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Poly(glycidol)-Based Analogues to Pluronic Block Copolymers. Synthesis and Aqueous Solution Properties

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ABSTRACT: Eight well-defined poly(glycidol)−poly(propylene oxide)−poly(glycidol) (PG−PPO−PG) block copolymers with PG contents from 20 to 84 wt % and fixed molecular weight of the middle PPO block of 2000 were prepared. The copolymers are considered as analogues to the commercially available Pluronic, poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) (PEO−PPO−PEO), block copolymers in which the PEO blocks are substituted by blocks of linear PG. They were prepared by means of anionic polymerization of ethoxyethyl glycidyl ether (protected glycidol) followed by cleavage of the protective groups. The resulting products bear hydroxyl groups in each repeating glycidol unit. In aqueous solution all studied copolymers were found to self-associate above a certain critical concentration (cmc), which depends on the PG content and temperature. The cmc values were found to decrease with increasing temperature and decreasing the content of the hydrophilic component less strongly than those of the corresponding Pluronic copolymers. According to the thermodynamic data, the substitution of the PEO blocks by blocks of linear PG reduces the enthalpic barrier to aggregation. The latter is entropically less favored compared to that of the Pluronics. The turbidity measurements reveal three types of transmittance vs temperature curve patterns. Two of them have been observed for some Pluronic copolymers. The third type, characterized by an increase of transmittance with increasing temperature, is exhibited only by the copolymers of higher (above 50 wt %) PG content. This behavior as well as other findings that deviate from the expectations can be understood with the well-documented in the present study fact that the interactions of the constituent blocks with water change with temperature in opposite manners.

Introduction

Glycidol, 2,3-epoxy-1-propanol (Figure 1a), is a hydroxyl epoxide that takes a special position among the other oxiranes. It is able to polymerize via an anionic mechanism, i.e., in the presence of alkoxide; however, because of repeating intra- and intermolecular transfer steps of the active sites to the primary hydroxyl groups, which subsequently propagate, typically branched oligomeric products are obtained.[1,2] A variety of copolymers with epoxide (propylene oxide,[3] ethylene oxide,[3] epichlorohydrine, isopropyl glycidyl ether, glycidyl phenyl ether, 1,2-epoxybutane[4]), cyclic (caprolactam[5]), and noncyclic (methyl acrylate,[6] *p*-chloromethylstyrene[7]) monomers in which the poly(glycidol) moieties consist of highly branched polyether scaffold have been reported. The linear products, homo- and copolymers, of glycidol are considerably less studied. In general, to obtain linear poly(glycidol), the hydroxyl group must be protected by a suitable group. It appears that for an anionic polymerization the ethoxyethyl protective group is most suitable as it is stable at basic conditions and easily removable by hydrolysis. There are few reports that document the synthesis of ethoxyethyl glycidyl ether, EEGE[8] (Figure 1b), as referred to as protected glycidol, its anionic (co)polymerization, and investigation of the resulting linear products.[9] A subsequent step could be cleavage of the protective group which yields linear poly(glycidol) moieties containing a hydroxyl group in each repeating unit.

The amphiphilic copolymers of the Pluronic family are commercially available in wide ranges of molecular weights and ratios between the hydrophilic and hydrophobic components. They are linear triblock copolymers of a poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) (PEO−PPO−PEO) architecture and probably the most extensively studied polymeric nonionic surfactants.[10−20] In aqueous solution they exhibit rich structural polymorphism. The microstructures resulting from the self-assembly of the copolymers can vary from normal micelles through body-centered cubic or face-centered cubic, hexagonal, bicontinuous cubic, and L3 to lamellar lyotropic liquid crystals. It is now well established that the parameters influencing their structural polymorphism are the total copolymer molecular weight, molecular weights, and hence the balance between the hydrophobic, PPO, and hydrophilic, PEO, components as well as temperature and concentration. The accumulated knowledge about the ability of these important copolymers to attain diverse microstructures and the properties of the microstructures is of great importance as the Pluronic copolymers are commercially available and find wide application in fields as diverse as medicine and petroleum industry. In the attempts to diversify the assortment copolymers, other, e.g., reverse and starlike, architectures have been commercialized. To the best of our knowledge, however, attempts have been made to substitute only the hydrophobic PPO block with structurally similar poly(butylene oxide).[21−24] With this in mind we initiated a study to create and investigate novel block copolymers which could be considered as analogues to Pluronic copolymers in which the hydrophilic blocks of PEO are substituted by blocks of linear poly(glycidol) (PG). In particular, in this first paper, we describe the synthesis and preliminary aqueous solution properties of a series of PG−PPO−PG block copolymers in which the PG content varies from 20 to 84 wt % whereas the degree of polymerization of the PPO block is 34. Thus, the resulting block copolymers are closest in composition to the Pluronic series

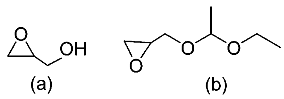

Figure 1. Structural formulas of (a) glycidol and (b) ethoxyethyl glycidyl ether (EEGE).

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L61−F68 and L72−F77. In forthcoming papers rheological properties and investigations based on scattering methods and electron microscopy of the copolymers of this series as well as copolymers of other series that differ in molecular weight of the central block of PPO will be presented.

Experimental Section

A. Materials. The solvents (methanol, methylene chloride) were purified by distillation. Glycidol (96%, Aldrich) was distilled under reduced pressure. Ethyl vinyl ether (99%, Aldrich), $AlCl_3·6H_2O$ (99%, Aldrich), and $CsOH·H_2O$ (99.95%, Acros Organics) were used as received. Ethoxyethyl glycidyl ether (EEGE) was obtained by a reaction of glycidol and ethyl vinyl ether as described elsewhere.[8] Fractions of EEGE of purity exceeding 98.5%, determined by gas chromatography, were used for polymerizations. Poly(propylene oxide) 2000 (Fluka) was dried by azeotropic distillation using toluene. A recent MALDI TOF analysis of the same product has shown that the exact number-average molecular weight is 2030.[25] A hydroxyl value of 47 has been determined as well.[25]

B. Synthesis of Block Copolymers. *1. Preparation of the Macroinitiator.* $CsOH·H_2O$ (0.202 g, 1.2 mmol) was added to PPO 2000 (1.48 g, 0.74 mmol) magnetically stirred at 90 °C in a reaction vessel equipped with argon and vacuum lines. After 2 h the reaction mixture was cooled to room temperature, and to remove the released water, 1 mL of dry benzene was added and vacuum was switched on for 2 h.

2. Polymerization (Synthesis of PEEGE−PPO−PEEGE Precursors). EEGE (2.92 g, 20 mmol) was introduced to the macroinitiator to obtain $(EEGE)_{13}(PO)_{34}(EEGE)_{13}$. The polymerization was carried out at 90 °C. The conversion of the monomer was followed by ^1H nuclear magnetic resonance spectroscopy. The syntheses of the other PEEGE−PPO−PEEGE precursors were carried out in analogy to this procedure.

3. Deprotection Reaction (Synthesis of PG−PPO−PG Copolymers). The procedure described below is similar to a method for deprotection of tetrahydropyranyl ether.[26] $(EEGE)_{13}(PO)_{34}(EEGE)_{13}$ (2.96 g, 20 mmol) was dissolved in methanol (7.5 mL, 160 mmol). $AlCl_3·6H_2O$ (0.04 g, 0.2 mmol) was added, and the mixture was stirred for 1 h at room temperature. Afterward, the reaction product was filtered through Hylfo Super Gel (diatomaceous earth), and the solvents were evaporated under reduced pressure. The syntheses of the other PG−PPO−PG copolymers were carried out in analogy to this procedure.

C. Analysis. *1. Gel Permeation Chromatography (GPC).* The GPC analysis was carried out with a Waters system consisted of four Styragel columns with nominal pore sizes of 100, 500, 500, and 1000 Å and a refractive index detector (R401). Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1 mL/min at 40 °C. Samples were prepared as solutions in THF. Toluene was used as the internal standard for indication of elution volume. Calibration was made versus polystyrene standards.

2. ^1H Nuclear Magnetic Resonance (NMR). ^1H NMR spectra were recorded at 250 MHz on a Bruker WM 250 spectrometer. The samples were prepared as solutions in $CDCl_3$, D_2O, or DMSO-d_6. The chemical shifts are given in ppm from tetramethylsilane. The spectra were recorded at different temperatures.

3. Turbidity Measurements. The turbidity was determined by measuring the transmittance at $\lambda = 500$ nm of aqueous solution of the copolymers with concentrations ranging from 1 to 10 wt % at different temperatures using a Specord UV−vis spectrophotometer. The samples were placed in a thermostated cuvette holder and heated slowly with a heating rate of 1 °C/min from ca. 15 to 90 °C.

4. Determination of the Critical Micellization Concentration (cmc). Aqueous solutions (2.0 mL) of a given triblock copolymer in the concentration range from 0.001 to 5 wt % were prepared at 0 °C. 1,6-Diphenyl-1,3,5-hexatriene, DPH (20 μL of a 0.4 mM solution in methanol), was added to each of the copolymer solutions. The solutions were incubated in the dark for 16 h at room temperature. The absorbance in the wavelength interval $\lambda = 300-500$ nm was followed at temperatures ranging from 25 to 60 °C on a Specord UV−vis spectrophotometer. The main absorption peak, characteristic for DPH solubilized in a hydrophobic environment, was at 356 nm.

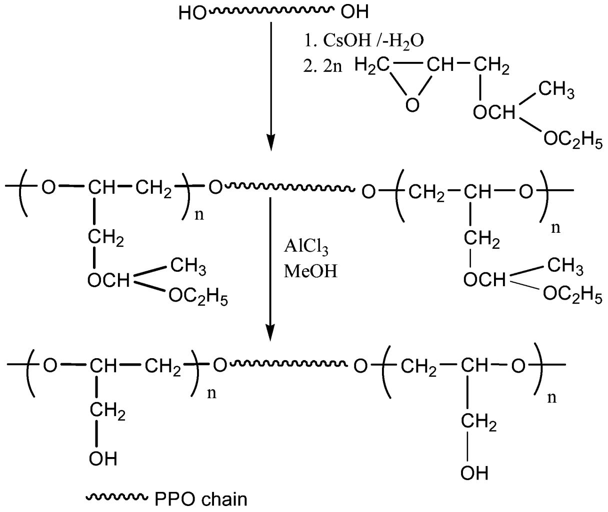

Figure 2. Synthesis of linear triblock copolymers of glycidol and propylene oxide.

Results and Discussion

Synthesis and Characterization of the Block Copolymer Precursors and the Targeting Poly(glycidol)−Poly(propylene oxide)−Poly(glycidol) Copolymers. To obtain the novel PG−PPO−PG copolymers, a two-step procedure was applied (Figure 2). In the first step PEEGE−PPO−PEEGE precursors were prepared, whereas the protective ethoxyethyl groups were cleaved in the second step to yield triblock copolymers with linear PG moieties. The precursors were obtained using an anionic polymerization of EEGE which has been shown possible,[9] close to living,[27] and applicable to obtain in a controlled way block copolymers of ethylene oxide and glycidol.[28,29]

To initiate the polymerization, we used PPO 2000 which was partially (80%) deprotonated. This approach is in analogy with a strategy based on a rapid exchange equilibrium between active chain ends and dormant, that is, potentially active, sites. After several propagation steps the active sites can be deactivated and reactivated again at some time which enables simultaneous growth of all chains, control of molecular weight, and narrowing the dispersity. The concept has been shown successful for ATRP, immortal polymerization of Inoue,[30] and polymerization of propylene oxide.[31] By reacting PPO 2000 with a suitable deprotonating agent, in particular CsOH, and removal of the released water, 80% of the hydroxyl groups were converted into alkoxide. Cesium alkoxide has been reported to be an efficient initiator for anionic polymerization of oxiranes and more active than the other alkali metal alkoxides.[9,27−29,32,33] In addition, the ring-opening anionic polymerization of EEGE does not involve side reactions, and (co)polymers of good yield and molecular weight distribution have been obtained.[9,27−29,32,33] A number of polymerizations were carried out aiming at preparing copolymers with varying contents of PG. The targeting PG contents were from 20 to 90 with an increment of 10 wt % (Table 1).

The block structure of the resulting PEEGE−PPO−PEEGE precursors was proved by GPC. The GPC analysis gave monomodal distributions with dispersity indices ranging from 1.04 to 1.28. The GPC traces of the starting PPO 2000 and two of the resulting copolymers are presented in Figure 3. Tiny low molecular weight tails are observed which have been previously attributed to homo-PPO and diblock copolymer impurities deriv-

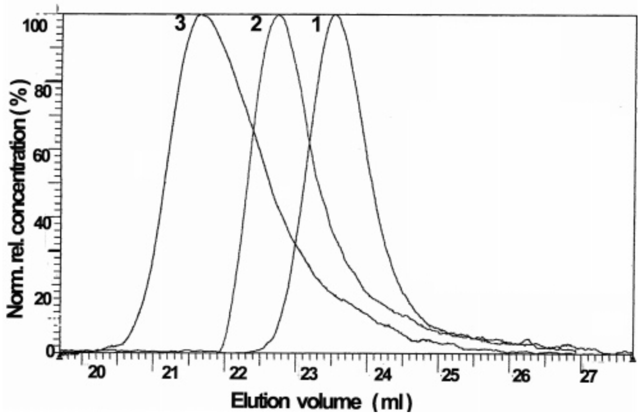

Figure 3. Gel permeation chromatography traces of poly(propylene oxide) 2000 (1) and poly(ethoxyethyl glycidyl ether)−poly(propylene oxide)−poly(ethoxyethyl glycidyl ether) copolymers with compositions 17−34−17 (2) and 70−34−70 (3).

ing most probably from monofunctional PPO contaminations[32] or irreversible inactivation of some of the active centers as a result of interactions with impurities introduced with the monomer.

The attempts to prepare well-defined block copolymers with degrees of polymerization (DPs) of the flanking blocks greater than 70, which corresponds to total copolymer molecular weight higher than 22 000, were unsuccessful. The GPC curves were highly asymmetric with clearly pronounced shoulders on the side of the low molecular weights (not shown). Apparently, this is the upper limit of the polymerization conditions (bulk, 90 °C) utilized in the present study. The experiments carried out at higher, that is above 90 °C, temperatures were of low reproducibility due most probably to cleavage of the protective group at such harsh conditions. In a forthcoming paper we use another deprotonating agent (potassium naphthalide) to prepare copolymers of molecular weights well above 22 000.

The compositions of the precursors were determined from the ^{1}H NMR data assuming an average DP of the PPO moieties of 34. A representative spectrum of a PEEGE−PPO−PEEGE copolymer is shown in Figure 4a. The theoretical and experimental DPs as well as the compositions of the PEEGE−PPO−PEEGE precursors are given in Table 1. The experimental DPs are in satisfactory agreement with the theoretical ones and with the values calculated from the feed.

The PEEGE blocks can be converted into PG blocks by hydrolysis of the protective ethoxyethyl groups. Ideally, the DPs of the PG blocks should be the same as the DPs of the PEEGE blocks of the corresponding precursors. Typically, the cleavage of the protective groups involves treatment with protonic acids, elevated temperatures, and long reaction times. At such harsh conditions destruction of the polyether backbone may occur, which largely limits the efficiency and applicability of the employed deprotection methods. Recently, a method for deprotection of tetrahydropyranyl ethers[26] has been adopted to cleave the ethoxyethyl groups of homo-PEEGE.[34] The same method was applied to the present PEEGE−PPO−PEEGE precursors. The cleavage was successful as evidenced by disappearance of the signals for the methine proton at 4.6−4.7 ppm and methyl protons at 1.1−1.2 and 1.3 ppm of the acetal group in the ^{1}H NMR spectrum of the resulting PG−PPO−PG copolymer (Figure 4b). It should be mentioned that the glycidol to propylene oxide ratio and hence the DPs of the PG blocks and copolymer molecular weights cannot be determined from the ratio of the signal intensities because, as shown later, depending

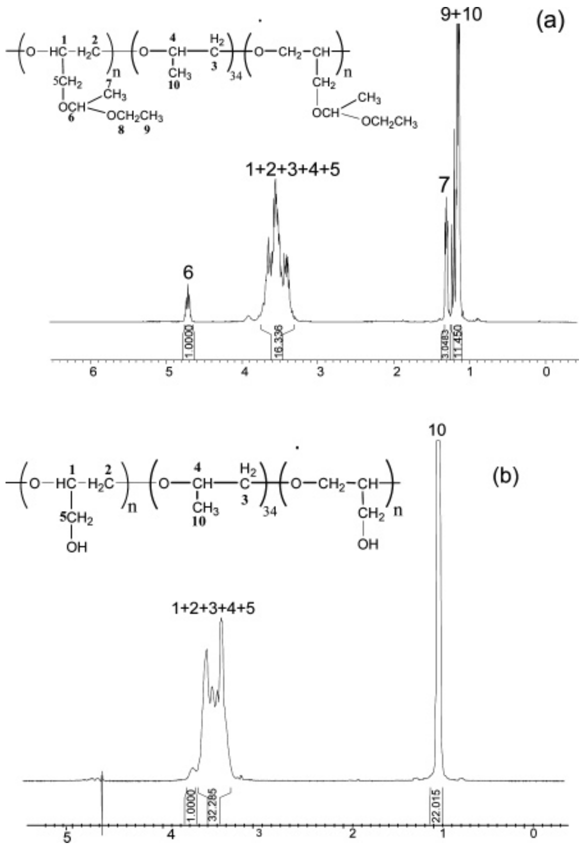

Figure 4. ^{1}H nuclear magnetic resonance spectra of $(EEGE)_6(PO)_{34}(EEGE)_6$ precursor in $CDCl_3$ (a) and the resulting $(G)_6(PO)_{34}(G)_6$ copolymer in D_2O (b).

Table 1. Targeting and Characterization Data of the Poly(glycidol)−Poly(propylene oxide)−Poly(glycidol) (PG−PPO−PG) Copolymers and the Corresponding Poly(ethoxyethyl glycidyl ether)−Poly(propylene oxide)−Poly(ethoxyethyl glycidyl ether) (PEEGE−PPO−PEEGE) Precursors

	total degree of polymerization of the PEEGE moieties				
targeting PG content (wt %)	theoretical	experimental[a]	copolymer composition[b]	experimental PG content (wt %)[c]	abbreviation
20	7	6	3−34−3	18	LGP62
30	12	11	6−34−6	29	LGP63
40	18	16	8−34−8	37	LGP64
50	27	26	13−34−13	49	LGP65
60	40	35	17−34−17	56	LGP66
70	63	52	26−34−26	66	LGP67
80	108	102	51−34−51	79	LGP68
90	242	141	70−34−70	84	LGP68+

[a] Determined from the ^{1}H NMR data of PEEGE−PPO−PEEGE precursors in $CDCl_3$. [b] 34 is the average degree of polymerization of the middle PPO block. The degrees of polymerization of the flanking blocks are the same for the precursors and final copolymers. [c] Determined from the ^{1}H NMR data of PG−PPO−PG precursors in DMSO-d_6.

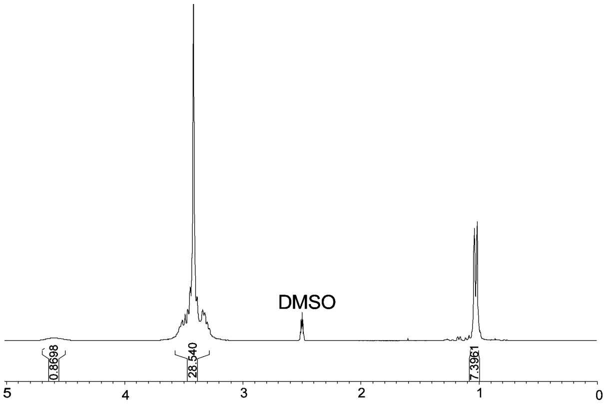

Figure 5. ^{1}H nuclear magnetic resonance spectrum of $(G)_6(PO)_{34}(G)_6$ copolymer in DMSO-d_6.

on temperature water is a selective solvent for the PG−PPO−PG copolymers. The DPs of the PG blocks were determined from the ^{1}H NMR spectra in DMSO-d_6 from the relative intensities of the resonances of the hydroxyl protons at 4.6 ppm of the glycidol units and methyl protons of the oxypropylene units at 1.1 ppm (Figure 5). The determined DPs are in excellent agreement with the DPs of the PEEGE blocks of the corresponding precursors (Table 1), implying that no destruction of the polyether backbone takes place during the deprotection reaction. The experimental PG contents are close to the targeting ones (with exception of the copolymer of the highest content as discussed above), which indicates that both the polymerization and the following modification proceed in a controllable and predictable way.

For easy presentation of the aqueous solution properties of the resulting PG−PPO−PG copolymers, we introduce abbreviation codes which are used also in forthcoming publications. The codes are given in the last column of Table 1. They consist of 3 characters and 2 digits. LGP is abbreviation of linear glycidol/propylene oxide copolymers. The last digit multiplied by 10 gives the targeting PG content in wt %. Similarly to the abbreviation of the Pluronic copolymers the first digit multiplied by 300 gives the molecular weight of the PPO block. In our case, however, the latter is slightly higher than the first digit indicates.

Aqueous Solution Properties. In this section we present preliminary aqueous solution properties to get some insight into the nature and behavior of these original copolymers. We start with determination of the critical micellization concentration and turbidity of dilute and semiconcentrated solutions. Detailed studies based on scattering methods, electron microscopy, rheology, etc., are underway and will be published in the near future.

Cmc Determination. The nonpolar dye DPH was used for determination of the cmc's of the copolymers. The absorbance of DPH is sensitive to changes in the microenvironment; it is minimal in water and substantially enhanced showing a characteristic maximum at 356 nm in hydrophobic environments. This property has been exploited to determine the cmc's of various conventional and polymeric, including Pluronic, surfactants.[11,35−37] Figure 6a shows UV−vis absorption spectra of DPH in the presence of increasing amounts of LGP64 taken at 25 °C. The well-pronounced maxima at 356 nm at higher copolymer concentrations indicate the presence of hydrophobic domains in which DPH is solubilized. The cmc values were determined from the break of the intensity vs copolymer concentration curves as shown in Figure 6b for LGP64 at three temperatures.

The cmc data for all copolymers studied are plotted as a function of temperature in Figure 7a. The plots represent micellization phase diagrams for each copolymer: below the micellization boundaries the copolymers presumably exist as unimers, that is, unassociated macromolecules, whereas hydrophobic domains, implying the presence of aggregates, are formed above the micellization boundaries. It should be noted that up to intermediate temperatures the cmc values are lower than those of the corresponding Pluronic copolymers, particularly the series L61−F68 and L72−F77.[13,38] This indicates that the substitution of the PEO blocks with PG blocks facilitates the formation of aggregates, which is somewhat counterintuitive keeping in mind that PG is considered more hydrophilic than PEO. No doubt, as Figure 7a reveals, the micelle formation of the LGP copolymers is sensitive to temperature, however, not as much as that of the Pluronic copolymers. The cmc's of the latter are known to decrease with an order of magnitude with a 10 °C increase in temperature.[39] The temperature sensitivity was found to depend on the PG content; whereas the cmc dependence on temperature for LGP62−66 is given by parallel curves exhibiting a characteristic break at 50 °C, that of the copolymers of higher PG content is nearly linear with slopes that decrease with increasing molecular weight of the PG blocks. The data in Figure 7a are replotted in Figure 7b to estimate the effect of the PG content. The cmc values at 25 and 40 °C show a gradual increase with increasing PG content, indicating that the micelle formation, although slightly, becomes more difficult. At higher temperatures a break in the dependence was observed, implying the existence of a critical PG content above which the micellization is suddenly hindered.

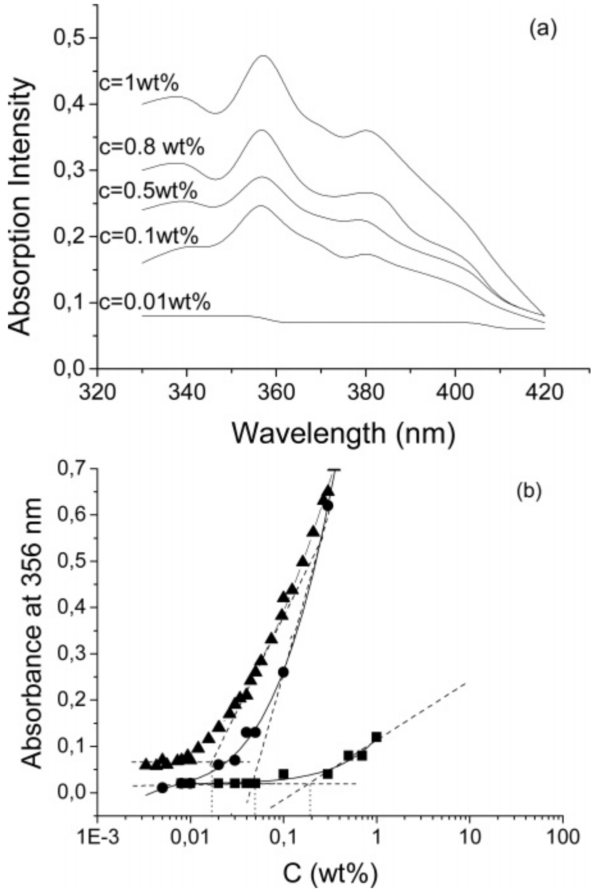

Figure 6. Effect of LGP64 concentration on (a) UV−vis absorption spectra of 1,6-diphenyl-1,3,5-hexatriene (DPH) taken at 25 °C and (b) absorption intensity at 356 nm at 25 (squares), 50 (circles), and 60 °C (triangles).

Thermodynamics of Micellization. The thermodynamic parameters of micellization can be extracted from the temperature dependence of the cmc.[40] Thus, the free energy of micellization,

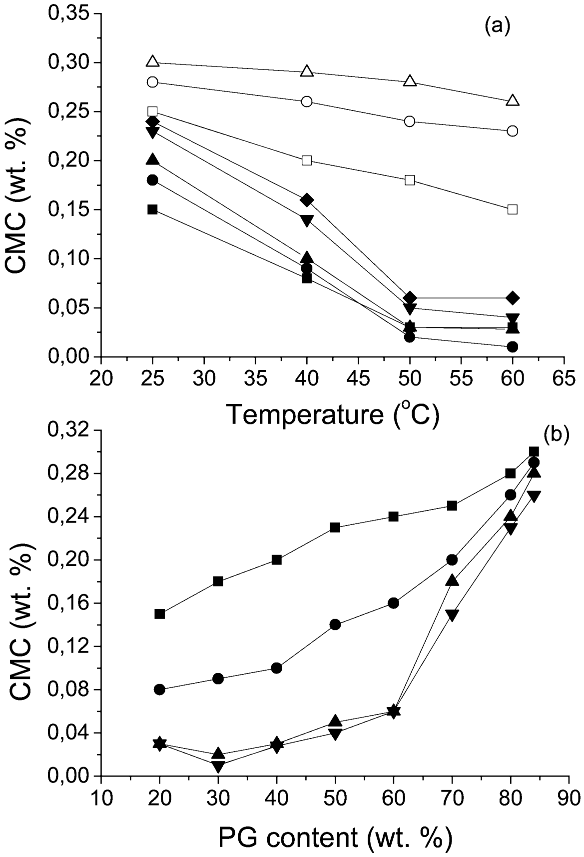

Figure 7. Critical micellization concentrations as a function of (a) temperature and (b) PG content. Symbols in (a): LGP62 (closed squares); LGP63 (closed circles); LGP64 (closed triangles); LGP65 (closed inverted triangles); LGP66 (closed diamonds); LGP67 (open squares); LGP68 (open circles); LGP68+ (open triangles). Symbols in (b): 25 °C (squares); 40 °C (circles); 50 °C (triangles); 60 °C (inverted triangles).

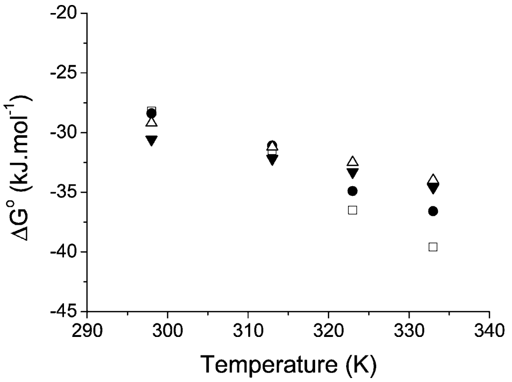

Figure 8. Micellization free energy, ΔG°, as a function of temperature for LGP63 (squares), LGP65 (circles), LGP 67 (open triangles), and LGP68+ (closed triangles).

ΔG°, is given by[40]

$$\Delta G^\circ = RT \ln(X_{\text{cmc}}) \tag{1}$$

where R is the gas law constant, T is the temperature in K, and X_{cmc} is the cmc in mole fractions at temperature T. ΔG° values for selected copolymers are plotted in Figure 8 as a function of temperature. The values are negative, indicating spontaneous formation of aggregates, and become more negative at higher temperatures. It is noteworthy that the ΔG° decrease with temperature is composition dependent. To further investigate this finding, the standard enthalpy of micellization, ΔH°, and the standard entropy of micellization, ΔS°, were calculated from the intercepts and the slopes, respectively, of the linear fits of the ΔG° vs T data according to eq 2[40]

Table 2. Enthalpy (ΔH°) and Entropy (ΔS°) of Micellization of the Investigated LGP Copolymers in Aqueous Solution

copolymer	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})
LGP62	64.25	0.308
LGP63	71.98	0.334
LGP64	50.87	0.265
LGP65	44.59	0.244
LGP66	36.57	0.218
LGP67	11.77	0.137
LGP68	4.94	0.118
LGP68+	3.28	0.113

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{2}$$

The ΔH° and ΔS° values are collected in Table 2. Similarly to the Pluronic copolymers[11,19,41] ΔH° is positive, indicating that the micellization is an enthalpically disfavored endothermic process; the positive entropy contribution is the driving force for the micellization of the present LGP copolymers. However, the ΔH° and ΔS° values are considerably lower than those of the Pluronics, which for the latter are in the 180−350 kJ mol^{-1} range and ca. 1 kJ mol^{-1} K^{-1}, respectively. Obviously, the micellization of the LGP copolymers is an enthalpically less disfavored with lower entropic contributions process compared to that of the Pluronic copolymers. It is seen from Table 2 that the PG content affects very consistently the magnitudes of ΔH° and ΔS° which were found to decrease with increasing PG content. This suggests that the increasing PG content reduces the enthalpic barrier to micellization and makes the latter an increasingly less entropy favored process. Nevertheless, the fundamental mechanism, that is entropic driving force, is not altered even for LGP68+.

Turbidity Measurements. The oligomeric polyoxyalkylene surfactants, including the Pluronic block copolymers, usually exhibit a lower critical solution temperature (LCST). At this temperature, which is experimentally observed as a cloud point (CP), the one-phase solution is separated into a dilute surfactant solution and a suspension of large aggregates that cause the appearance of milky-white opalescence. Solutions based on homo-PEO typically exhibit CPs over 100 °C,[42] whereas those of PPO cloud at considerably lower temperatures. The CPs of PPO are found to decrease with increasing molecular weight, and in particular, PPO 2000 exhibits a CP at about 20 °C.[32] The CPs of the Pluronic copolymers depend strongly on the copolymer composition and only weakly on the concentration.[43] Typically, copolymers of higher, e.g. above 70%, PEO content do not cloud at temperatures up to 100 °C.

To further investigate the properties of the LGP copolymers at semiconcentrated (1−10 wt %) solutions we monitored the variations of the incident light intensity transmitted through the solutions with temperature. Representative transmittance vs temperature curves are shown in Figure 9. The curve patterns can be divided broadly into three types. Type I (Figure 9a) is displayed by the copolymers of lower PG content, that is LGP62 and LGP63. It is a typical clouding process presented by sigmoidal curves and corresponding to a thermally induced phase separation. Compared to the clouding curve of PPO 2000 those of LGP62 and LGP63 are less sharp and shifted to higher temperatures. Type II is displayed by the copolymers of PG content above 50% (Figure 9b). These copolymers do not cloud, and as seen from Figure 9b the transmittance increases with temperature. The increase can be gradual as shown for the 1 wt

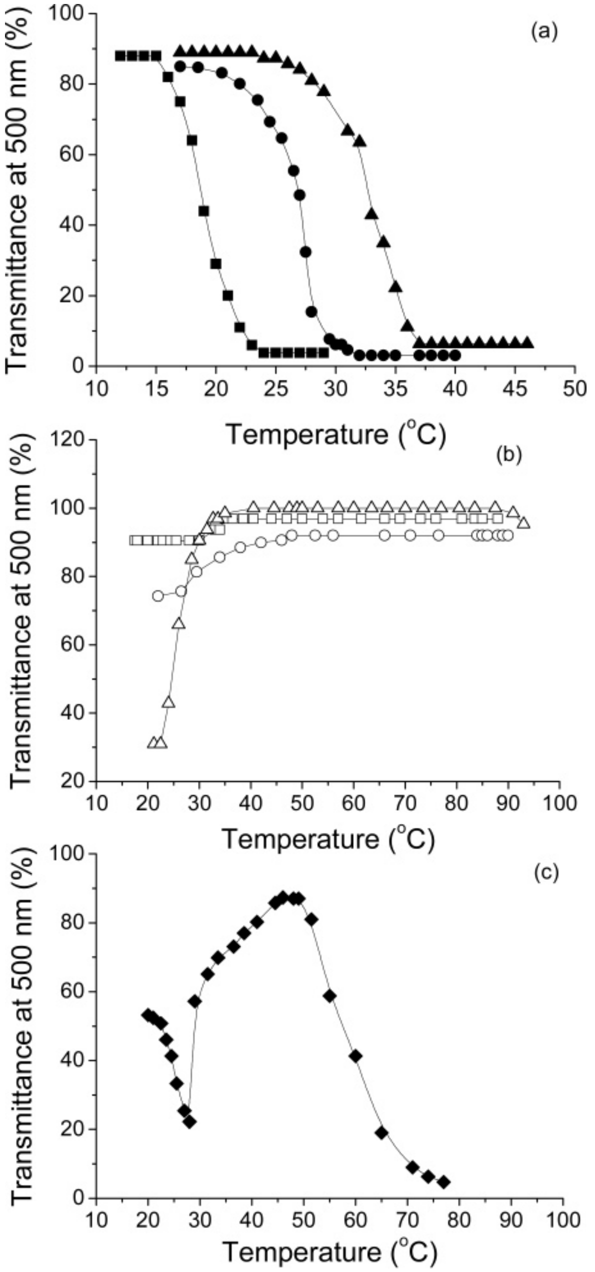

Figure 9. Transmittance vs temperature curves for aqueous solutions of 1 wt % of PPO 2000 (closed squares), 1 wt % of LGP62 (closed circles), and 1 wt % of LGP63 (closed triangles) in (a), 1 wt % of LGP65 (open squares), 5 wt % of LGP66 (open circles), and 5 wt % of LGP67 (open triangles) in (b), and 5 wt % of LGP64 (closed diamonds) in (c).

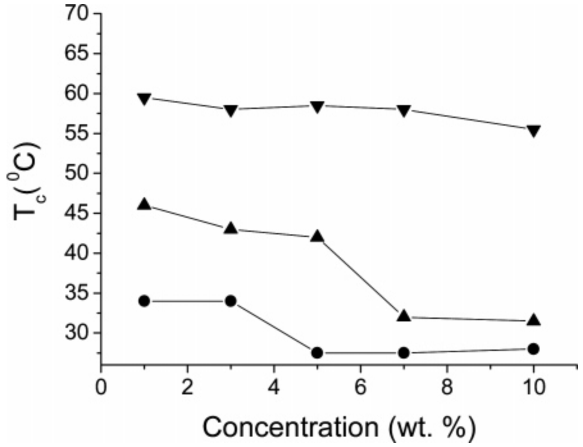

Figure 10. Variations of T_c with concentration of LGP67 (circles), LGP68 (triangles), and LGP68+ (inverted triangles). T_c is the critical temperature at which the appearance of the solutions changes. See text for more information.

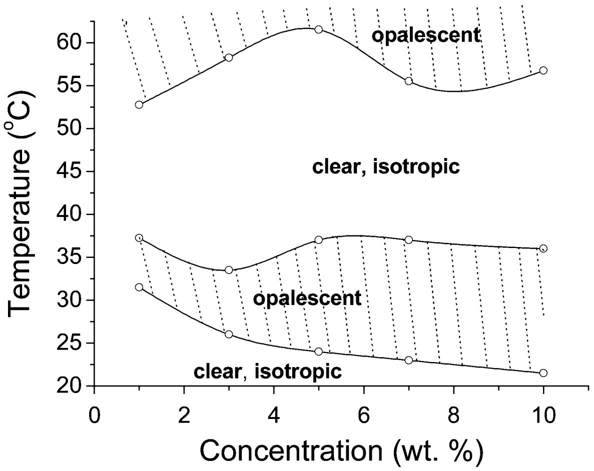

Figure 11. Partial phase diagram of LGP64 in water. The dashed regions represent opalescent phases. See text for more information.

% solution of LGP65, reminiscent of the materials exhibiting upper critical solution temperature (UCST) properties (LGP67) or less sharp compared to the latter but still with a detectable critical temperature (LGP66). The existence of critical temperatures (T_c) at which the appearance of the solutions changes made it possible to follow the dependence of T_c with concentration (Figure 10). The curves, in fact, represent boundaries between solutions with (slightly) different opalescence; the regions above the curves are less opalescent than those below the curves. Interestingly, the critical temperatures were found to decrease with increasing copolymer content, indicating that the solutions are less opalescent at higher concentrations.

Unique for this series of LGP copolymers is the behavior of LGP64, which features the third type of transmittance vs temperature curve patterns (Figure 9c). Over a certain concentration range two CPs and, consequently, two highly opalescent regions in the partial phase diagram depicted in Figure 11 are observed. As seen, the solutions in the investigated concentration range underwent several transitions upon heating: the initially clear solutions got highly opalescent at moderate temperatures, then the turbidity disappeared, and the solutions remained optically clear up to around 55−60 °C, above which they clouded out again. Such a behavior is unique for this series of LGP copolymers but not for some Pluronic copolymers. Two cloud points have been observed earlier for Pluronic L62[39,44] and explained in terms of presence of a more hydrophobic component that causes the first CP. Similar is the interpretation of Zhou and Chu[10] for the anomalous micellization behavior of Pluronic L64; although the solutions were clear, they showed strong scattering before the onset of micellization. In our opinion it is the composition of LGP64, rather than the presence of hydrophobic contaminants, that is responsible for the peculiar behavior. We carried out filtration experiments, the same as those carried out by Zhou and Chu,[10] and the results presented in Figure 9c were reproduced within 5%. Moreover, our preliminary results with other LGP copolymers comprising PPO of molecular weight both lower and higher than that of the present copolymers indicate quite similar behavior of the copolymers with moderate PG contents.

Attempting to generalize the cloud-point behavior of the LGP copolymers and to make a comparison with the reference

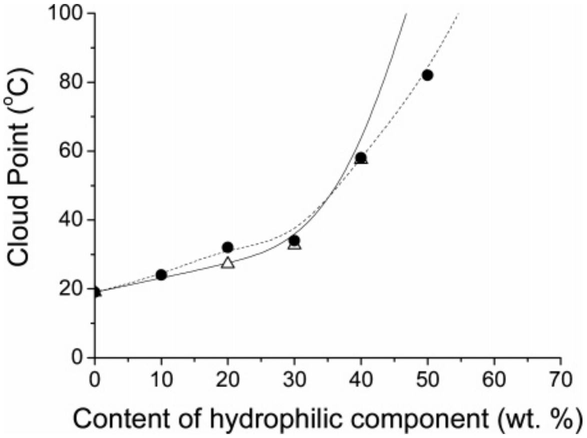

Figure 12. Variations of the CPs of 1 wt % aqueous solutions with the content of the hydrophilic component: LGP copolymers (triangles and solid line); Pluronic copolymers of the series L61−F68 (circles and dashed line). The hydrophilic components are PEO and PG for the Pluronic and LGP copolymers, respectively. The copolymers of higher hydrophilic component contents do not cloud at temperatures up to 100 °C. The CP data for the Pluronic copolymers are taken from ref 43.

Pluronic copolymers, we plotted the CPs as a function of the content of a hydrophilic component (Figure 12). For both groups of copolymers the CPs increase with increasing content of the hydrophilic component. Up to 40% the CPs of the LGP and Pluronic copolymers slightly differ being somewhat lower for the former. Then a crossover was observed, and the two curves diverged.

^{1}H NMR Spectroscopic Measurements. In many aspects the behavior of the LGP copolymers is similar to that of the corresponding Pluronic copolymers. There are, however, a number of differences which, at first sight, are somewhat inconsistent with the view of highly hydrophilic PG blocks soluble in water in the whole temperature range from 0 to 100 °C. Some of the experimental results that deviate from the expectations are as follows: (i) Erratic values of the degrees of polymerizations and, hence, copolymer compositions, determined from the ^{1}H NMR spectra in D_2O. (ii) Lower cmc values at ambient/moderate temperatures than those of the corresponding Pluronic copolymers, implying easier aggregation. (iii) The magnitude of the exothermic interactions increases whereas the positive entropy contributions decrease upon increasing PG content. The effect of the PG content is similar to that of a structure-breaker added to aqueous solutions of Pluronic.[41] In light of the easier aggregation suggested above these trends are somewhat unexpected. (iv) Lower thermosensitivity and the enhanced role of the PG blocks at elevated temperatures. As seen from Figure 7b, the linear increase of the PG content leads to an exponential cmc increase. (v) Type II of the CP behavior exhibited by the copolymers of higher, i.e., above 50 wt %, PG content.

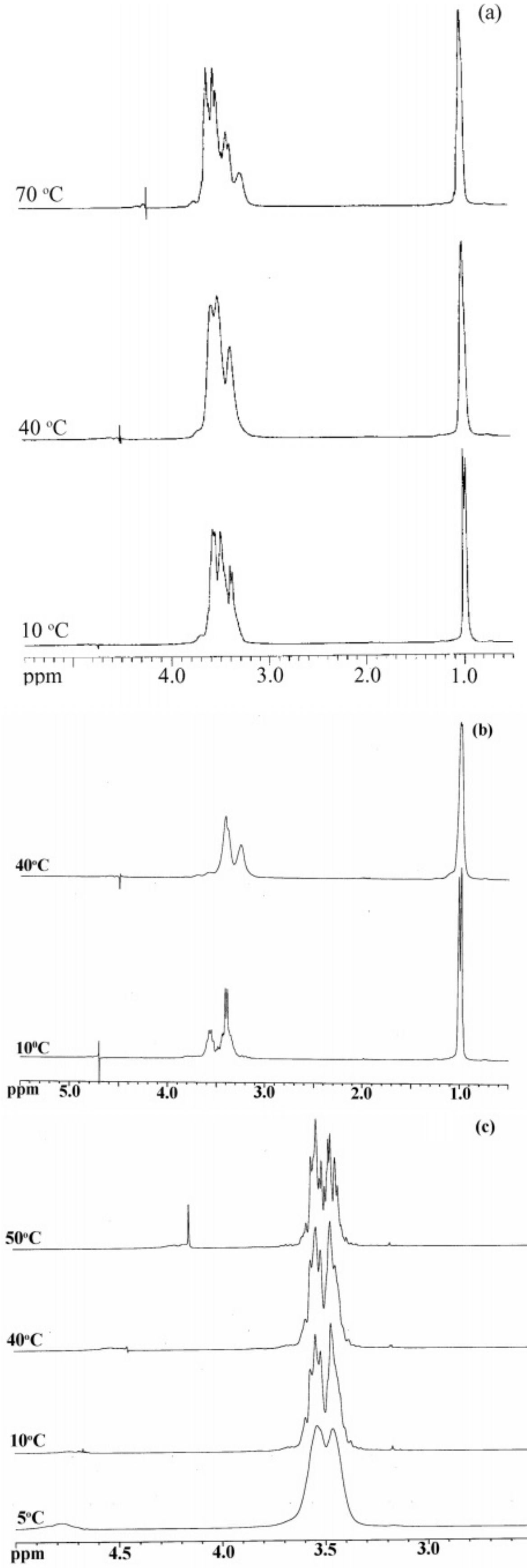

Figure 13. ^{1}H nuclear magnetic resonance spectra of 1 wt % solutions of LGP65 (a), homo-PPO (b), and homo-PG (c) in D_2O at various temperatures indicated.

To elucidate these peculiarities, we carried out ^{1}H NMR measurements in D_2O of the copolymers as well as of the homopolymers PPO and PG at different temperatures. Figure 13a shows the ^{1}H NMR spectra of a 1 wt % solution of LGP65 taken at 10, 40, and 70 °C. Each spectrum contains two resonances: a doublet at about 1.0 ppm assigned to the methyl protons of the PO units and a composite band from about 3.2 to 3.8 ppm in which the CH_2CH protons from the PO units are superimposed by the large peaks of the methylene and methine protons of the glycidol units. The bands change drastically with temperature: at 40 °C the peak at 1.0 ppm is almost unrecognizable that it was a doublet, and the hyperfine structure of the composite band centered at about 3.5 ppm disappears. At 70 °C the latter is partially restored; however, the band keeps changing with at least one peak shifted toward lower ppm values. Such a shift has been observed previously for Pluronic F127 at temperatures higher than the temperature of micellization[12] and attributed to the reduced mobility of the PO units resulting from the micellization. With the spectra shown in Figure 13b we unambiguously prove the above suggestion; here, the different features of the spectra taken at 10 and 40 °C, that is, below and above the LCST of PPO 2000, respectively, are attributed to a decrease in the solubility upon increasing temperature. The spectra of homo-PG shown in Figure 13c reveal just the opposite trend: the bands with a clearly visible hyperfine structure at 70 °C progressively broaden with decreasing temperature, and the latter completely disappears at 5 °C. This finding suggests that the mobility of the glycidol units decreases with decreasing temperature due to lowering of the solubility of the PG chains and/or strong H-bonding involving the hydroxyl groups.

In summary, the ^{1}H NMR results show that the interactions of the constituent blocks with water change with temperature in completely opposite manners, which explains the deviating from the expectations findings outlined in the beginning of this section.

Conclusions

In this paper we report our first study on a series of novel copolymers that can be considered as analogues to the commercially available polymeric surfactants Pluronic, in which the hydrophilic PEO blocks are substituted by blocks of linear PG. In particular, the synthesis and preliminary aqueous solution properties are reported. Eight well-defined PG−PPO−PG copolymers were prepared applying a two-step procedure. In the first step using a macroinitiator technique and by anionic polymerization of EEGE, as referred to as protected glycidol, triblock copolymeric precursors of the type PEEGE−PPO−PEEGE were prepared. The protective groups were successfully cleaved in the second step, thus yielding linear PG−PPO−PG triblock copolymers. Both the polymerization and modification reactions were found to proceed in a controllable and predictable way. The final copolymers are of total molecular weight ranging from 2400 to 12 400, molecular weight distribution below 1.28, and PG contents of 20, 30, 40, 50, 60, 70, 80, and 84 wt %; the molecular weight of the middle block of PPO was always 2000.

The thermodynamic data evidence that the aggregation in water of the novel copolymers is an entropy-driven process. Although the increasing PG content reduces the enthalpic barrier to the aggregation and makes the latter entropically less favored, the fundamental mechanism of the aggregation is not altered. Compared to the Pluronic copolymers, the cmc values of the present LGP copolymers at ambient to intermediate temperatures are lower; a less dramatic decrease with increasing temperature was observed. The PG content was found to determine the cmc values, which showed an increase with increasing content. The effect of the PG content, however, was much more pronounced on the cloud-point behavior of the copolymers: three types of transmittance vs temperature curve patterns were observed. The most important finding is that the interactions of the PPO and PG blocks with water change in opposite manners as strongly evidenced by the ^{1}H NMR spectroscopy, which depending on the delicate balance between the constituent blocks imparts a number of peculiar aqueous solution properties of the copolymers.

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