Synthesis of Polyglycidol-Based Analogues to Pluronic L121−F127 Copolymers. Self-Assembly, Thermodynamics, Turbidimetric, and Rheological Studies

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ABSTRACT: The fifth paper of a series, which is focused on polyglycidol-based analogues to Pluronic copolymers, describes the synthesis of another group of eight well-defined polyglycidol−poly(propylene oxide)−polyglycidol (PG−PPO−PG) block copolymers with PG contents varying from 10 to 80 wt % and fixed molecular weight of the middle PPO block of 4000. In composition these copolymers are closest to the Pluronic copolymers of the highest molecular weight of PPO, L121−F127. The copolymers were prepared by means of anionic polymerization of ethoxyethyl glycidyl ether (protected glycidol) followed by cleavage of the protective groups. In aqueous solutions the copolymers were found to self-associate above a certain critical concentration (CMC). The CMC variations with temperature and PG content as well as the thermodynamic parameters of the self-assembly were compared to those of the corresponding Pluronic copolymers and related PG-based copolymers studied earlier. The turbidity measurements carried out in the temperature range from −10 to 60 °C revealed four types of transmittance vs temperature curve patterns depending on PG content. Formation of qualitatively different self-assembled structures was suggested to explain the different curve patterns. Dilute and concentrated aqueous solutions were investigated by means of rheology. Shear thinning was observed for all copolymers even in the dilute (0.5−2.0 wt %) limit which imparts high magnitudes of the zero shear viscosity. The mechanical properties of the high concentrated solutions (33 wt %) were studied by frequency-dependent oscillatory experiments. The solutions of all copolymers invariably behaved as fluids and elastic gels at low (15 °C) and elevated (60 °C) temperatures, respectively.

Introduction

A number of our previous studies[1−4] have focused on the synthesis and aqueous solution properties of novel polyglycidol−poly(propylene oxide)−polyglycidol (PG−PPO−PG) block copolymers. The latter can be considered analogues to the commercially available and widely investigated by a number of research groups and variety of experimental techniques[5−29] Pluronic, poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) (PEO−PPO−PEO), copolymers, in which the flanking PEO blocks are substituted by the structurally similar PG. Figure 1 shows the chemical structures of the monomer units of PEO, PPO, and PG. The PG analogues were nominally based on PPO of constant molecular weight of 2000 and were prepared in different PG contents covering the range from 20 to 84 wt %. Their aqueous solution properties in wide temperature and concentration ranges were investigated as a function of the PG content.[1−4] It is remarkable that significant differences in the aqueous solution properties can arise from seemingly small alterations in the chemical structure of the hydrophilic block. For example, compared to Pluronic copolymers, the self-assembly of the PG-based copolymers is entropically less favored with a lower enthalpic barrier; the critical micellization concentration (CMC) values decrease with increasing temperature less strongly; an increase of transmittance with increasing temperature for solutions of higher (above 50 wt %) PG content was observed.[1] Responsible for these peculiarities is the well-documented fact that the interactions of PPO and PG with water change upon heating in opposite manners,[1] in contrast to the reverse solubility of both constituent blocks of the Pluronic copolymers.

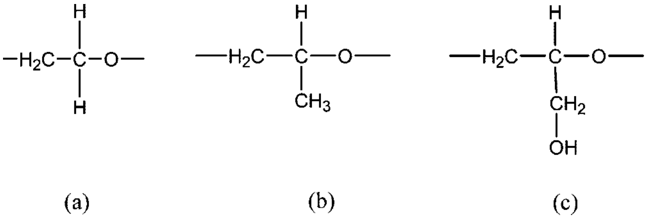

Figure 1. Monomer units of (a) poly(ethylene oxide), (b) poly(propylene oxide), and (c) linear polyglycidol.

Furthermore, the PG-based analogues (hereinafter LGP60 copolymers) formed in aqueous solution nanosized particles. Their dimensions and aggregation numbers were considerably larger than those of the corresponding Pluronic copolymers as revealed by light scattering.[2] The interior of these large particles, as studied by small-angle neutron scattering,[3] consisted of slightly prolate spherical PPO domains that coexisted with individual, nonassociated copolymer chains. The striking difference was attributed to the strong hydrogen bonding promoted by the numerous hydroxyl groups. Thus, hydrophobic interactions of the PPO blocks and multiple intra- and interchain hydrogen bonds in the PG moieties were equally involved in the formation of the large compound particles.[2] The rheological properties of the LGP60 copolymers were largely dictated by the size and structure of the large compound particles as well as by their dependence on temperature and PG content.[4]

Whereas in the previous studies[1−4] the investigations were made with a special emphasis to the effect of the PG content, little is known about the effect of PPO. Therefore, we expanded the study by creating more series of PG−PPO−PG copolymers nominally based on PPO of molecular weights 1000 and 4000. In this paper the synthesis of a series of copolymers with a middle block based on PPO 4000 (degree of polymerization of

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68) and PG content varying from 10 to 80 wt % is described. The resulting block copolymers are closest in composition to the Pluronic series L121−F127. The preliminary aqueous solution properties in wide temperature and concentration intervals are investigated by CMC determination, turbidimetry, and rheology.

Experimental Section

A. Materials. The solvents (methanol, methylene chloride, tetrahydrofuran) were purified by distillation. Glycidol (96%, Aldrich) was distilled under reduced pressure. Ethyl vinyl ether (99%, Aldrich), $AlCl_3 \cdot 6H_2O$ (99%, Aldrich), and $CsOH \cdot H_2O$ (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.[30] Fractions of EEGE of purity exceeding 98.5%, determined by gas chromatography, were used for polymerization. Poly(propylene oxide) 4000 (Fluka) was dried by azeotropic distillation using toluene. Potassium naphthalide was prepared by adding potassium in small portions to a solution of naphthalene in anhydrous tetrahydrofuran under stirring in an inert atmosphere until the mixture is colored in the typical dark green color.

B. Synthesis of Block Copolymers. *1a. Preparation of the Macroinitiator for the Synthesis of Copolymers of PG Contents ≤60 wt %.* $CsOH \cdot H_2O$ (0.084 g, 0.5 mmol) was added to PPO 4000 (1.248 g, 0.312 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.

1b. Preparation of the Macroinitiator for the Synthesis of Copolymers of PG Contents of 70 and 80 wt %. A 160 mL solution of potassium naphthalide (67 mg of naphthalene, 20 mg of potassium) in tetrahydrofuran was titrated under stirring in an inert atmosphere with a solution of PPO 4000 (1 g, 0.25 mmol) in tetrahydrofuran (5 mL) until the dark green color disappeared.

2a. Polymerization (Synthesis of PEEGE−PPO−PEEGE Precursors for Targeting PG Contents ≤60 wt %). EEGE (3.65 g, 25 mmol) was introduced to the macroinitiator obtained in **1a** to synthesize $(EEGE)_{40}(PO)_{68}(EEGE)_{40}$. The polymerization was carried out in bulk at 90 °C. The conversion of the monomer was followed by ^1H nuclear magnetic resonance spectroscopy. The syntheses of the rest of the PEEGE−PPO−PEEGE precursors were carried out in analogy to this procedure.

2b. Polymerization (Synthesis of PEEGE−PPO−PEEGE Precursors for Targeting PG Contents of 70 and 80 wt %). EEGE (4.6 g, 31.5 mmol) was introduced to the macroinitiator obtained in **1b** to synthesize $(EEGE)_{63}(PO)_{68}(EEGE)_{63}$. The polymerization was carried out in tetrahydrofuran at reflux for 48 h. The conversion of the monomer was followed by ^1H nuclear magnetic resonance spectroscopy. The synthesis of the $(EEGE)_{135}(PO)_{68}(EEGE)_{135}$ precursor was carried out analogously.

3. Deprotection Reaction (Synthesis of PG−PPO−PG Copolymers). The procedure was adopted from a method for deprotection of tetrahydropyranyl ether, described elsewhere.[31] 3.92 g of $(EEGE)_{40}(PO)_{68}(EEGE)_{40}$, containing 20 mmol of EEGE units, was dissolved in methanol (7.5 mL, 160 mmol). $AlCl_3 \cdot 6H_2O$ (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 deprotection reactions for the rest of the copolymers were carried out analogously.

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 was used as an eluent at a flow rate of 1 mL/min at 40 °C. Samples were prepared as solutions in tetrahydrofuran. Toluene was used as the internal standard for indication of elution volume. Calibration was made with polystyrene standards.

2. 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 thermostated cuvette holder and heated slowly with heating rate of 1 °C/min from −10 to 60 °C. The temperature was controlled with accuracy of ±0.1 °C.

3. Determination of the Critical Micellization Concentration (CMC). Aqueous solutions (2.0 mL) of a given triblock PG−PPO−PG copolymer in the concentration range from 0.001 to 5 wt % were prepared at 0 °C. 20 μL of a 0.4 mM solution of 1,6-diphenyl-1,3,5-hexatriene (DPH) 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 spectrometer. The main absorption peak, characteristic for DPH solubilized in a hydrophobic environment, was at 356 nm.

4. Rheology. Oscillatory shear and steady shear experiments were carried out on a Thermo Haake 600 rheometer equipped with cone/plate and plate/plate geometry, respectively. The diameter and the gap width of the rotating inner bob were 60 and 2 mm, respectively, whereas the cone sensor diameter was 25 mm. Both series of experiments were carried out in a controlled stress mode. Copolymer solutions were transferred to the instrument and carefully overlaid with a low-viscosity silicone oil to minimize water evaporation. Oscillatory experiments were performed for high-viscosity samples (concentrated solutions). The storage modulus (G') and the loss modulus (G'') were measured over the frequency range 0.01−1000 Hz. The values of the stress amplitude were checked in order to ensure that all measurements were performed within the linear viscoelastic region, where the dynamic moduli are independent of the applied stress. For low-viscosity samples (dilute solutions), steady shear experiments were performed in the range 0.01−2000 s^{-1}. The measurements were performed at different temperatures ranging from −10 to 70 °C. The temperature was controlled with accuracy of ±0.1 °C.

Results and Discussion

Synthesis and Characterization of the Precursors and Targeting Copolymers. The syntheses of the present triblock copolymers were carried out using the same two-step procedure described earlier:[1] in the first step PEEGE−PPO−PEEGE precursors were prepared by anionic polymerization of EEGE using (partially) deprotonated PPO 4000 as a macroinitiator and cleavage of the protective groups in the second step, thus yielding linear PG−PPO−PG triblock copolymers. The majority of the precursors were prepared in bulk at 90 °C using CsOH as a deprotonating agent. This approach, however, has shown some limitations as far as the syntheses of copolymers of molecular weight higher than 22 000 are concerned.[1] The limitations are related to bad reproducibility of the results, low yields, relatively high molecular weight distributions, appearance of asymmetry, shoulders, and even additional peaks in the GPC curves, etc. Therefore, to prepare precursors of total molecular weight above 22 000, potassium naphthalide was used as a deprotonating agent of PPO 4000 and the polymerization of EEGE was carried out in tetrahydrofuran at reflux.

The block structure of the resulting PEEGE−PPO−PEEGE copolymer precursors was proved by GPC. The GPC traces for the starting PPO 4000 and two of the resulting copolymers are presented in Figure 2. Traces 2 and 3 in Figure 2 correspond to copolymers prepared in bulk at 90 °C and in tetrahydrofuran at reflux using CsOH and potassium naphthalide, respectively, as deprotonating agents for PPO 4000. The dispersity indices, also determined by GPC, ranged from 1.05 to 1.22 for the whole series of copolymers (for details see Supporting Information).

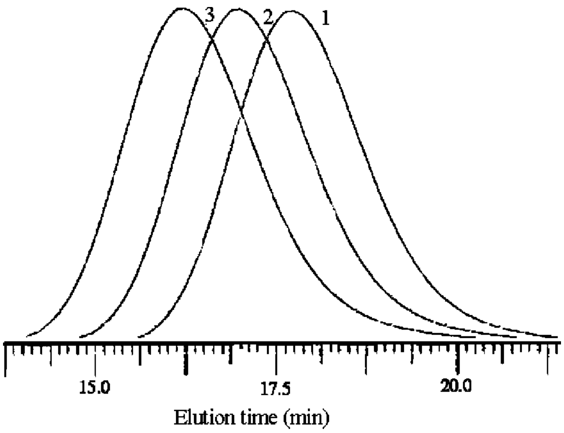

Figure 2. Gel permeation chromatography traces of PPO 4000 (1) and two poly(ethoxyethyl glicidyl ether)−poly(propylene oxide)−poly(ethoxyethyl glicidyl ether) copolymer precursors with compositions 27−68−27 (2) and 135−68−135 (3).

The ^{1}H nuclear magnetic resonance spectra of the precursors, from which their compositions are determined, are qualitatively similar to those shown earlier.[1] An example is presented in the Supporting Information. To obtain the targeting PG−PPO−PG copolymers, the PEEGE blocks of the precursors should be converted into PG blocks by cleavage of the protective ethoxyethyl groups. It has been shown[1,32] recently that no destruction of the polyether backbone takes place during the deprotection reaction. The degrees of polymerization of the PG blocks determined from the ^{1}H nuclear magnetic resonance spectra in DMSO-d_6 (see Supporting Information for an example of a spectrum in DMSO-d_6) are in excellent agreement with those of the PEEGE blocks of the corresponding precursors and the theoretical ones (Table 1). Considering the composition, the present polyglycidol-based copolymers are closest in composition to the Pluronic series L121−F127. In the following the collective abbreviation LGP130 copolymers will be used.

Aqueous Solution Properties. The preliminary aqueous solution properties, in particular determination of the critical micellization concentration and turbidity measurements, were studied in wide ranges of concentrations and temperatures.

CMC Determination. For determination of the CMCs at different temperatures the properties of the hydrophobic dye 1,6-diphenyl-1,3,5-hexatriene (DPH) were exploited. DPH is sensitive to changes in the microenvironment: its absorbance is minimal in water, whereas in hydrophobic environments substantially increases showing a characteristic maximum at 356 nm. DPH has been first employed to study the fluidity of membranes and dynamic phenomena in vesicles[33−36] and later on for determination of CMC of conventional and polymeric surfactants.[1,5,37−40] A typical plot of DPH absorbance at 356 nm vs copolymer concentration, from which CMC was determined, is presented in Figure 3. The CMC data for all copolymers studied are plotted in parts a and b of Figure 4 as functions of temperature and PG content, respectively. Each of the curves in Figures 4a,b represents a boundary above which hydrophobic domains are detected. The CMC values are invariably below ca. 0.09 wt %, which is lower than the CMC values of the LGP60 copolymers.[1] Considering the higher molecular weight of the present copolymers, this finding was in line with the expectations. Compared to the corresponding Pluronic copolymers they self-associate easier (lower CMC values); however, the micellization is less sensitive to temperature. As clearly seen in Figure 4a, the CMCs are only slightly (copolymers of higher PG content) or practically not affected by temperature.

The shapes of the curves in Figure 4b are qualitatively similar to those for the LGP60 copolymers observed at 50 and 60 °C.[1] The break indicates the existence of a critical content of polyglycidol above which the micellization is suddenly hindered, evidenced by the sharp increase in the CMCs. In contrast to the previous series the break is observed for all investigated temperatures, and it is shifted toward the lower PG contents. The critical contents, determined as the PG content at which the curves departed from the lower region of CMCs, are 50 and 70 wt % for LGP130s and LGP60s, respectively, corresponding to LGP135 and LGP67. However, what is more interesting is that the degrees of polymerization of the PG blocks of LGP135 and LGP67 are the same: 26−27. Apparently, that critical degree of polymerization at which the properties of the PG blocks become more influential, and as a result the copolymers suddenly become more hydrophilic, is universal for the two series of copolymers. Experiments are in progress to prove the applicability of this finding to another series of copolymers nominally based on PPO 1000.

Thermodynamics of Micellization. The free energy of micellization ($\Delta G°$) is related to the CMC via the equation[41]

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

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. Figure 5 depicts the variations of $\Delta G°$ for two copolymers with temperature. The $\Delta G°$ values for all copolymers are negative, which indicates spontaneous micellization. As clearly seen from Figure 5, $\Delta G°$ becomes more negative with increasing temperature and/or decreasing PG content. The standard enthalpy of micellization ($\Delta H°$) and the standard entropy of micellization ($\Delta S°$) were determined according to eq 2,[41] and the values are collected in Table 2.

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

The data in Table 2 indicate that the aggregation of the copolymers is an entropy-driven process; however, compared to the copolymers Pluronic, it is entropically less favored (lower $\Delta S°$ values) with a reduced enthalpic barrier (lower $\Delta H°$ values). A feature that makes the present copolymers different from the copolymers of the previous series[1] is the way the values of $\Delta H°$ and $\Delta S°$ change with PG content. In contrast to the latter for which both $\Delta H°$ and $\Delta S°$ were found to gradually increase with decreasing PG content, here, a stepwise increase at critical PG contents of 50 and 10 wt % is observed (Table 2). The stepwise increase reflects the variations of CMC (X_{CMC}, respectively) with the copolymer composition.

Turbidity Measurements. The measurements of turbidity were carried out on solutions in the concentration interval from 1 to 10 wt %. It is known that the cloud point and, in general, the variations in turbidity of solutions of polyoxyalkylenes depend only weakly on solute concentration. Typically, the clouding of 1 wt % solutions is presented as a characteristic value in the scientific literature and industrial brochures and reports.

The variations of transmittance with temperature for the present copolymers can be broadly divided into four types (Figure 6). Whereas the solutions of the copolymers of low (≤30 wt %) PG content are opaque but homogeneous in the whole temperature interval investigated, those of the copolymers of PG content ≥70 wt % showed no clouding with transmittance of above 90%. The solutions of LGP135 and LGP136 are more temperature sensitive, exhibiting a detectable critical temperature around 17−18 °C at which the transmittance slightly but sharply increases. The remarkable bell-like curve observed for LGP134 complements the entire picture; similarly to its composition analogue, LGP64,[1] LGP134 exhibits two highly opalescent

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

	total degree of polymerization of the flanking blocks				
		experimental			
targeting PG content (wt %)	theoretical	PEEGE[c]	PG[d]	copolymer composition	abbreviation[e]
10[a]	6	6	6	$(G)_3(PO)_{68}(G)_3$	LGP131
20[a]	14	14	14	$(G)_7(PO)_{68}(G)_7$	LGP132
30[a]	24	22	24	$(G)_{12}(PO)_{68}(G)_{12}$	LGP133
40[a]	36	33	36	$(G)_{18}(PO)_{68}(G)_{18}$	LGP134
50[a]	54	50	54	$(G)_{27}(PO)_{68}(G)_{27}$	LGP135
60[a]	80	77	80	$(G)_{40}(PO)_{68}(G)_{40}$	LGP136
70[b]	126	123	126	$(G)_{63}(PO)_{68}(G)_{63}$	LGP137
80[b]	270	262	270	$(G)_{135}(PO)_{68}(G)_{135}$	LGP138

[a] The precursors were obtained in bulk at 90 °C using CsOH as a deprotonating agent. [b] The precursors were obtained in tetrahydrofuran at reflux using potassium naphthalide as a deprotonating agent. [c] Determined from the ^{1}H NMR spectra of PEEGE−PPO−PEEGE precursors in $CDCl_3$ assuming an average degree of polymerization of the middle block of PPO of 68. [d] Determined from the ^{1}H NMR spectra of PG−PPO−PG in DMSO-d_6 assuming an average degree of polymerization of the middle block of PPO of 68. [e] The last digit multiplied by 10 gives the PG content in wt %.

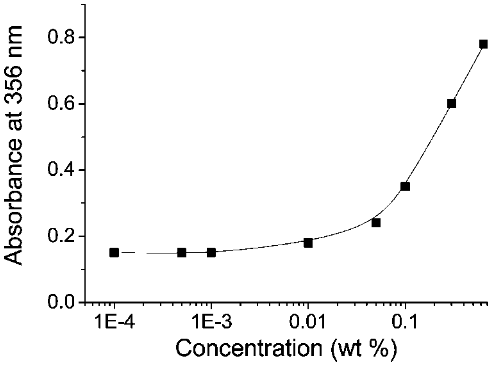

Figure 3. Variations of the absorbance of DPH at 356 nm with LGP135 concentration at 25 °C.

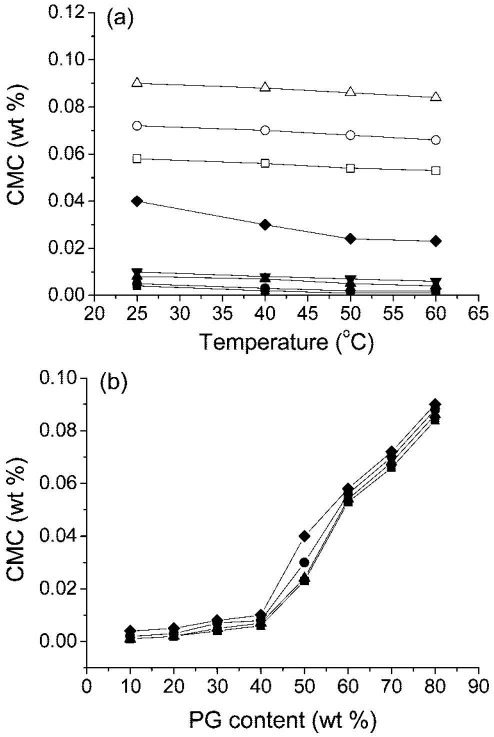

Figure 4. Critical micellization concentrations as a function of (a) temperature and (b) PG content. Symbols in (a): LGP131 (closed squares), LGP132 (closed circles), LGP133 (closed triangles), LGP134 (closed inverted triangles), LGP135 (diamonds), LGP136 (open squares), LGP137 (open circles), and LGP138 (open triangles). Symbols in (b): 25 °C (squares), 40 °C (triangles), 50 °C (circles), and 60 °C (diamonds).

regions separated by a window in which the solutions appear clear and isotropic. It is notable that this type of behavior is observed for copolymers that considerably differ in total molecular weight but have the same (40 wt %) PG content. This confirms our earlier suggestion[1] that the specific copolymer composition, rather than the presence of impurities (the trivial explanation for the presence of double clouding for some Pluronic copolymers[8,11,42]), is responsible for the peculiar behavior. We must point out here that the results for both LGP64[1] and LGP134 were reproduced within the experimental error following filtration through tight filters.

A prominent feature of copolymers LGP131, LGP132, and LGP133 is that sigmoidal curve patterns typical for materials with low critical solution temperature (LCST) properties as those observed earlier for their composition analogues LGP62 and LGP63[1] were not observed (Figure 6). The sudden increase in solubility of the latter copolymers upon cooling arises from the proximity of the investigated concentration range to the CMCs; CMCs in the range 0.15−0.20 wt % at 25 °C were determined.[1] Taking into account that the LCST of PPO 2000 is about 19 °C, one may expect that the aggregates that LGP62 and LGP63 formed would easily dissociate upon further cooling. The curve patterns of these molecular solutions reflect the expected behavior of materials based on PPO 2000.[1] The CMC range of copolymers LGP131, LGP132, and LGP133 is about 2 orders of magnitude lower than the concentration interval investigated in the present section. In addition, the LCST of PPO 4000 is about 11 °C. In other words, the aggregates that LGP131, LGP132, and LGP133 form are much more stable with regard to both concentration and temperature compared to those of LGP62 and LGP63. The temperature decrease would stabilize them because of the well-documented lowering of the solubility of the PG chains and/or strong H-bonding involving the hydroxyl groups.[1] Thus, even at temperatures at which PPO 4000 is presumably soluble, formation of molecular solutions is not expected. Instead, supposedly not well-defined, large and loose aggregates (hereinafter clusters) are formed. The cluster formation based on H-bonding nullifies the effect of enhanced solubility of PPO 4000, and as a consequence no clearing of the solutions upon cooling was observed. The next question to be answered is why clusters, rather than the better-defined structures (micelles), are formed on cooling. It is known that a critical molecular weight/degree of polymerization of the insoluble block should be reached to make the micelle formation possible. For the present series of copolymers such a critical degree of polymerization is obviously 27, corresponding to PG content of 50 wt % or copolymer LGP135. A strong indication clearly seen from Figure 6 is that the solution of LGP135 only slightly but notably changes its appearance on cooling, in sharp contrast to the copolymer of slightly lower degrees of polymerization of the PG blocks, LGP134. The micelles, as noted

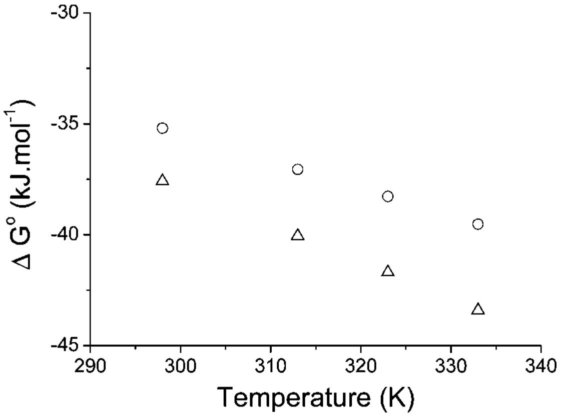

Figure 5. Micellization free energy, $\Delta G°$, as a function of temperature for LGP138 (circles) and LGP134 (triangles).

Table 2. Enthalpy ($\Delta H°$) and Entropy ($\Delta S°$) of Micellization of the Investigated LGP130 Copolymers in Aqueous Solution

copolymer	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ mol^{-1} K^{-1})
LGP131	30.652	0.235
LGP132	16.043	0.183
LGP133	11.103	0.173
LGP134	11.940	0.176
LGP135	12.002	0.180
LGP136	1.249	0.118
LGP137	1.365	0.119
LGP138	1.571	0.123

elsewhere,[43] are significantly more soluble than the clusters, which explains the differences in the transmittance of LGP135 and LGP131−LGP134 in the temperature range below, e.g., 20 °C. In that context the low- and high-temperature parts of the transmittance curve of LGP135 in Figure 6 can be attributed to structures formed as a result of lowered solubility of the PG chains and/or strong H-bonding and self-association due to hydrophobic interactions of PPO, respectively. Even a transition temperature of around 18 °C can be detected, which remarkably coincides with the transition temperature for LGP134 as shown in Figure 6. This indicates that the same phenomena are behind the experimental facts. Analogously, the low-temperature part of the transmittance curve of LGP134 can be attributed to presence of clusters due to H-bonding and/or lowered solubility of the PG chains. Upon heating, a transition interval is observed in which the mobility of the PG chains and hydrophobicity of PPO simultaneously increase. The superposition of the two opposite processes leads to rearrangement of the particles; thus, the clearing can be associated with formation of better defined self-assembled structures with PPO interior and PG chains extending into aqueous phase. Upon further heating, PPO becomes increasingly hydrophobic; the PG chains are obviously not long enough to counteract the increased hydrophobicity and, consequently, not able to provide steric stabilization of the particles which results in secondary aggregation, leading to a sharp drop in transmittance. The uneventful curve for LGP137 (and LGP138) can be explained with the size similarities of the structures formed at lower and elevated temperatures, that is, with PPO and PG, respectively, in the outer regions. Experiments based on scattering methods with a special attention to the low temperature interval are underway.

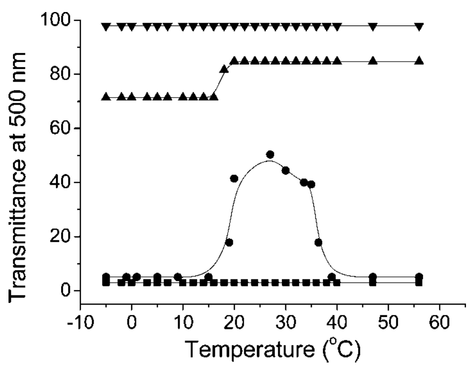

Figure 6. Transmittance vs temperature curves for 1 wt % aqueous solutions of LGP132 (squares, representative for LGP131 and LGP133), LGP134 (circles), LGP135 (triangles, representative for LGP136), and LGP137 (inverted triangles, representative for LGP138). The lines through the data are drawn to guide the eye.

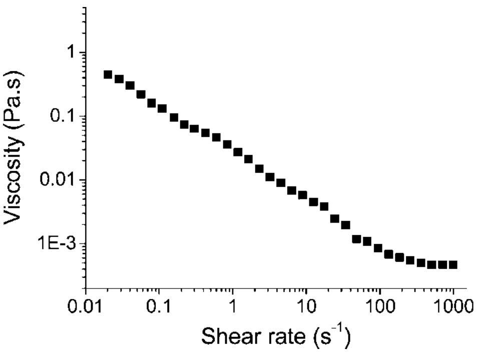

Figure 7. Viscosity vs shear rate for 0.5 wt % aqueous solution of LGP135 at 50 °C.

Rheology of Aqueous Solutions. To investigate the effects of the PG content and temperature, two limiting concentration ranges were explored. These particular intervals, dilute (0.5−2.0 wt %) and concentrated (33 wt %), were selected to compare the rheological properties of the present LGP130 copolymers with those of the related LGP60 copolymers studied earlier.[4]

Dilute Solutions. Steady shear viscosity measurements reveal that the solutions despite the low but invariably above the CMCs concentrations normally behave as non-Newtonian fluids. Figure 7 shows a steady shear viscosity profile that is representative for all LGP130 copolymers in the temperature (25−60 °C) and concentration (0.5−2 wt %) intervals studied. The results indicate that the solutions are non-Newtonian over at least 3 decades of shear rates; at shear rates typically above 100 s^{-1} a Newtonian region, in which the viscosity is independent of shear rate, is observed. The rheothining behavior of the present copolymers in the dilute limit is the first main difference from the related LGP60 copolymers studied earlier.[4] The second ones are the magnitudes of the zero shear viscosity, η_0. The latter was obtained by extrapolating the linear, non-Newtonian, part of the viscosity curves to zero shear rate. The values of η_0 are several orders of magnitude larger than those of the LGP60 copolymers at the same conditions.[4] The variations of η_0 with PG content and temperature of 0.5 wt % solutions are presented as a 3D plot in Figure 8. The temperature dependence of η_0 is the next feature that makes the present copolymers different: the zero shear viscosity was found to generally increase upon heating being more pronounced for the copolymers of intermediate PG content, LGP135 and LGP136. Similarly to the copolymers reported previously,[4] pronounced maxima, especially in the 40−60 °C range, were observed at a PG content of 50 wt %.

Concentrated Solutions. The mechanical properties of the concentrated solutions were investigated by frequency-dependent oscillatory experiments carried out at temperatures 15 and 60 °C, concentrations of 33 wt %, and constant shear stress. The copolymers of PG contents ≤30 wt % form two-phase systems at that concentration and therefore were not investigated. The mechanical spectra of the solutions of the rest of the copolymers

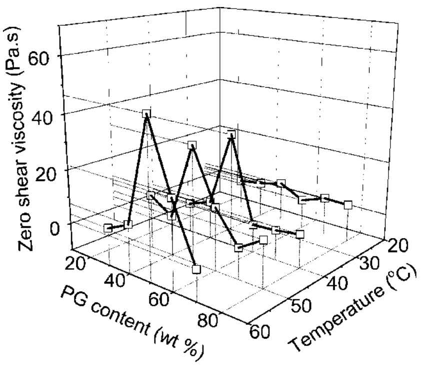

Figure 8. Zero shear rate viscosity as a function of PG content and temperature for aqueous solutions of PG−PPO−PG block copolymers at concentration of 0.5 wt %.

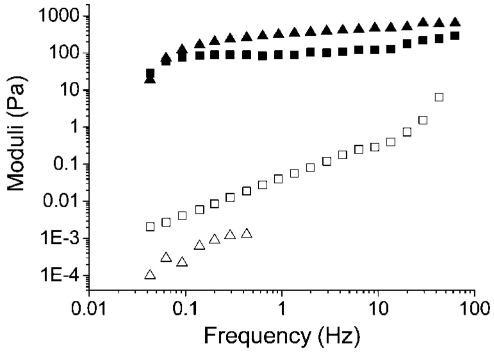

Figure 9. Storage, G' (triangles), and loss G'' (squares), moduli as a function of frequency at 15 °C (open symbols) and 60 °C (closed symbols) for LGP138. Copolymer concentration 33 wt %.

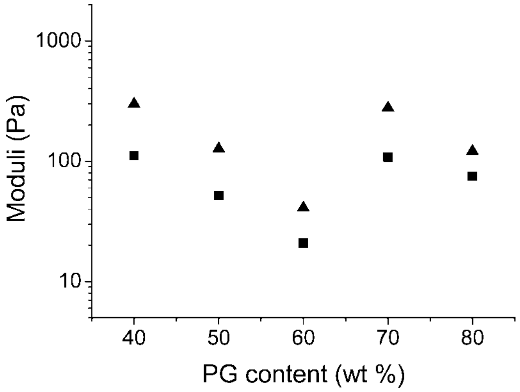

Figure 10. Storage, G' (triangles), and loss, G'' (squares), moduli as a function of PG content at a frequency of 0.1 Hz and temperature of 60 °C. Copolymer concentration 33 wt %.

are similar and differ only in minor details. A typical spectrum is shown in Figure 9; more spectra are presented in the Supporting Information. Invariably at 15 °C the solutions behave as fluids with a loss modulus, G'', larger than the storage modulus, G', whereas at 60 °C the moduli curves are rather flat and the elastic character of the solutions is predominant as $G' > G''$. Only at lower frequency a flow zone at 60 °C is possibly observable. At a given frequency and 60 °C slight variations in moduli values with PG content were exhibited as shown in Figure 10. The evolution of the moduli at a frequency of 0.1 Hz (Figure 10) shows very nicely the differences with the related LGP60 copolymers,[4] e.g., the invariably elastic character at 60 °C and the larger magnitudes of both moduli of the concentrated solutions of the LGP130 copolymers.

Concluding Remarks

In this paper we report a study on the synthesis and preliminary aqueous solution properties of a novel series of LGP, that is, linear polyglycidol−poly(propylene oxide)−polyglycidol, copolymers. In composition, given by the formula $(G)_n(PO)_{68}(G)_n$ where $n = 3-135$, G and PO represent the glycidol and propylene oxide monomer units, respectively, they are closest to the Pluronic series L121−F127. The copolymers were obtained by applying a two-step synthetic procedure. In the first step triblock copolymeric precursors PEEGE−PPO−PEEGE were obtained by anionic polymerization of EEGE applying a macroinitiator technique, whereas in the second step the protective groups of the PEEGE blocks were successfully cleaved, yielding linear PG−PPO−PG triblock copolymers. The resulting copolymers are of total molecular weight ranging from 4400 to 24 000, molecular weight distribution below 1.22, and PG contents in the interval from 10 to 80 wt %. The copolymeric precursors for targeting PG contents up to 60 wt % were obtained in bulk at 90 °C using CsOH as a deprotonating agent. This technique, however, was demonstrated to be nonapplicable for the synthesis of copolymers of higher molecular weight. Therefore, the PEEGE−PPO−PEEGE precursors for LGP137 and LGP138 were prepared in tetrahydrofuran using potassium naphthalide as a deprotonating agent.

The present LGP130 copolymers self-associate in aqueous solution easier (lower CMC values) than both related LGP60 copolymers studied earlier and corresponding Pluronic copolymers. Their micellization, however, is less temperature sensitive compared to the latter. The self-assembly is an entropy-driven process as the thermodynamic data evidence though it is entropically less favored and the enthalpic barrier is further reduced compared to the related LGP60 copolymers. The turbidity measurements carried out in an extended (from −10 to 60 °C) temperature interval reveal that the transmittance vs temperature curves are featured by four different patterns depending on PG content. To explain the peculiar curve patterns, we speculate on the formation of qualitatively different structures comprising interiors made of PG and PPO at lower and elevated temperatures, respectively.

In strong contrast to the related LGP60 copolymers, the copolymers of the present series behave as non-Newtonian fluids in the dilute limit as steady shear viscosity measurements reveal. They are characterized by considerably higher magnitudes of the zero shear viscosity. The latter was found to generally increase with increasing temperature—a feature that is closer to the behavior of the Pluronic rather than to that of the related LGP60 copolymers. The concentrated solutions are invariably elastic at 60 °C and are typified by larger magnitudes of both moduli compared to LGP60 copolymers. The different properties of the LGP130 copolymers may be explained with large differences in the structure, density, and compactness of the aggregates that LGP130 copolymers form as preliminary studies based on scattering methods and electron microscopy indicate.

Critical changes in the properties of the aqueous solutions studied as a function of PG content were repeatedly observed at PG content of 50 wt %, corresponding to LGP135. Some of the experimental facts are (i) a sudden increase in CMC, $\Delta H°$, and $\Delta S°$, (ii) pronounced maxima of η_0, and (iii) transition to qualitatively different transmittance vs temperature curve patterns. Apparently, these peculiar properties origin from the delicate and changeable balance between constituent blocks whose solubilities change in opposite manners.

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Supporting Information Available: Experimental details. The material is available free of charge via the Internet at http://pubs.acs.org.

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