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Synthesis and self-association in aqueous media of poly(ethylene oxide)/poly(ethyl glycidyl carbamate) amphiphilic block copolymers

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Abstract

New temperature sensitive AB, ABA, and BAB amphiphilic block copolymers consisting of hydrophilic poly(ethylene oxide) and hydrophobic poly(ethyl glycidyl carbamate) blocks were synthesized by anionic polymerization followed by chemical modification reactions. The self-association of the block copolymers in aqueous media was studied by UV–vis spectroscopy and dynamic and static light scattering. The obtained block copolymers spontaneously form micelles in aqueous media. The critical micellization concentration varied from 0.5 to 4 g/L depending on the copolymer architecture and composition. The influence of the temperature upon the self-association of the block copolymers was investigated. The increase of temperature did not affect the value of the critical micellization concentration, but led to the formation of better defined micelles with narrow size distribution.

Keywords: Anionic polymerization; Polyethers; Amphiphilic block copolymers

1. Introduction

The self-association of amphiphilic block copolymers in aqueous media is an entropy driven process, which in the majority of cases leads to formation of spherical micelles comprising hydrophobic core and hydrophilic shell [1,2]. The most extensively studied is the micellization of block copolymers of hydrophilic poly(ethylene oxide)—PEO and hydrophobic polyoxiranes such as poly(propylene oxide)—PPO or poly(butylene oxide)—PBO [3,4]. In the case of PEO–PPO copolymers, the micellization is a temperature dependent process [5,6], as PPO exhibit the lower critical solution temperature at a relatively low temperature [7,8]. In the majority of cases, the temperature is typically not so important for the micellization of PEO–PBO block copolymers [3,9]. For some copolymer architectures and compositions even athermal micellization was observed [10,11].

Polyglycidol—PG is a polyoxirane that carries one primary hydroxyl functional group per monomeric unit and resembles PEO by its hydrophilicity. Well defined linear polyglycidol polymers have been obtained by anionic polymerization of ethoxyethyl glycidyl ether—EEGE followed by successive mild cleavage of the protective ethoxyethyl group [12]. In recent years, various polyglycidol based random [13], block [14], star-block [15], brush-like [16], and arborescent [17–21] copolymers have been synthesized.

The hydroxyl functionality of PG opens versatile synthetic routes of selective chemical modification leading to new materials of desired physicochemical properties. Up to now only few modifications of the hydroxyl groups of the glycidol monomeric units have been performed. High molar mass PEO–PG block copolymers were modified with stearic acid aiming for rheology builders [22]. Superabsorbing hydrogels were obtained after chemical cross-linking of hydrophilic PEO–PG triblock copolymers [14,23]. Temperature sensitive copolymers with controllable cloud points have been achieved by tuned hydrophobization of high molar mass polyglycidol or PG–PEO–PG block copolymers [13,24].

Block copolymers of ethylene oxide—EO and glycidol—G of different architecture are suitable precursors for new class amphiphilic block copolymers when the hydrophilic groups of the glycidol units are reacted with hydrophobic compounds. In the present article, we investigate the synthesis of well defined di- and triblock copolymers of EO and ethyl glycidyl

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carbamate—EGC of different hydrophilic/hydrophobic balance. Their self-association properties in aqueous media is studied as a function of temperature by using UV–vis spectroscopy and dynamic and static light scattering.

2. Experimental

2.1. Materials

All solvents were purified by standard methods. $CsOH \cdot H_2O$ 99.5% (Aldrich) and *t*-BuOK 97.0% (Aldrich) were used as received. Diethylene glycol—DEG (Aldrich) was distilled under reduced pressure prior to use. Poly(ethylene glycol)—PEG of $\bar{M}_n = 12{,}000$ g/mol and $\bar{M}_w/\bar{M}_n = 1.03$ (Aldrich) and poly(ethylene glycol)monomethyl ether—MPEG of $\bar{M}_n = 11{,}000$ g/mol and $\bar{M}_w/\bar{M}_n = 1.02$ (Polysciences) were precipitated in hexane. Ethoxyethyl glycidyl ether was synthesized according to procedure described elsewhere [25] and purified by vacuum distillation. Fractions of purity exceeding 99.8% (GC) were used for polymerizations. Ethylene oxide (Aldrich) was kept over CaH_2 and distilled under vacuum prior to polymerization. Dibuthyltin dilaurate 95% (Aldrich) and ethyl isocyanate 98% (Aldrich) were used as received.

2.2. Synthesis of block copolymers

2.2.1. Synthesis of di- and triblock copolymers

Cesium alkoxides of PEG and MPEG were used as initiators for the polymerization of EEGE in order to obtain copolymers of $EEGE_nEO_mEEGE_n$ and $EEGE_nEO_m$ architectures. Details are given elsewhere [14].

Block copolymers—$EO_mEEGE_nEO_m$ were obtained using sequential polymerization of EEGE and EO initiated by potassium alkoxide of diethylene glycol. Schlenk tube equipped with teflon seals, teflon sealed ampoules and high vacuum (10^{-4} bar) were used for the polymerizations. Stock solution of *t*-BuOK (0.026 g, 2.3×10^{-4} mol) in 10 mL of DMSO was prepared at room temperature in a calibrated ampoule. 1.4 mL of the stock solution containing 3.34×10^{-5} mol *t*-BuOK was added dropwise under vacuum to the polymerization ampoule containing diethylene glycol (0.125 g, 1.18×10^{-3} mol) dissolved in another 5 mL of DMSO. The reaction mixture was stirred at room temperature and occasionally slightly heated for 1 h under vaccum in order to remove the released *t*-BuOH. The EEGE monomer (6.8 g, 4.7×10^{-2} mol or 13.7 g, 9.4×10^{-2} mol for $DP_{EEGE} = 40$ and $DP_{EEGE} = 80$, respectively), was added and the polymerization continued for 48 h at 60 °C. After taking a sample for analysis, the temperature was lowered to 0 °C and EO (12.5 mL, 0.25 mol) was transferred under vacuum to the ampoule. The EO was polymerized initially at room temperature (24 h), then at 40 °C (48 h) and finally at 65 °C (24 h).

2.2.2. Deprotection of the ethoxyethyl groups

EO/EEGE copolymer was dissolved in acetone (polymer concentration was 150 g/L). Oxalic acid dissolved in water was added and after 1 h of stirring at room temperature the reaction mixture was neutralized with aqueous solution of $Ca(OH)_2$. The molar ratio [EEGE]:[oxalic acid]:[$Ca(OH)_2$] was 1:0.5:1. The suspension formed by insoluble calcium oxalate was removed by filtration and the polymer solution was concentrated under reduced pressure. The polymer was dialyzed against deionised water. The resulting EO/G copolymers were dried under reduced pressure at 50 °C.

2.2.3. Chemical modification of copolymers of ethylene oxide and glycidol with ethyl isocyanate

While maintaining dry conditions, ethyl isocyanate was added to a DMF solution of EO/G block copolymers and dibutyltin dilaurate (DBTL) catalyst at room temperature (polymer concentration in DMF was 150 g/L). The molar ratio [glycidol units]:[DBTL]:[ethyl isocyanate] was 1:0.02:2. The reaction leading to block copolymer of ethylene oxide and ethyl glycidyl carbamate was carried out at 40 °C for 48 h. DMF was exchanged with water via dialysis for 12 h. The water was evaporated under vacuum. The residue was dissolved in small amount of methylene chloride and precipitated in diethyl ether. After several precipitation procedures the final product was dried under vacuum.

2.3. Measurements

2.3.1. NMR

^1H NMR spectra were recorded at 25 °C on a Varian Unity-Inova spectrometer operating at 300 MHz. $CDCl_3$ and D_2O were used as solvents.

2.3.2. Size exclusion chromatography (SEC)

The setup for SEC measurements consisted of differential refractive index detector Δn-1000 RI WGE DR Bures and a multiangle laser light scattering (MALLS) detector DAWN EOS from Wyatt Technologies. Four PSS SDV columns of nominal pore sizes 1×10^5, 1×1000, 2×100 Å were used for measurements in THF. THF was used as a mobile phase in the case of homopolymers of EO, EEGC, EGC and their block copolymers. Also four PSS GRAM columns of nominal pore sizes 1×3000, 1×1000, 1×100, and 1×30 Å were used for measurements in DMF with 5 mmol/L LiBr. DMF was used as a mobile phase in the case of PG and its block copolymers with EO. Measurements were preformed at 30 °C for THF and at 45 °C for DMF/LiBr. The nominal flow rate of the eluent was 1 mL/min. The specific refractive index increment (d*n*/d*c*) of polymer samples was measured at 30 °C using a differential refractive index detector Δn-1000 RI WGE DR Bures from Wyatt Technologies. SEC results were collected and evaluated by ASTRA software from Wyatt Technologies and WINGPC software from PSS.

2.3.3. Dynamic light scattering (DLS)

DLS 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 were made at angles from 40 to 140° to the incident beam at different temperatures. The autocorrelation functions from DLS were analyzed by the constrained regularized CONTIN method [26] to obtain distributions of decay rates (Γ). The decay rates gave distributions of apparent diffusion coefficient ($D_{\mathrm{app}}=\Gamma/q^2$, where q is the magnitude of the scattering vector $q=(4\pi n/\lambda)\sin(\Theta/2)$). The mean hydrodynamic radii were obtained by the Stokes–Einstein equation:

$$R_{\mathrm{h}} = kT/(6\pi\eta D_0) \tag{1}$$

where k is the Boltzmann constant, η is the viscosity of water at temperature T and D_0 is the diffusion coefficient at infinite dilution. The apparent hydrodynamic radii (R_{h}^{90}) obtained at scattering angle $\theta=90°$ were calculated by Eq. (1) where the corresponding apparent diffusion coefficients were used.

2.3.4. Static light scattering (SLS)

SLS measurements were carried out using the Brookhaven instrument described above at angles ranging from 40 to 140° to the incident beam at different temperatures. The SLS data analyses were performed by the Zimm plot software (BI-ZPW) provided from Brookhaven Instruments using the Rayleigh–Gans–Debye equation:

$$\frac{Kc}{R_\theta} = \frac{1}{M_{\mathrm{w}}}\left(1+\frac{R_{\mathrm{g}}^2 q^2}{3}\right) + 2A_2 c \tag{2}$$

where $K \equiv 4\pi^2 n_0^2 (\mathrm{d}n/\mathrm{d}c)^2/N_{\mathrm{A}}\lambda^4$ is an optical parameter with n_0 being the refractive index of toluene, N_{A} is the Avogadro's constant, λ is the laser wavelength (632.8 nm); R_θ is the Rayleigh ratio of the polymer solution at a given angle; $\bar{M}_{\mathrm{w}}$ is the mass-average molar mass of the solute; R_{g} is the radius of gyration and A_2 is the second virial coefficient. The refractive index increment dn/dc for every copolymer was measured in water in separate measurement as described in Section 2.3.2.

2.3.5. Preparation of micellar solutions

Micelles of EO/EGC block copolymers were prepared at 25 °C by direct dissolution in deionized water filtered through 0.02 μm Whatman ANOTOP membrane. An initial stock solution of 20 g/L was diluted in order to obtain a series of solutions with concentrations reaching down to 0.01 g/L. To remove possible dust impurities, the micellar dispersions were filtered through 0.1 μm Whatman PURADISC syringe filters.

2.3.6. Hydrophobic dye solubilization

Aqueous solutions (2 mL) of a block copolymer in the concentration range from 0.01 to 10 g/L were prepared as described above. Twenty microliter of a 0.4 mM solution of a hydrophobic dye 1,6-diphenyl-1,3,5-hexatriene (DPH) in methanol were added to each of the copolymer solutions. Solutions were incubated in the dark for 16 h at 25 °C. The absorbance in the range of $\lambda=300$–500 nm was measured using a Helwett Packard 8452 UV–vis spectrometer at temperature from 25 to 60 °C. Before recording the spectra, the samples were thermostated for 10 min, after which the intensity of the characteristic absorption peak at 356 nm for DPH solubilized in a hydrophobic domain remained constant [5].

2.3.7. Cloud point measurements

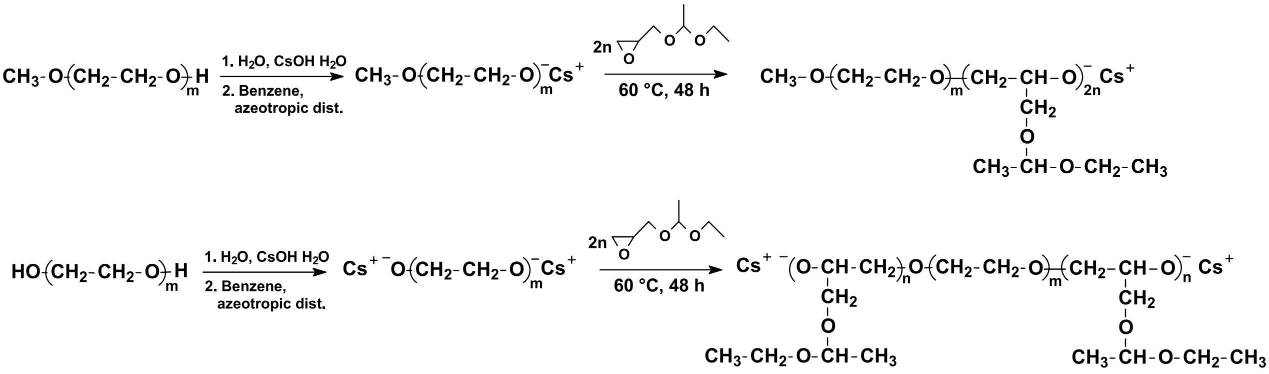
Cloud points (CP) of 10 g/L aqueous copolymer solutions were determined using a Jasco V-530 UV–vis spectrophotometer. The transmittance was measured as a function of temperature at wavelength $\lambda=500$ nm. The cuvette was thermostated by Medson MTC-P1 thermocontroller with a stability of ±0.05 °C. Cloud points were determined as the temperature at which the transmittance was 50%.

3. Results and discussion

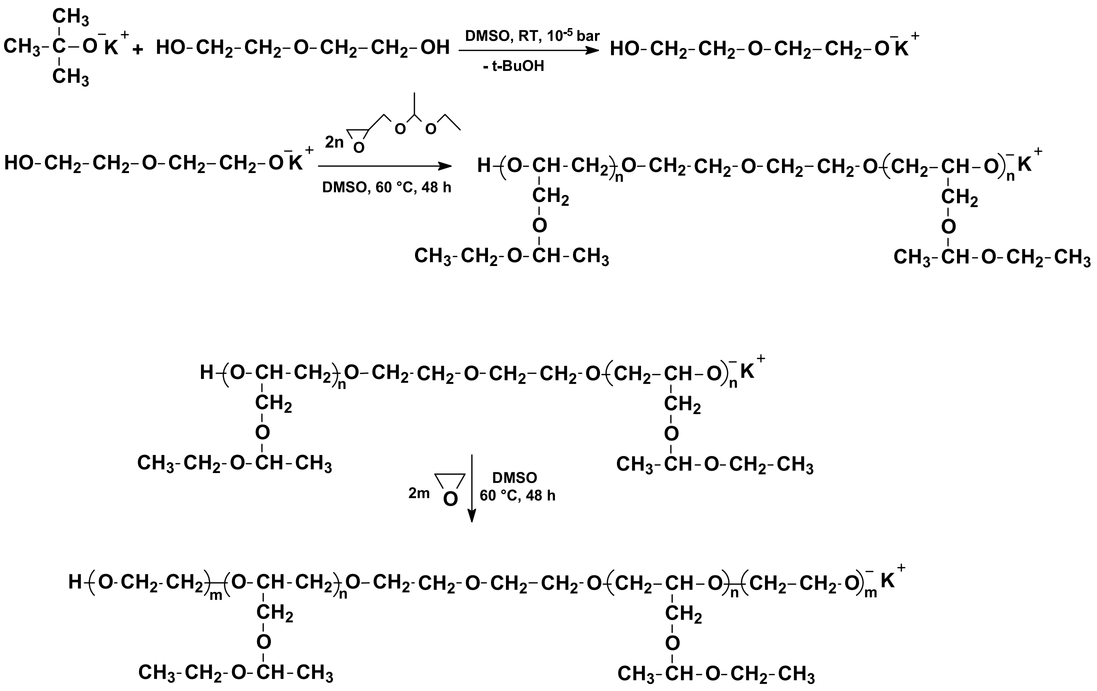
3.1. Synthesis of block copolymers

As described previously [12,14,16], the anionic polymerization of EEGE can be effectively controlled and is close to living. Polymers with predictable degrees of polymerization and narrow molar mass distributions can be obtained. In order to achieve linear block copolymers of three different architectures two anionic polymerization techniques were used.

Poly(ethylene oxide)-*b*-poly(ethoxyethyl glycidyl ether) and poly(ethoxyethyl glycidyl ether)-*b*-poly(ethylene oxide)-poly(ethoxyethyl glycidyl ether) block copolymers were obtained in the bulk polymerization of EEGE initiated



Scheme 1. Synthesis of $\mathrm{EO}_m\mathrm{EEGE}_n$ and $\mathrm{EEGE}_n\mathrm{EO}_m\mathrm{EEGE}_n$ block copolymers.



Scheme 2. Synthesis of $EO_mEEGE_nEO_m$ block copolymers.

by MPEG and PEG cesium alkoxides, respectively, (Scheme 1) [14].

The synthesis of poly(ethylene oxide)-*b*-poly(ethoxyethyl glycidyl ether)-*b*-poly(ethylene oxide) block copolymers requires sequential anionic polymerization of EEGE and EO initiated by a bifunctional low molar mass initiator (Scheme 2). The initiator itself (potassium alkoxide of diethylene glycol) was prepared in a reaction of diethylene glycol and potassium *t*-butoxide, followed by removal of *t*-butanol [17]. In order to keep the initiator soluble in DMSO and therefore, to provide homogeneous conditions for the polymerization of EEGE, only 10% of the hydroxyl groups of diethylene glycol were ionized. The exchange of hydrogen cations between hydroxyl groups is much quicker than the propagation, which allows simultaneous growth of all of the polymer chains.

After quantitative and mild deprotection of the ethoxyethyl groups from the EEGE monomeric units, highly hydroxyl functional EO/G block copolymers of equivalent degrees of polymerization were derived.

The hydroxyl groups of the polyglycidol blocks were reacted with ethyl isocyanate (Scheme 3) to obtain the final amphiphilic block copolymers: AB type—EO_mEGC_n; BAB type—$EGC_nEO_mEGC_n$ and ABA type—$EO_mEGC_nEO_m$.

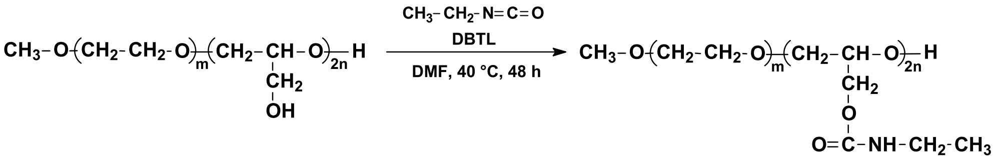
The basic molar mass characteristics from SEC–MALLS and ^1H NMR of the synthesized copolymers are collected in Table 1. The refractive index increments of the block copolymers, needed for the determination of $\bar{M}_n$ by SEC–MALLS, were estimated from the measured values of the corresponding homopolymers and the weight fraction (ϕ) of different blocks by assuming simple additivity:

$$dn/dc = \phi_A(dn/dc)_A + \phi_B(dn/dc)_B \tag{3}$$

The measured d*n*/d*c* values of PEEGE = 0.045 mL/g (THF), PG = 0.054 mL/g (DMF) and PEGC = 0.0796 mL/g (THF) were used for the calculation. d*n*/d*c* for PEO = 0.063 mL/g (THF) or 0.05 mL/g (DMF) were taken from [27].

The SEC chromatograms of precursors (MPEG and PEEGE) and the final copolymers ($EO_{264}EGC_{32}$ and $EO_{108}EGC_{38}EO_{108}$, respectively), are shown in Fig. 1, as an example. At each synthetic stage leading to EO_mEGC_n and EGC_nEO_m-EGC_n block copolymers the peaks obtained from the SEC analysis were narrow and symmetrical. No unreacted PEG or MPEG macrointiator has been left in the system. In the case of $EO_mEGE_nEO_m$ block copolymers, a small tail at the low molar mass region of the chromatograms was observed (Fig. 1(b)) and it was present even after fractional precipitation in hexane and diethyl ether. In no case it made more than 5% of the total yield. It was assumed that the low molar mass impurity was represented by EO rich di- or triblock copolymers.

The chemical composition of the EO/EEGE and EO/G precursor copolymers and the EO/EGC final copolymers was followed by ^1H NMR spectroscopy (Fig. 2).



Scheme 3. Chemical modification of EO/G block copolymers with ethyl isocyanate.

Table 1
Composition and molar masses of the block copolymers

Composition (NMR and SEC)	d*n*/d*c* (mL/g)	$\bar{M}_n$ (NMR)	$\bar{M}_n$ (SEC–MALLS)	$\bar{M}_w/\bar{M}_n$ (SEC–MALLS)
EO_{270}	0.063	–	12,000	1.03
$EEGE_{23}EO_{270}EEGE_{23}$	0.057	18,700	18,600	1.07
$G_{23}EO_{270}G_{23}$	0.051	15,400	15,000	1.04
$EGC_{22}EO_{270}EGC_{22}$	0.070	18,400	17,400	1.04
EO_{264}	0.063	–	11,600	1.02
$EO_{264}EEGE_{32}$	0.058	16,300	16,800	1.02
$EO_{264}G_{32}$	0.050	14,000	13,000	1.02
$EO_{264}EGC_{32}$	0.070	16,000	16,000	1.02
EO_{264}	0.063	–	11,600	1.02
$EO_{264}EEGE_{18}$	0.059	14,500	14,000	1.04
$EO_{264}G_{18}$	0.050	13,000	11,400	1.02
$EO_{264}EGC_{18}$	0.066	14,500	14,600	1.01
$EEGE_{81}$	0.045	–	11,800	1.07
$EO_{125}EEGE_{81}EO_{125}$	0.059	27,600	20,000	1.04
$EO_{125}G_{81}EO_{125}$	0.051	15,000	17,000	1.12
$EO_{125}EGC_{80}EO_{125}$	0.071	27,400	22,000	1.06
$EEGE_{38}$	0.045	–	5500	1.03
$EO_{108}EEGE_{38}EO_{108}$	0.057	15,500	14,000	1.02
$EO_{108}G_{38}EO_{108}$	0.050	13,000	13,400	1.04
$EO_{108}EGC_{38}EO_{108}$	0.069	15,500	15,000	1.02

SEC–MALLS measurements of EO/EEGE and EO/EGC block copolymers were done in THF and of EO/G block copolymers were done in DMF/LiBr.

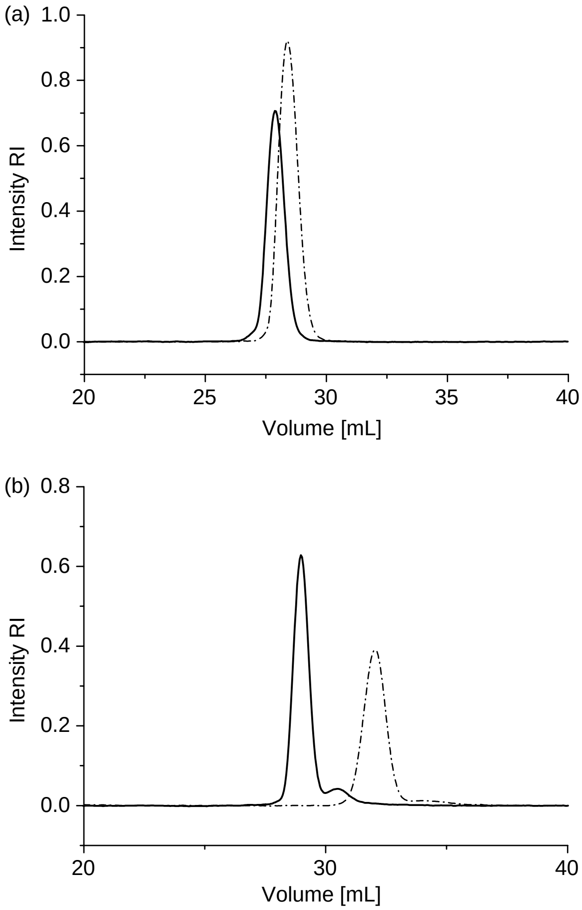


Fig. 1. (a) SEC curves of MPEG precursor (dashed line) and $EO_{264}EGC_{32}$ final block copolymer (black line); (b) SEC curves of PEEGE first block (dashed line) and $EO_{108}EGC_{38}EO_{108}$ final block copolymer (black line) (THF, 1 mL/min).

Molar masses of the final copolymers calculated by ^{1}H NMR were determined from $\bar{M}_n$ of the starting block and copolymer composition measured by NMR. They are in good agreement with SEC–MALLS results.

3.2. Aqueous solution properties of ethylene oxide and ethyl glycidyl carbamate block copolymers

3.2.1. Cloud point measurements

The cloud points of 10 g/L aqueous solutions of block copolymer are collected in Table 2. One can expect that the clouding temperature would depend on the tendency for the formation of intermicellar aggregates, which decreases with increased stability of the micelles. In the case of AB type block copolymers (EO_mEGC_n), which possess the highest ability to form stable micelles [1], the solutions remained clear up to 90 °C, the upper limit temperature of measurements. ABA block copolymers ($EO_mEGC_nEO_m$) clouded at relatively high temperature—above 80 °C and the difference in the EGC units content did not influence the cloud points significantly. Most likely the clouding process in the case of ABA architecture is influenced not only by the hydrophobic effect of the middle block, but also by the dehydration of the PEO chains at such a high temperature.

As seen in Fig. 3, the BAB block copolymer $EGC_{22}EO_{270}EGC_{22}$ underwent a transition at 46 °C, which is much lower than the clouding temperature of $EO_{108}EGC_{38}EO_{108}$ copolymer of similar chemical composition, but ABA architecture. In many cases, BAB block copolymers, which are also sometimes described as 'reverse architecture', form flower-like micelles [28,29]. Depending on the conditions, one or more copolymer macromolecules can participate in more than one micelle, thus forming linked micelles [30] and also higher aggregates [31], which at certain critical dimensions cause the clouding of the solution at much lower temperature than observed for AB and ABA architectures of the same overall ratio of hydrophilic and hydrophobic units.

3.2.2. Micellization studied by hydrophobic dye solubilization

The solubilization of the hydrophobic dye DPH is a convenient and widely used method for determination of the critical micellization concentration (cmc) and the critical micellization temperature (cmt) for a variety of water soluble non-ionic amphiphilic block copolymers [5]. Cmcs of EO/EGC block copolymers were determined from the inflection of the DPH absorption intensity at $\lambda = 356$ nm versus copolymer concentration (Fig. 4(a)) between 25 and 60 °C. It was found that the temperature influenced the cmcs for all of the EO/EGC block copolymers very slightly, and therefore, only values obtained at 25 °C are presented in Table 2. As expected, for a given architecture the cmc is lower for the block copolymer with longer hydrophobic block.

As mentioned above and shown in Fig. 4(a), temperature was not an important factor for the cmc values of the EO/EGC block copolymers. In the case of temperature driven micellization, such as for block copolymers of EO and propylene oxide (PO), a temperature shift of 10 °C usually

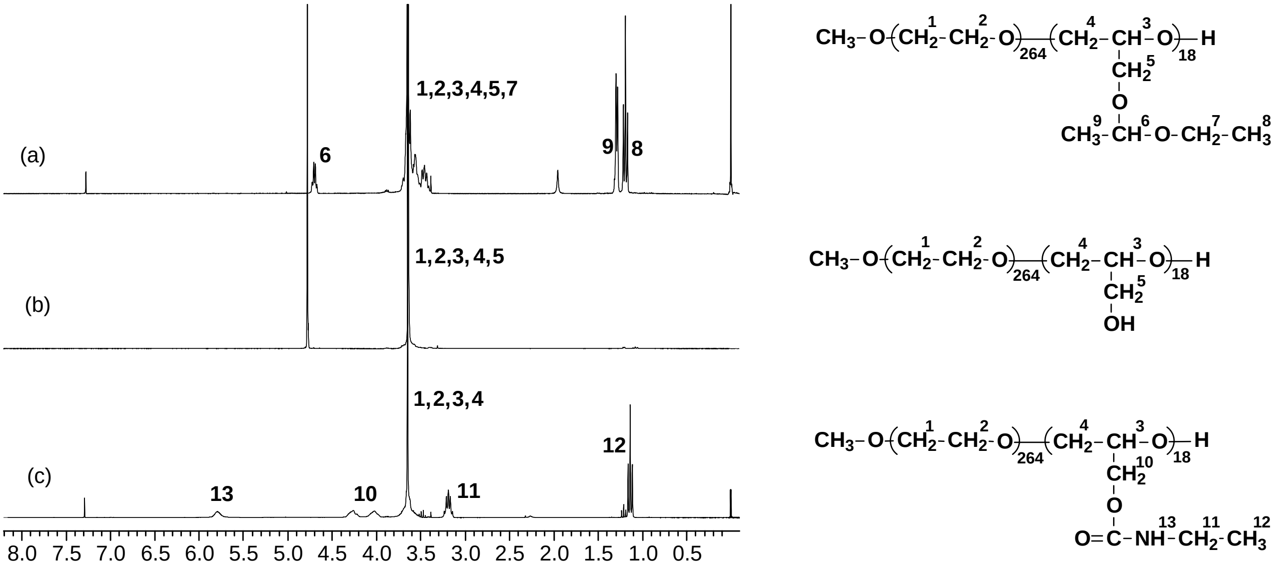


Fig. 2. ^{1}H NMR spectra of (a) initial $EO_{264}EEGE_{18}$ block copolymer (300 MHz, $CDCl_3$), (b) $EO_{264}G_{18}$ precursor, obtained after deprotection reaction of the ethoxyethyl groups of the copolymer 'a' (300 MHz, D_2O) and (c) final $EO_{264}EGC_{18}$ amphiphilic block copolymer (300 MHz, $CDCl_3$).

causes a change of cmc by about one order of magnitude [5] and the standard enthalpy of micellization, ΔH^0_{mic}, quantifing the decrease of cmc with increase of temperature, exceeds 200 kJ/mol [5]. Provided that the aggregation number of the micelles is large and temperature independent, the standard enthalpy of micellization can be obtained from the following equation [3]:

$$\Delta H^0_{\text{mic}} = R\frac{\mathrm{d}\ln(X_{\text{cmc}})}{\mathrm{d}(1/T)} \qquad (4)$$

where R is the universal gas constant, X_{cmc} is the cmc in mole fraction and T is the temperature.

As seen later from SLS results the above mentioned requirements are not fully met for the investigated copolymers. Therefore, the values of ΔH^0_{mic} (Table 2), obtained from the slope of the dependence $\ln X_{\text{cmc}}$ versus $1/T$ (Fig. 4(b)), can be considered as apparent. The values of the apparent enthalpy of micellization, $\Delta H^0_{\text{mic,app}}$, from Table 2 are very low, if compared to conventional temperature sensitive micellar systems. Athermal micellization was observed for copolymer $EO_{108}EGC_{38}EO_{108}$ as $\Delta H^0_{\text{mic,app}}$ approached zero.

Although temperature did not seem to play any significant role for the cmc values of the studied EO/EGC block copolymers, the reorganization in micellar system itself seems to be temperature sensitive. For concentrations above cmc, a transition of the DPH absorption around 40 °C was observed for EO/EGC copolymers, except for $EO_{264}EGC_{18}$ copolymer (an example for $EO_{125}EGC_{80}EO_{125}$ is shown in Fig. 5).

The increase of the absorption at temperatures above 40 °C may be attributed to the increasing number of the hydrophobic domains able to solubilize DPH. This can result either from incorporation of unassociated unimers into micelles or from the increasing hydrophobicity of the environment of the solubilized DPH molecules due to dehydration of the micellar cores. In Section 3.2.3, we attempt to address the importance of each of these possible factors.

3.2.3. Light scattering measurements

Dynamic light scattering. In order to obtain the basic hydrodynamic properties for each of EO/EGC block copolymers DLS measurements in aqueous solutions were performed at 25 and 40 °C for several copolymer concentrations over cmc in the angular region from 40 to 140°. The diffusion coefficients for each concentration were determined as slopes of the linear fit of the relaxation rates Γ versus $\sin^2(\theta/2)$ (Fig. 6(a)). The mean hydrodynamic radii were calculated from Eq. (1) taking $D_{\text{o}} = \lim D_{c\to 0}$ (Fig. 6(b)). DLS results are summarized in Table 3.

The intensity fraction distributions of solutions prepared from samples 1, 3, and 4 from Table 3 are bimodal at 25 °C (Fig. 7).

Table 2
Cloud point and cmc data for EO/EGC block copolymers

No.	Composition	EGC units content (mol%)	CP (°C)	Cmc at 25 °C		$X_{\text{cmc}}\times 10^6$ (mol fr.)	$\Delta H^0_{\text{mic,app}}$ (kJ/mol)
				(g/L)	(mol/L)$\times 10^4$		
1	$EO_{264}EGC_{18}$	6.4	–	4.0	2.8	5.0	n.d.
2	$EO_{264}EGC_{32}$	10.5	–	3.3	2.1	2.0	4.2
3	$EGC_{22}EO_{270}EGC_{22}$	14.0	46	2.4	1.3	2.4	4.8
4	$EO_{108}EGC_{38}EO_{108}$	14.9	84	1.9	1.2	2.2	0
5	$EO_{125}EGC_{80}EO_{125}$	27.6	80	0.5	0.2	0.4	8.7

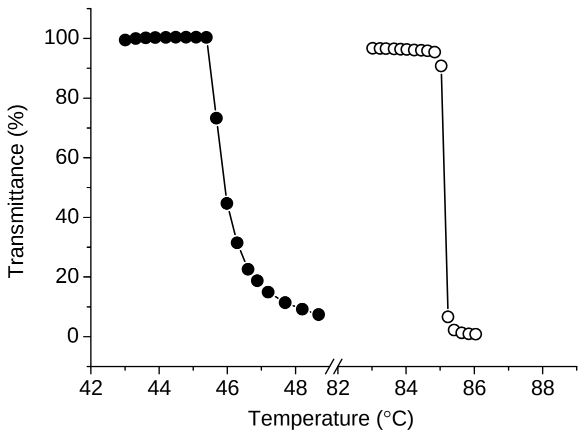


Fig. 3. Transmittance at $\lambda = 500$ nm versus temperature for aqueous solution of $EGC_{22}EO_{270}EGC_{22}$ (filled circles) and $EO_{108}EGC_{38}EO_{108}$ (open circles). Polymer concentration 10 g/L.

In all cases, the observed two modes were diffusive, as judging from the linear dependence of Γ versus $\sin^2(\theta/2)$ passing through the (0,0) point. It was possible to derive R_h values for both types of aggregates (Table 3). Here, we attribute the smaller aggregates to micelles, while the loose, larger aggregates are presumably of non-micellar nature and the origin of the latter is not completely clear. In the case of $EGC_{22}EO_{270}EGC_{22}$ and $EO_{108}EGC_{38}EO_{108}$, the large particles disappeared when solutions were heated to 40 °C (Fig. 7). Having this in mind, it may be suggested that the loose aggregates are formed due to hydrogen bonding mediated by water molecules and the polar carbamate groups from the poly(ethyl glycidyl carbamate) block(s). The association process resulting in loose aggregates was presumably not due

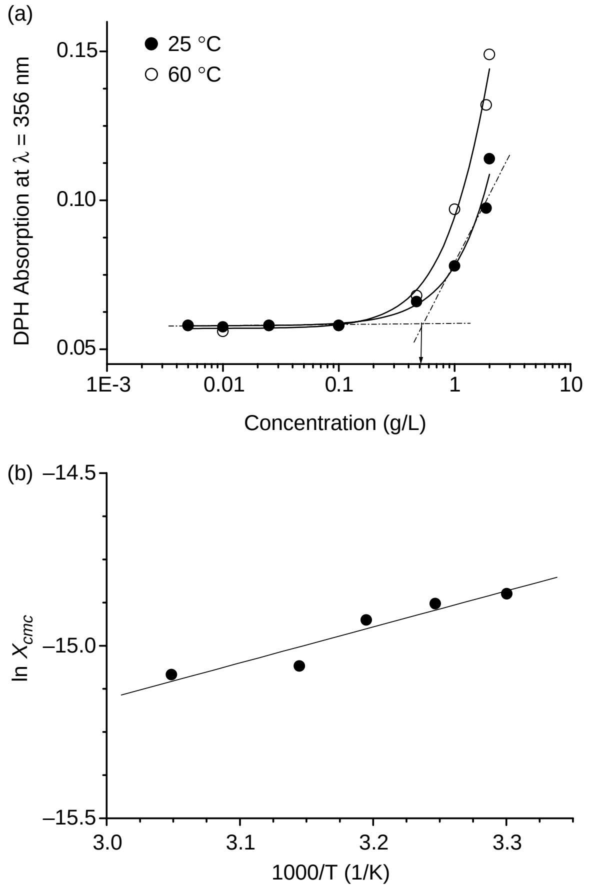


Fig. 4. (a) Cmc curves and (b) cmc in mole fraction (X_{cmc}) as a function of temperature obtained for copolymer $EO_{125}EGC_{80}EO_{125}$.

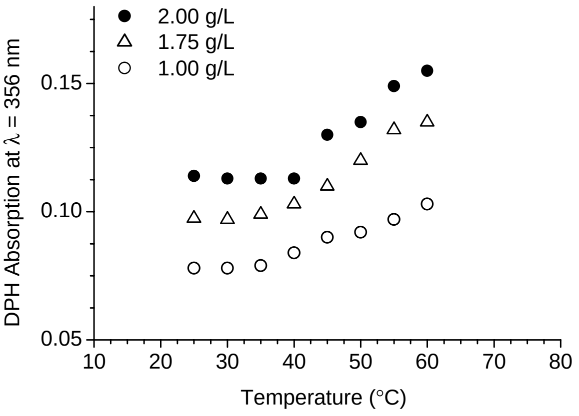


Fig. 5. Temperature dependence of DPH absorbance at 356 nm for $EO_{125}EGC_{80}EO_{125}$ aqueous solutions of 1 g/L (open circles), 1.75 g/L (triangles) and 2 g/L (full circles).

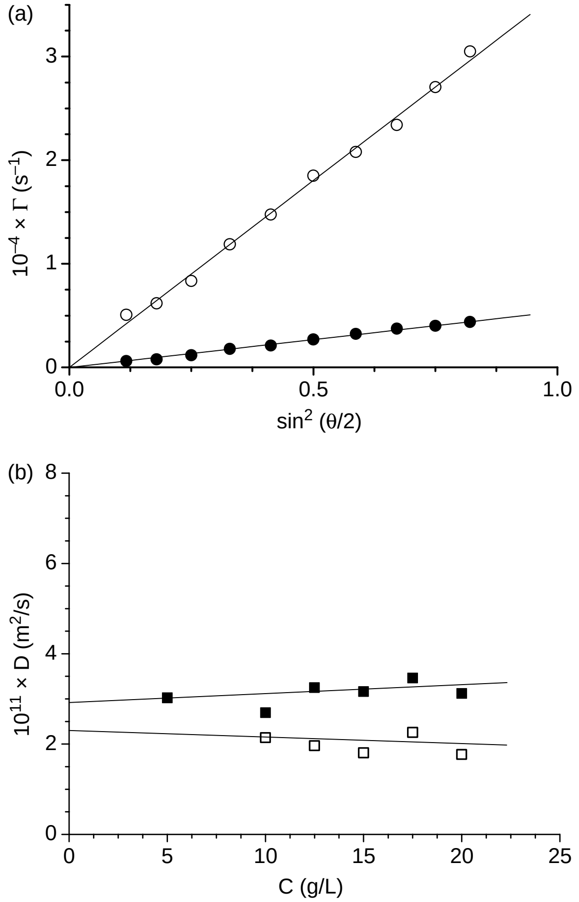


Fig. 6. (a) Relaxation rate (Γ) for fast mode (open circles) and slow mode (full circles) as a function of $\sin^2(\theta/2)$ for 7.5 g/L aqueous solution of $EO_{264}EGC_{18}$ at 25 °C; (b) Concentration dependence of apparent diffusion coefficients for $EO_{264}EGC_{32}$ micelles (fast mode) at 25 °C (open squares) and at 40 °C (squares). The lines through the points are linear fits.

Table 3
DLS results for EO/EGC block copolymers

No.	Composition	EGC units content (mol%)	R_h at 25 °C (nm)	R_h^* at 25 °C (nm)[a]	R_h at 40 °C (nm)
1	$EO_{264}EGC_{18}$	6.4	4	74.0	12.1[b]
2	$EO_{264}EGC_{32}$	10.5	10.8	–	12.6
3	$EGC_{22}EO_{270}EGC_{22}$	14.0	14.8	110.0	15.2
4	$EO_{108}EGC_{38}EO_{108}$	14.9	3.6	30.0	5.3
5	$EO_{125}EGC_{80}EO_{125}$	27.6	9.7	–	10.7

[a] R_h^* denotes the radii of loose, large non-micellar aggregates.
[b] Determined at 70 °C.

to hydrophobic interactions. Moreover, another observation supports the occurrence of hydrogen bonding and the lack of association driven by the hydrophobic interactions. No adsorption of DPH below cmc for $EO_{264}EGC_{18}$ copolymer solutions indicated that there is no hydrophobic environment necessary for solubilization of DPH and thus it was homogeneously solubilized in the sample. At higher temperature the hydrogen bonds break and the released unimeric macromolecules are incorporated into the already existing micelles. Most probably this is the reason for the slight increase of the hydrodynamic radii of the micelles at 40 °C (Table 3). Solutions of the copolymer of the lowest amount of EGC units, $EO_{264}EGC_{18}$ gave monomodal distribution of the intensity fraction distribution at temperatures as high as 70 °C.

Micelles formed by block copolymers of AB and ABA architectures with longer hydrophobic blocks ($EO_{264}EGC_{32}$ and $EO_{125}EGC_{80}EO_{125}$) were larger and their size distributions were monomodal at 25 °C. The increase of the temperature to 40 °C caused only a slight increase of R_h, which may result from an increase of the aggregation number, as confirmed by the SLS data (Section 4).

In order to obtain more detailed information about the temperature induced reorganization in the micellar systems of EO/EGC block copolymers, the intensity of the scattered light at $\theta = 90°$, I^{90} and the apparent hydrodynamic radii, R_h^{90}, were followed for a chosen copolymer concentrations above cmc at several temperatures between 25 and 60 °C. The values of R_h^{90} determined at 25 and 40 °C correlate well with the corresponding mean R_h determined previously.

The apparent hydrodynamic radii of micelles formed by EO_mEGC_n and $EO_mEGC_nEO_m$ block copolymers gradually increased up to 40 °C, after which the radii remained constant until the upper temperature of measurements (Fig. 8(a)). This is not observed only for $EO_{264}EGC_{18}$. This behavior describes different stages of association—below 40 °C the exchange of unimers between growing micelles is a favored process. At 40 °C, the temperature driven micellization process has already ended and possible quasi-equilibrium exchange of unimers had no importance on the system properties. R_h^{90} changes only slightly by no more than 1.8 nm (Fig. 8(a)). The plateau at 40 °C is consistent with the temperature dependence of the absorption of DPH, solubilized in the hydrophobic micellar cores (Fig. 5). At 40 °C a transition of the I^{90} readings was observed, although at higher temperatures I^{90} continues to rise due to the formation of more compact micellar aggregates, which results from the dehydration of both core and shell of the micelles.

The micellization process of the block copolymer of 'reverse' architecture, $EGC_{22}EO_{270}EGC_{22}$ is quite different (Fig. 8(b)). In the temperature interval from 25 to 38 °C bimodal distribution of the hydrodynamic radius was observed (Table 3) and at the same time the I^{90} readings were low. At temperatures above 38 °C the intensity distribution became monomodal and the values of I^{90} rapidly increased until the clouding of the solution at 46 °C. The values of R_h^{90} were also greatly affected by temperature. While raising the temperature

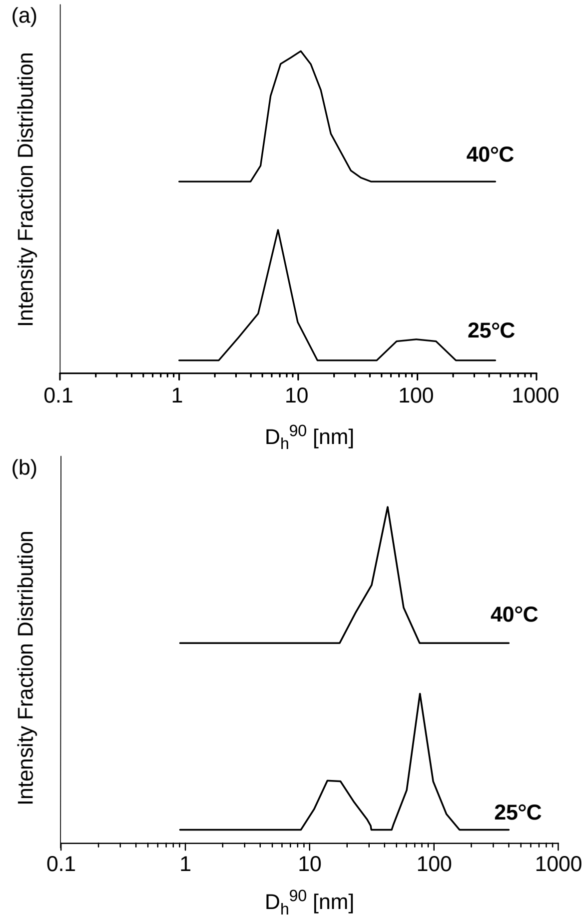


Fig. 7. Temperature dependence on the intensity fraction distribution of the hydrodynamic diameter obtained at $\theta = 90°$ for (a) $EO_{108}EGC_{38}EO_{108}$ and (b) $EGC_{22}EO_{270}EGC_{22}$ micellar systems. Concentration of the solutions is 10 g/L.

from 38 to 44 °C the values of R_h^{90} gradually increased from 15 to 22 nm. In contrast with the copolymers from AB and ABA architectures, no temperature interval of stability of R_h^{90} was observed for $EGC_{22}EO_{270}EGC_{22}$ micelles.

Static light scattering. SLS measurements of aqueous solutions of EO/EGC block copolymer were performed at 25 and 40 °C and within relatively broad concentration region above the cmc. In most cases below a certain concentration the presence of unimers in the system disrupted the linearity of the Debye plots (Fig. 9(a)) due to the resulting higher values for K_c/R_θ [32,33]. Therefore, the molar masses of the micelles $\bar{M}_w^{mic}$ were calculated by the Zimm plots where concentrations only from the linear region of the corresponding Debye plots were used (Fig. 9(b)). In the aqueous solutions of copolymers $EGC_{22}EO_{270}EGC_{22}$ and $EO_{108}EGC_{38}EO_{108}$ two populations of aggregates coexisted at 25 °C (see DLS data) and therefore, the molar masses were determined only at 40 °C, at which the distributions were monomodal. The copolymer of the lowest EGC content, $EO_{264}EGC_{18}$ was investigated at 70 °C, as at lower temperatures the particle distribution was bimodal. Due to the small dimensions of the EO/EGC micelles (isotropic scatterers at the applied laser wavelenght) it was impossible to determine their radii of gyration by SLS.

The weight average aggregation number N_{agg} of the micelles was obtained from the following relationship:

$$N_{agg} = \bar{M}_w^{mic}/\bar{M}_w^{uni} \quad (5)$$

where $\bar{M}_w^{uni}$ is the weight average molar mass of the unimers determined by SEC–MALLS (Table 1).

The aggregation number of EO/EGC micelles depends on copolymer architecture as well as on the length of the hydrophobic blocks. Only values obtained at 40 °C will be discussed, since at lower temperatures not every copolymer was able to associate into uniform micelles. Diblock copolymers are reported to posses the strongest ability to self-associate [34]. This is clearly seen for copolymer $EO_{264}EGC_{32}$ (Table 4, entry 2), which has the same N_{agg} as the copolymer of the highest EGC content, but of ABA architecture (Table 4, entry 5).

The hydrodynamic radius and aggregation number of the polymers entries 1 and 4 in Tables 3 and 4 are relatively small. The aggregation numbers approximately determined by the ratio of the molar masses of the unimer to the molar mass formed structures do not exceed 4. However, they seem to be organized micellar structures, consisting of a dense hydrophobic core and a hydrophilic shell. This behavior, characteristic for micelles, was confirmed by the DPH solubilization measurements (Table 2). A distinct cmc is observed, indicated by profound increase of the DPH absorption at 356 nm. The formation of small micelles has been observed for similar systems before [3,6,35].

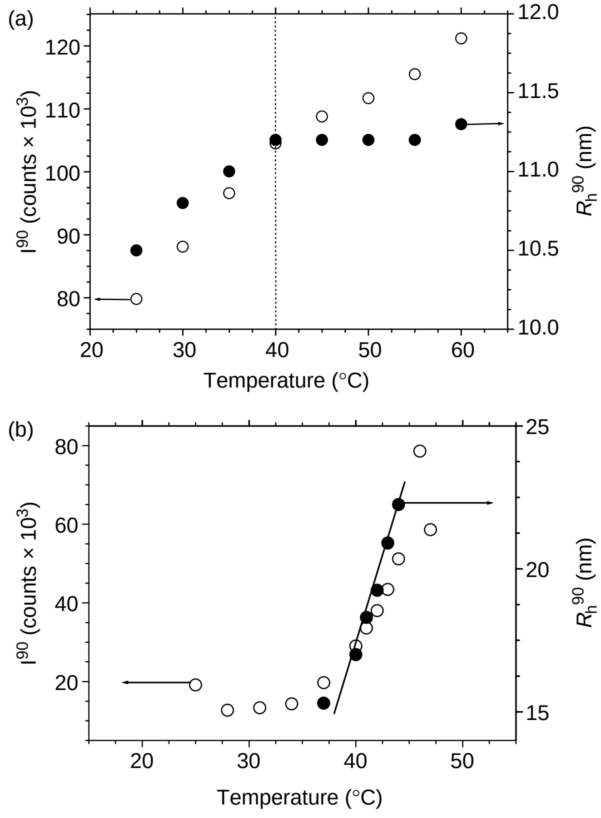


Fig. 8. Temperature dependence of the intensity of scattered light, I^{90}, (open circles) and the apparent hydrodynamic radius, R_h^{90}, (full circles) at $\theta = 90°$ for (a) $EO_{125}EGC_{80}EO_{125}$, concentration 1.75 g/L and (b) for $EGC_{22}EO_{270}EGC_{22}$ micelles, concentration 10 g/L.

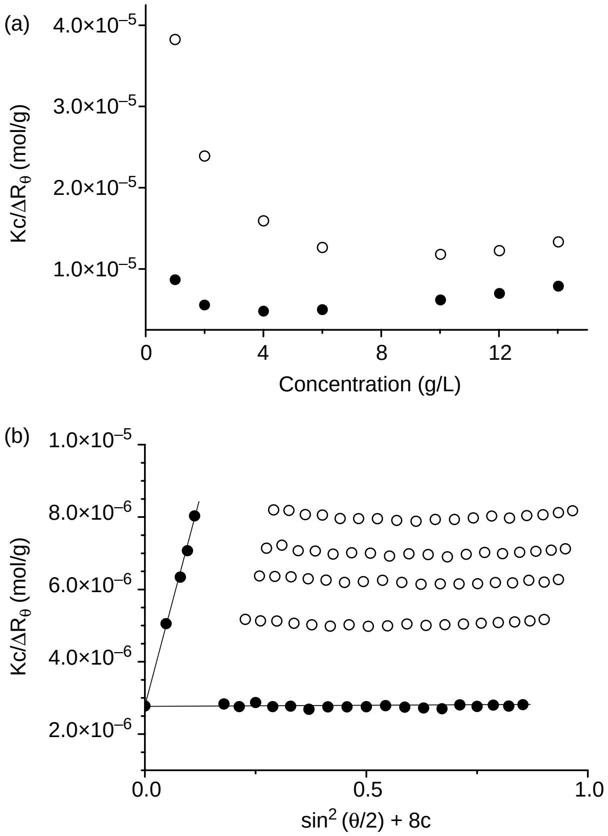


Fig. 9. (a) Debye plots for $EO_{264}EGC_{32}$ block copolymer at 25 °C (open circles) and at 40 °C (circles), $\theta = 90°$ (b) Zimm plot for $EO_{264}EGC_{32}$ at 40 °C.

Table 4
SLS measurements of EO/EGC block copolymer micelles

No.	Composition	EGC content (mol%)	$\bar{M}_w^{uni}$ (g/mol)	$\bar{M}_w^{mic}$ at 25 °C (g/mol)	$\bar{M}_w^{mic}$ at 40 °C (g/mol)	N_{agg} at 25 °C	N_{agg} at 40 °C
1	$EO_{264}EGC_{18}$	6.4	15,100	–[a]	62,000[b]	–[a]	4[b]
2	$EO_{264}EGC_{32}$	10.5	17,300	130,000	360,000	8	21
3	$EGC_{22}EO_{270}EGC_{22}$	14.0	19,200	–[a]	150,000	–[a]	8
4	$EO_{108}EGC_{38}EO_{108}$	14.9	15,300	–[a]	42,000	–[a]	3
5	$EO_{125}EGC_{80}EO_{125}$	27.6	24,000	440,000	500,000	18	21

[a] Not determined because of bimodal particle distribution (from DLS).
[b] Determined at 70 °C.

For polymer entry 1 (Table 4) most likely the degree of polymerization of EGC hydrophobic block equal to 18 is not enough to provide the hydrophobicity needed for the spontaneous formation of uniform micelles. To promote this the solution must be heated to 70 °C, at which the overall hydrophobicity of the copolymers becomes higher due to partial dehydration of the copolymer chain. Even at such conditions the value of N_{agg} remained low for this copolymer and the micelles contained only ca. four copolymer macromolecules.

The copolymer $EO_{108}EGC_{38}EO_{108}$ is suitable for the evaluation of the influence of both of the architecture and the content of hydrophobic units, since it can be directly compared to the copolymer of 'reverse architecture' $EGC_{22}EO_{270}EGC_{22}$ and to a copolymer of the same architecture, but with longer hydrophobic block—$EO_{125}EGC_{80}EO_{125}$. From these three block copolymers, $EO_{108}EGC_{38}EO_{108}$ had the lowest value of N_{agg} (Table 4), which is in good agreement with previous results obtained for other polyoxyalkylenes [3]. Copolymer $EO_{125}EGC_{80}EO_{125}$ contain twice longer hydrophobic block, which resulted in much higher value of the N_{agg} of the micelles.

As seen from Table 4, the increase of the temperature leads to increase of N_{agg} for all copolymers, which agrees with the observed increase of R_h obtained from DLS. This tendency can most clearly be seen for the copolymers $EO_{264}EGC_{32}$ and $EO_{125}EGC_{80}EO_{125}$, for which the SLS measurements were possible at 25 °C, where the intensity distribution (DLS) was monomodal.

4. Conclusions

The aqueous solution properties of new well defined AB, ABA, and BAB amphiphilic block copolymers of EO and EGC were investigated by cloud point measurements, hydrophobic dye solubilization and dynamic and static light scattering.

Apart from block copolymer architecture and the content of hydrophobic units, temperature played the dominating role in the process of micelle reorganization. At room temperature systems were either bimodal, or at non-equilibrium state of self-association. The micellization of the AB (excluding $EO_{264}EGC_{18}$) and ABA block copolymers completed at temperatures near 40 °C, above which micelles were stabilized and no change of hydrodynamic radii was observed. The ability to form micelles influenced the cloud point of copolymer solutions. There were no cloud point observed for diblock copolymers and for ABA copolymers it was about 80 °C. Solution prepared from the copolymer of BAB architecture clouded at relatively low temperature of 46 °C. Micelles from this copolymer never entered a temperature region of stability, as the values of hydrodynamic radius constantly elevated while increasing the temperature.

For $EO_{264}EGC_{32}$ and $EO_{125}EGC_{80}EO_{125}$ the number of aggregation obtained from SLS had relatively high values. The number of aggregation for the other copolymers was not calculated at 25 °C due to the bimodal distribution but at 40 °C the number of aggregation had low value.

Copolymers of shorter hydrophobic blocks tend to form loose non-micellar aggregates at low temperature. The nature of those aggregates is still not clear. A possible explanation for this phenomenon is the presence of intermolecular hydrogen bonding between carbamate groups of the chains mediated by water molecules.

To elucidate the above suggestion the influence of pH at constant ionic strength and at different temperatures upon the self-association process of EO/EGC copolymers and the evaluation of the relative hydrophobicity of copolymers of ethylene oxide and glycidol substituted with different alkyl glycidyl carbamate groups are under way.

Acknowledgements

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