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ORIGINAL PAPER

Nanosized colloidal particles from thermosensitive poly(methoxydiethyleneglycol methacrylate)s in aqueous media

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Abstract The formation of well-defined colloidal particles (mesoglobules) from the thermosensitive polymer poly(methoxydiethyleneglycol methacrylate) was observed in dilute aqueous solutions (0.5–1.0 g/L) by turbidimetry and dynamic light scattering (DLS). DLS measurements were performed at 70 °C and showed a strong influence of polymer molecular weight: the hydrodynamic diameters of the mesoglobules increased from ca. 160 to 330 nm with a relatively small, i.e., from 6,400 to 14,000, increase in molecular weight. The addition of sodium dodecyl sulfate (SDS) at surfactant/polymer ratios (*s*/*p*, g/g) ranging from 0.3 to 0.5 practically inhibited the clouding of the solutions as the initial transmittance decreased by only 10–30%. Furthermore, a dramatic shift of the original cloud point values taken as a 10% decrease in transmittance, by approximately 20–60 °C was registered upon the surfactant addition. The presence of SDS resulted in size reduction by 52–90% as indicated by DLS.

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Introduction

A class of water-soluble thermosensitive polymers exhibits a lower critical solution temperature (LCST), at which the individual polymer chains undergo a coil-to-globule transition as a result from dehydration of the chains due to worsening of the thermodynamic quality of water as a solvent. Thus, the formed polymeric globules quickly aggregate, ultimately resulting in the appearance of a macroscopic phase separation. Typical LCST polymers are poly(*N*-isopropylacrylamide) (PNIPAm), poly(propylene oxide), polyoxazolines, poly(oligoethyleneglycol (meth)acrylate)s, and many others [1]. However, conditions can be found, at which well-defined colloidal globular aggregates of low size dispersity and dimensions ranging from tens to hundreds of nanometers are formed instead of macrophase separation. These aggregates, referred to as *mesoglobules* [2], in particular have been extensively investigated for development of intelligent applications in nanotechnology and biotechnology including gene and drug delivery.

The most studied LCST polymer so far is PNIPAm. The reason is not only that PNIPAm is commercially available and displays an LCST that is close to body temperature; its LCST has been shown to be slightly sensitive to environmental conditions such as pH, concentration, chemical environment, etc. For PNIPAm, below the overlapping polymer concentration, colloidal mesoglobules of spherical shape are reportedly formed [1, 2]. Moreover, mesoglobules of low size dispersity and dimensions ranging from 50 to 200 nm can form even at higher polymer concentrations [3, 4]. The size of mesoglobules could be effectively controlled by the polymer concentration and the rate of heating of the polymer solution. In general, smaller aggregates are formed at lower concentrations and/or faster heating rates [3, 4]. The presence of surfactants has also been reported to decrease the size of mesoglobules [5].

A promising alternative to PNIPAm are various poly(meth)acrylates possessing rather short oligo(ethylene glycol) side chains [6–9]. Their LCSTs and, in general, aqueous solution properties can be tuned by varying the length of the side chains or by copolymerizing monomers with different numbers of pendant ethylene oxide units. These (co)polymers typically exhibit a narrower transition than that of PNIPAm and almost lack of hysteresis during heating–cooling cycles [10] Recently, we have shown that well-defined mesoglobules from LCST polymers are attractive as templates for formation of nanoparticles containing cores of different natures, hollow nanospheres and for preparation of nanocapsules, intended for delivery of bioactive molecules [11]. The formation of nanotemplates from thermosensitive polymers is a relatively unexplored field and only examples for PNIPAM and poly(ethoxytriethylene glycol acrylate)s (PETEGA) exist up to date [10, 12].

In the present contribution, we explore the possibilities for formation of nanotemplates from another thermosensitive polymer—poly(methoxydiethylene-glycol methacrylate) (PDEGMA). The latter has an LCST of around 25 °C, regardless polymer's molecular weight, i.e., PDEGMA like PNIPAM and PETEGA is also type II LCST polymer [10]. The formation of mesoglobules was observed by turbidimetry and dynamic light scattering (DLS) of aqueous solutions of PDEGMA in the molecular weight range from 6,400 to 14,000 in the absence or in the presence of sodium dodecyl sulfate (SDS).

Experimental

Materials

Deionized water was obtained by Millipore MilliQ system. Sodium dodecyl sulfate (SDS, 98.5%, Aldrich), 1-methoxy-3-(trimethylsilyloxy)-2-methyl-1-propene (MTS, 99.9+%, ABCR, Karlsruhe, Germany), calcium hydride (CaH_2, 99.99 %, Aldrich), activated neutral aluminum oxide (Al_2O_3, Aldrich), sodium metal (Na, ≥99%, Aldrich), and potassium metal (K, ≥99%, Aldrich) were used as received.

Methoxydiethyleneglycol methacrylate (DEGMA, Aldrich, 99%) was activated by passing through an aluminum oxide column. After flushing with argon, it was stored over CaH_2 degassed and distilled under high vacuum. The initiator MTS was degassed by three freeze–pump–thaw cycles prior to use.

Tetrahydrofuran (THF, ≥99.9%, Adrich) was refluxed over potassium and distilled in a two-step distillation still. After degassing, the solvent was stirred over Na/K alloy and distilled in vacuo prior to use.

The catalyst trisdimethylaminosulfonium bifluoride (TAS HF_2) was prepared according to the literature procedure [13].

Polymerization of DEGMA

PDEGMA was synthesized by group transfer polymerization (GTP) under TAS HF_2 catalysis at room temperature. Molar masses of the final polymers were controlled by the monomer to initiator ratio. The polymerization was performed in an Argon-filled glove box (MBraun, Garching, Germany) at room temperature. Typically, 5 mL (5.1 g, 27.1 mmol) of DEGMA monomer and an appropriate amount of the initiator MTS (Table 1) were dissolved in 50 mL THF. The polymerization was started by addition of 5 mL of TAS HF_2 solution in THF (concentration 10^{-4} mol/L). After 3 h reaction time, the polymerization was terminated with methanol and the obtained polymer was precipitated in heptane.

Table 1 Molecular weight properties of PDEGMA

#	[DEGMA]/[MTS]	M_n	PDI
PDEGMA-5K	27.65	6,400	1.5
PDEGMA-10K	55.31	11,400	1.4
PDEGMA-15K	79.71	14,000	1.4

Preparation of mesoglobules

PDEGMA mesoglobules were formed in situ in deionized water, at temperatures higher than 25 °C. For DLS measurements, 3 mL aqueous solution of molecularly dissolved polymer (at temperatures below 25 °C) with appropriate concentration was added to 6 mL milliQ water at 70 °C.

Methods

Size exclusion chromatography (SEC)

SEC measurements were performed at room temperature in THF using 5 μ PSS SDV gel columns (10^2, 10^3, 10^4, 10^5 Å, 8 × 300 mm each, PSS GmbH, Mainz, Germany) at a flow rate of 1.0 mL/min (VWR-Hitachi 2130 pump). A Waters 2410 refractive index detector ($\lambda = 930$ nm) was used for concentration detection. Samples were injected employing a Waters 717 autosampler (injection volume 50 μL). To compensate for flow-rate fluctuations, 20 ppm 2,6-di-*tert*-butylhydroxytoluene (BHT) was added as internal standard to each sample. Raw data were processed using PSS WinGPC Unity software package. Elugrams are flow-rate corrected; poly(methyl methacrylate) calibration was used to calculate the apparent molecular weight distribution and the corresponding averages.

Dynamic light scattering (DLS)

DLS measurements were performed on a Brookhaven BI-200 goniometer with vertically polarized incident light of wavelength $\lambda = 633$ 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 ($c = 0.5$ g/L) were made at an angle of 90° to the incident beam at 70 °C. The autocorrelation functions were analyzed by the constrained regularized CONTIN method to obtain the apparent hydrodynamic diameters, D_h [14]. DLS measurements were also carried out on a Zetasizer Nano-ZS instrument (Malvern Instruments), equipped with a He–Ne laser ($\lambda = 633$ nm) with a scattering angle of 173°.

Turbidimetry

Cloud points of 0.5 and 1.0 g/L 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 thermocontroller with a stability of $\leq$0.05 °C. The temperature range was from 10 to 85 °C and heating/cooling rates were 1 °C/min.

Results and discussion

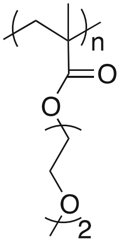
Synthesis of PDEGMA polymers

Controlled polymerizations of methoxydiethyleneglycol methacrylate, DEGMA, and its mono- and trisethyleneglycol analogs have been reported employing an anionic polymerization route. Ishizone et al. investigated the influence of various counterions and additives on the molar mass distribution as well as tacticity and even accomplished the synthesis of a polystyrene-*b*-PDEGMA block copolymer by sequential monomer addition technique [15–17, 22]. The similarity of their findings to an anionic polymerization of *tert*-butyl methacrylate indicated the possibility, that DEGMA could be polymerized using a group transfer mechanism (GTP) [18–20] which circumvents the necessity to work at low temperatures. Despite the polymerization of *tert*-butyl methacrylate (*t*BMA) via anionic polymerization is a straightforward process; reports on the synthesis of P*t*BMA via GTP are scarce. Doherty and Müller [21] reported that the GTP of *t*BMA could only be accomplished, if the trisdimethylaminosulfonium bifluoride (TAS HF_2) catalyst is repeatedly added during the reaction. Based on their results, DEGMA was polymerized in the presence of the same catalyst; however, TAS HF_2 was solely added to initiate the polymerization.

The results of the polymerization are compiled in Table 1. Molecular weights can be controlled by variation of the monomer to initiator ratio; the polydispersity indices in the range of 1.5 indicate some deviations from an idealized GTP process.

Turbidity measurements

PDEGMA is a low T_g (−40 °C)[22] thermosensitive polymer with a hydrophobic aliphatic backbone surrounded by hydrophilic diethylene glycol pendant chains (Scheme 1). The sigmoidal turbidity curves of PDEGMA in water in the absence of SDS were abrupt with a decrease of transmittance window of approx. 5 °C (Fig. 1a, c). The heating and cooling curves were very close and almost overlapped in a similar fashion as in the aqueous solutions of PETEGA at similar experimental conditions [10]. The cloud point (CP) values of aqueous PDEGMA solutions with or without added surfactant (SDS) were determined as the point at which the transmittance decreased by 10%. They are collected in Table 2. As seen from Table 2, the CPs were not significantly influenced by concentration or molecular weight variations of the polymers, which confirmed that PDEGMA is a type II LCST polymer. The CP value



Scheme 1 Structure formula of PDEGMA

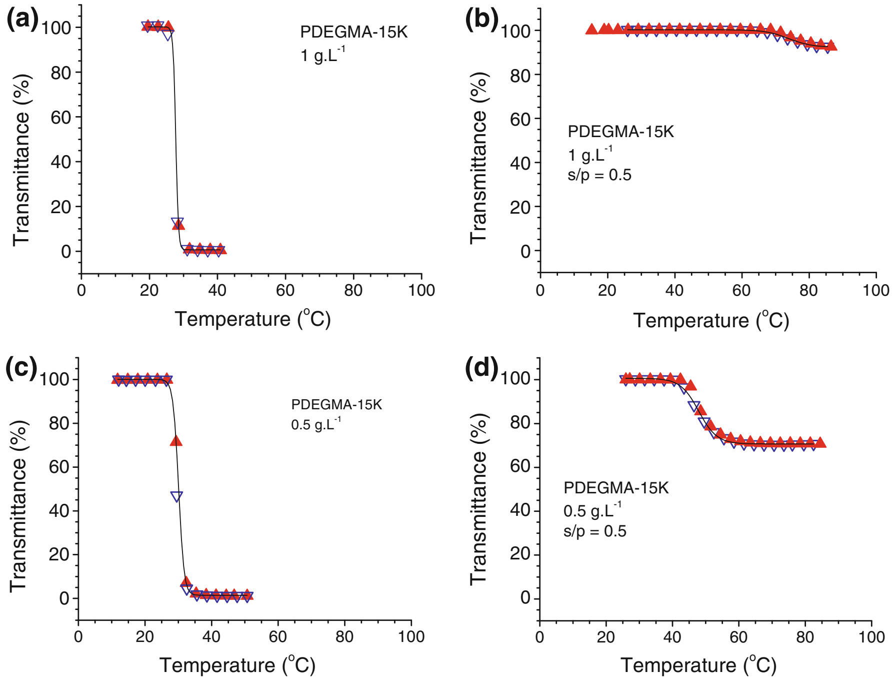


Fig. 1 Turbidity curves for **a** PDEGMA-15K, 1 g/L, **b** PDEGMA-15K, 1 g/L in the presence of SDS, *s*/*p* = 0.5 (g/g), **c** PDEGMA-15K, 0.5 g/L, **d** PDEGMA-15K, 0.5 g/L in the presence of SDS, *s*/*p* = 0.5 (g/g). *Filled triangles* are data points for heating cycle, *hollow triangles* are data points for cooling

Table 2 Cloud points of PDEGMA aqueous solutions

No.	Sample #	Concentration (g/L)	Surfactant/ polymer (*s*/*p*) (g/g)	CP (°C)	Reported CP (°C)
1.	PDEGMA-5K	1.0	0.0	29	21 [24]
2.	PDEGMA-10K	1.0	0.0	26	–
3.	PDEGMA-15K	1.0	0.0	26	27 [22]
4.	PDEGMA-15K	1.0	0.5	85[a]	–
5.	PDEGMA-15K	0.5	0.0	26	–
6.	PDEGMA-15K	0.5	0.5	45[b]	–

[a] Solutions were not completely cloudy, transmittance decreased to 90%

[b] Solutions were not completely cloudy, transmittance decreased to 70%

of PDEGMA-15K agreed very well with values already reported in the literature (Table 2), whereas a difference as high as 8 °C was observed for PDEGMA-5K when compared to PDEGMA of $M_n = 6{,}000$ and PDI = 1.3 [22]. CP values from the literature are for higher molecular weights of $M_n = 37{,}000$, PDI = 1.08 and $M_n = 31{,}000$, PDI = 1.48 are 26 and 25 °C, respectively [22, 23].

The addition of SDS to aqueous solutions of PNIPAm [11] and PETEGA [10, 12] has been shown to shift the original clouding curves to higher temperatures; the initially transparent solutions eventually turned into milky white dispersions with practically zero transmittance. In contrast, the addition of the same surfactant at the same quantities (hereinafter expressed as a surfactant-to-polymer, *s*/*p*, w/w ratio) to aqueous solution of PDEGMA did not result in appearance of strong opalescence upon increasing temperature (Fig. 1b, d). Instead, formation of stable colloidal aggregates of presumably sub-micron dimensions up to temperatures as high as 85–90 °C was observed. For example, the transmittance versus temperature curve for PDEGMA-15K at $c = 1$ g/L and $s/p = 0.5$ started to decrease at about 65 °C and up to the upper temperature limit of our experiments (85 °C) only a 10% decrease in transmittance was registered (Fig. 1b). This temperature was taken as a CP (Table 1). At the same *s*/*p* ratio but lower polymer concentration and, consequently, lower overall SDS content, the onset of transmittance decrease was shifted to lower temperatures—42 versus 65 °C—and more pronounced decrease in transmittance—90 versus 70%—was observed (Fig. 1b, d). CP of 45 °C was determined for that sample (Table 2). The difference between the two experiments is most likely due to the lower overall concentration of SDS, which solubilizes the PDEGMA chains and prevents them from collapsing with each other. The lack of hysteresis during the heating–cooling cycles regardless on the presence of SDS is noteworthy as well. The peculiar behavior in the presence of SDS, in particular, the substantial increase of CPs and insignificant to slight decrease in transmittance is so far unique for PDEGMA and, to the best of our knowledge, has not been reported elsewhere neither for the investigated concentration region nor for other LCST polymers.

Dynamic light scattering (DLS)

The DLS measurements of the aqueous dispersions were done at 70 °C, since at this temperature the formation of a thin cross-linked shell on the surface of nanotemplates based on thermosensitive or ionic (co)polymers is typically performed [12]. The polymer concentration was fixed at 0.5 g/L. The presence of a surfactant, in particular SDS, has been very important in controlling the size of the nanotemplates or mesoglobules in general aspect. Therefore, two *s*/*p* ratios—0.3 and 0.5—corresponding to overall SDS concentrations of 0.15 and 0.25 g/L, respectively, were explored. Figure 2 shows size distribution of PDEGMA mesoglobules obtained from the three polymers via abrupt heating of presumably molecular solutions (see "Experimental" section). The distributions were invariably monomodal and relatively narrow (<0.1), corresponding to average hydrodynamic diameters (D_h) of mesoglobules of 163, 185, and 329 nm for PDEGMA-5K, PDEGMA-10K, and PDEGMA-15K, respectively (Table 3). Similar to other systems [2–4, 10–12], the D_hs of PDEGMA mesoglobules were found to increase with increasing molecular weight of the polymers. While for PETEGA polymers, for example, the effect of molecular weight within the range from 7,000 to 40,000 was not obvious [10], the striking result for PDEGMA is the substantial increase in dimensions within considerable narrower molecular weight interval. We can assume

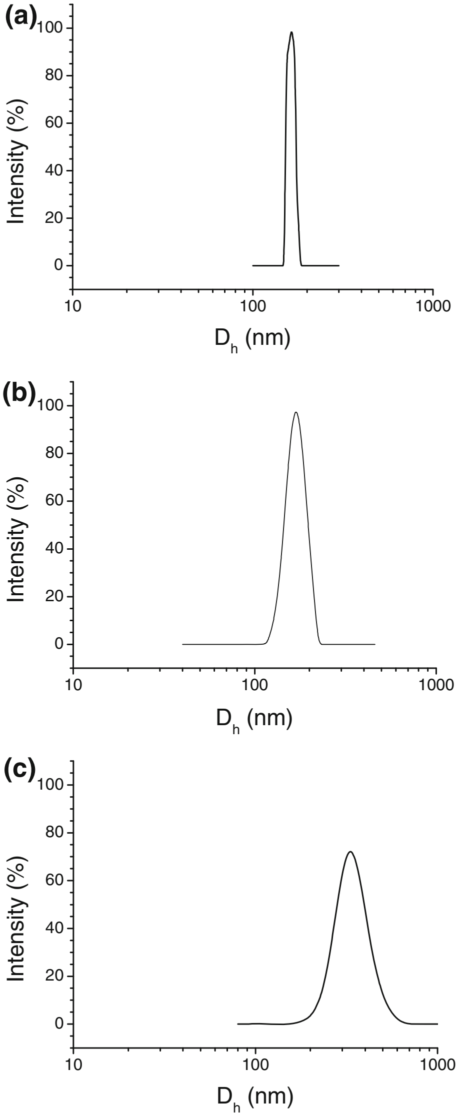


Fig. 2 Typical DLS diameter distributions of mesoglobules obtained from **a** PDEGMA-5K, **b** PDEGMA-10K, and **c** PDEGMA-15K. Polymer concentration $c = 0.5$ g/L, temperature of preparation and measurements 70 °C

that the more hydrophobic nature of PDEGMA compared to PETEGA (2 vs 3 EO units in the side chains and polymethacrylic versus polyacrylic backbone) is behind the well documented more pronounced molecular weight dependence of mesoglobule dimensions.

The added SDS had a dramatic effect on the mesoglobules dimensions as well. For all PDEGMA polymers at the two *s*/*p* ratios studied (0.3 and 0.5 at polymer concentration of 0.5 g/L) the particle size distributions remained monomodal, as exemplified in Fig. 3 for PDEGMA-15K at *s*/*p* 0.5, which indicated the existence of only one population of particles implying that all SDS molecules are effectively

Table 3 Hydrodynamic diameters of mesoglobules prepared from PDEGMA polymers of different molecular weights and at SDS-to-polymer (*s*/*p*) ratios of 0.3 and 0.5

#	D_h (nm)	D_h (nm) $s/p = 0.3$[a]	D_h (nm) $s/p = 0.5$[a]
PDEGMA-5K	163	78 (52)	22 (86)
PDEGMA-10K	185	82 (56)	24 (87)
PDEGMA-15K	329	100 (70)	32 (90)

Polymer concentration $c = 0.5$ g/L, temperature of preparation and measurements 70 °C

[a] Size reduction in % is given in parenthesis

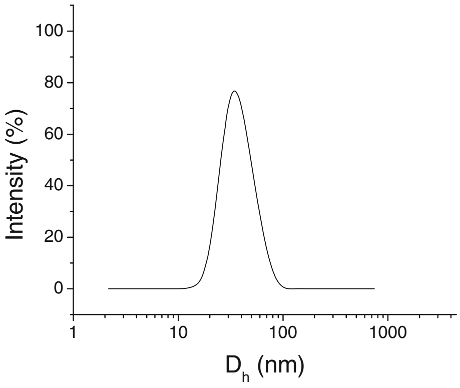


Fig. 3 Size distribution of mesoglobules obtained from PDEGMA-15K in the presence of SDS at *s*/*p* ratio of 0.5. Polymer concentration $c = 0.5$ g/L, temperature of preparation and measurements 70 °C

bound to the mesoglobules. Since the overall SDS content is below the critical micellization concentration, we can presume unimer binding, rather than micellar binding, of SDS to hydrophobic sites of PDEGMA macromolecules and collective formation of mesoglobules, which resemble a polyelectrolyte type polymer–surfactant complex. In these particles, the repulsive intra-particle electrostatic interactions between SDS molecules become dominant and increasingly pronounced with increasing SDS content, respectively, *s*/*p* ratio, so that the system would relax with formation of more curved, respectively, smaller in size, structures. Indeed, as evidenced by Table 3, a substantial (52–90%) particle size reduction was observed. The formation of considerably smaller mesoglobules in the presence of SDS is in line with the turbidimetric curves showing only slight decrease in transmittance at elevated temperatures.

Conclusions

The thermal behavior of well-defined PDEGMA homopolymers of molecular weight ranging from 6,400 to 14,000 was investigated in dilute aqueous solutions. The polymers exhibit LCST properties with sharp and reversible transitions within a narrow temperature window and lack of hysteresis. They are molecularly dissolved below the transition and form stable nanosized mesoglobules above it. The cloud point values (26–29 °C) were insensitive to molecular weight variations in contrast to mesoglobule dimensions, which were found to strongly increase with increasing molecular weight. The addition of small quantities of anionic surfactant (sodium dodecyl sulfate, SDS) did not compromise the (lack of) hysteresis in the heating–cooling cycles but had a strong effect on the (i) CP values which were found to shift to higher temperatures by tens of degrees; (ii) macroscopic phase separation which was completely inhibited as the transmittance of the dispersions showed only a slight decrease; and (iii) mesoglobule dimensions which displayed reduction up to 90%. To the best of our knowledge, such strong influence of polymer molecular weight and surfactant addition has not been reported for other LCST polymers.

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