 5a. However, for a better representation, a data selection that includes particle diameter versus temperature plots was re-drawn in Fig. 5b. As

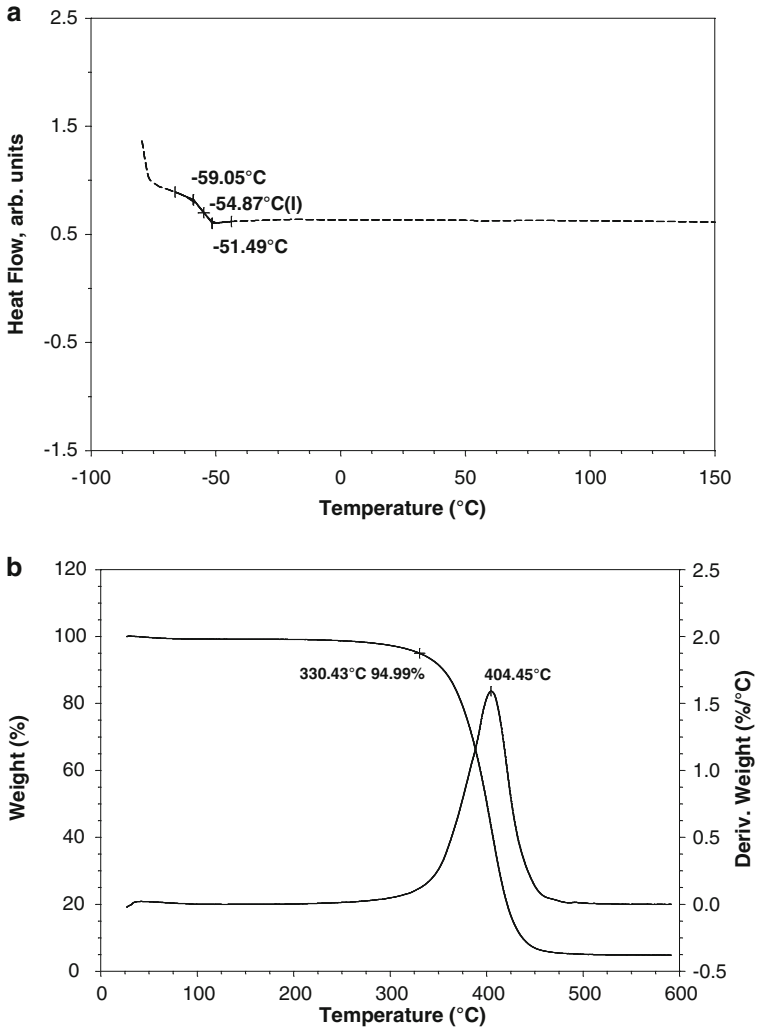



**Fig. 2** DSC (**a**, entry 1) and TGA (**b**, entry 6) curves of PETEGA polymers

**Table 2** DSC and TGA data of selected PETEGA homopolymers varying in molecular weights

| Entry # | $T_{d5\%}$ (°C)[a] | $T_{dmax}$ (°C)[b] | $V_{dmax}$ (°C $min^{-1}$)[b] | $T_g$ (°C) |
|---|---|---|---|---|
| 1 | 321 | 404 | 1.68 | −57.2 |
| 5 | 330 | 406 | 1.60 | −55.7 |
| 6 | 341 | 409 | 1.58 | −54.9 |

[a] Initial degradation temperature that corresponds to weight loss of 5%

[b] Maximum degradation temperature ($T_{dmax}$) and maximum degradation rate ($V_{dmax}$) that correspond to weight loss of 50%

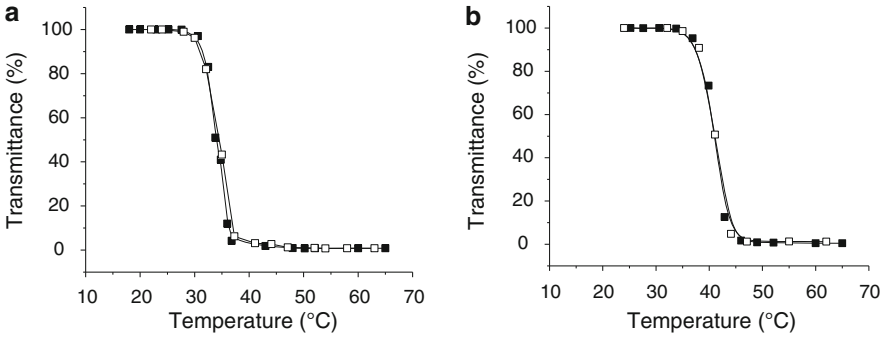



**Fig. 3** Transmittance versus temperature curves for aqueous solution of **a** PETEGA (sample # 2) and **b** the same polymer in a 1:0.5 wt ratio with SDS: heating (*filled symbols*), cooling (*open symbols*), concentration 1 g $L^{-1}$, heating/cooling rate 1 °C $min^{-1}$

**Table 3** Cloud point transitions in aqueous media of PETEGA polymers; PETEGA concentration 1 g $L^{-1}$

| Entry # | $M_n$ | $M_w/M_n$ (SEC) | Cloud point (°C) |
|---|---|---|---|
| 1 | 7,000 | 1.2 | 37 |
| 2 | 8,000 | 2.3 | 35 |
| 3 | 20,000 | 1.3 | 39 |
| 4 | 24,000 | 1.2 | 37 |
| 5 | 36,000 | 1.3 | 37 |
| 6 | 40,000 | 1.3 | 35 |

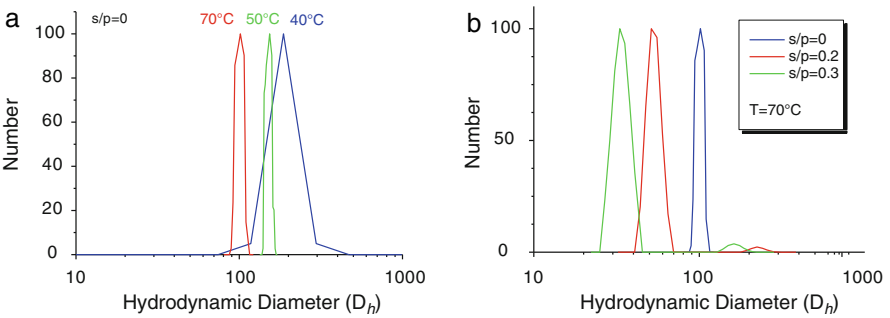



**Fig. 4** Hydrodynamic diameter distributions measured at an angle of 90°: **a** mesoglobules formed by PETEGA of molecular weight of 8000 (entry 2) in aqueous solution at different temperatures indicated and **b** the same polymer in the presence of SDS at different surfactant-to-polymer (s/p) ratios indicated; Concentration of PETEGA was 1 g $L^{-1}$

seen, upon heating from 40 to 70 °C the diameters were found to decrease abruptly. For the majority of samples, the typical reduction in size in this temperature interval was about 53 ± 3%. The decrease was less pronounced (e.g., about 25%) for the mesoglobules formed by the polymer of the lowest molecular weight.

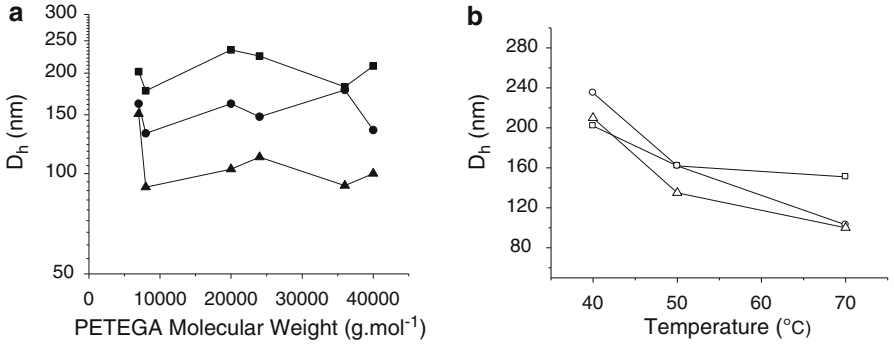



**Fig. 5** Variations of mesoglobule hydrodynamic diameters with **a** molecular weight of PETEGA at certain temperatures and **b** temperature at certain molecular weight. *Symbols* in (**a**): *filled squares*, *filled circles*, *filled triangles* at 40, 50, and 70 °C, respectively. *Symbols* in (**b**): *open squares*, *open circles*, *open triangles* at PETEGA molecular weight of 7,000; 20,000; and 40,000, respectively; Concentration of PETEGA was 1 g $L^{-1}$

The effect of surfactant addition was also evident. As seen from Fig. 4b the presence of SDS substantially decreased the particle dimensions: the higher the surfactant-to-PETEGA ratio, the smaller the mesoglobules. It should be noted here that the SDS concentration was invariably kept below the critical micellization concentration. At SDS/PETEGA ratios $\geq 0.2$, a tiny fraction of large particles typically appeared (Fig. 4b); the latter can be easily removed by filtration through appropriate pore size filters.

## Conclusions and outlook

Thermo-sensitive PETEGA homopolymers of molecular weights ranging from 7,000 to 40,000 were synthesized by ATRP, RAFT, and anionic polymerization. PETEGA was molecularly dissolved in water at temperatures lower than 35 °C and, above its LCST, PETEGA formed stable nano-sized mesoglobules. A very important observation is that the aqueous solution properties, in particular, CPs and size of the mesoglobules, are not substantially influenced by PETEGA molecular weight. Insensitivity to molecular weight variations can be considered advantageous as far as applications of PETEGA homopolymers as templates or for packaging of large biomacromolecules such as DNA or proteins are envisaged. The presence of additives is an effective instrument to influence the properties of the materials. By adding an anionic surfactant (SDS) in fixed amounts, the CPs increased by 4–6 °C and the mesoglobules were tuned to desirable dimensions. In further studies, the development of vectors for delivery and release of DNA or other biologically active molecules, hollow nano-spheres, and DNA nano-traps based on PETEGA are planned.

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