Supplementary Information

Influence of hydrophilic block length on aggregation properties of polyglycidol-polystyrene-polyglycidol copolymers

Łukasz Otulakowski[1*], Maciej Kasprow[1], Mariusz Gadzinowski[2], Stanislaw Slomkowski[2], Tomasz Makowski[2], Teresa Basinska[2], Aleksander Forys[1], Marcin Godzierz[1], Barbara Trzebicka[1]

[1]Centre of Polymer and Carbon Materials, Polish Academy of Sciences, M. Curie-Skłodowskiej 34, Zabrze, 41-819, Poland

[2]Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland

*Corresponding author: Łukasz Otulakowski

Synthesis of polyglycidol-polystyrene-polyglycidol (PGL-PS-PGL) copolymers

Synthesis of difunctional initiator (1,1-diphenylethylene dimer with lithium counterions) used for preparation of HO-PS-OH difunctional macroinitiator

The difunctional initiator was obtained in reaction of 1,1-diphenylethylene (DPE) with lithium in dry THF [1]. Recipe: 1.485 g (0.00824 mol) of DPE (purified with n-BuLi and distilled under high vacuum) was dissolved in 5 ml of dry THF and 0.35 g (0.05 mol, excess) of freshly cut lithium pieces were added. After 30 min. of stirring color of the mixture was changed to deep blue and after next several minutes - to deep red, due to rapid dimerization of DPE radical anions. The mixture was stirred further during 24 hours at room temperature. The above reaction is quantitative. The solution was separated from residual lithium and immediately used for polymerization of styrene.

Synthesis of HO-PS-OH difunctional macroinitiator

The whole amount of the aforementioned initiator solution was added to 250 ml of dry toluene containing 24.7 g (0.2375 mol) of dried styrene. The mixture was prepared in vial in inert (air-free) atmosphere and anionic living polymerization was carried out with stirring in argon atmosphere at 0-5°C for 1h. The reaction vial was then opened under argon atmosphere and an excess of dry ethylene oxide was added (about 10 ml). After 15 min. an excess of formic acid solution in THF (15 ml 10%) was added to convert living alkoxide centers at the polymer ends into hydroxyl groups. The resulting bi-sided hydroxyl-terminated polystyrene (HO-PS-OH macroinitiator) was precipitated into methanol and dried under vacuum (with yield=95 %). Plot of the relevant 1H NMR spectrum is shown in Figure SI1. Expected molar mass calculated from monomers (polystyrene, initiator feed incorporates poly(ethylene oxide)) was 6490 g/mol.

Synthesis of PGL-PS-PGL copolymers

In the first step the HO-PS-OH macroinitiator was used for anionic polymerization of glycidol with blocked hydroxyl groups (1-ethoxyethyl glycidyl ether (GLB)). Prior to polymerization, 1,1-ethoxyethyl glycidyl ether (GLB) was prepared in reaction of glycidol with ethyl vinyl ether according method described by Fitton at al.[2].

Four samples of linear copolymers (PGLB-PS-PGLB) were prepared in the following way. The macroinitiator was dissolved in ca. 25 ml of dry THF in air-free vial and activated by freshly prepared potassium mirror within 24h. This procedure allowed transformation of hydroxyl end groups into alkoxide anions. The resulting solution was poured into next vial under vacuum and various amounts of GLB (regarding to the desired molar mass of PGLB block) were added. Polymerization was carried out at 45°C for 4 days and then alkoxide living centers on chains ends were terminated by adding excess of water. The resulting copolymer was precipitated into warm water. The crude viscous products were dried in vacuum. The ^{1}H NMR spectra of obtained copolymers in $CDCl_3$ were recorded. These spectra are shown in Figures SI2 – SI5. The amounts of reagents used in synthesis of each type of copolymer and their molar masses are listed in Table SI1.

Table SI1. Amounts of reagents used for synthesis of copolymers, molar masses and compositions of obtained copolymers determined from ^{1}H NMR spectra.

	PGLB-PS-PGLB(1)	**PGLB-PS-PGLB(2)**	**PGLB-PS-PGLB(3)**	**PGLB-PS-PGLB(4)**
HO-PS-OH (M_n=6600 g/mol)	4.85 g (0.000730 mol)	2.70 g (0.000410 mol)	0.500 g (0.0000758 mol)	2.90 g (0.000440 mol)
GLB	2.358 g (0.0162 mol)	3.220 g (0.0220 mol)	0.924 g (0.00633 mol)	7.373 g (0.0505 mol)
M_n [g/mol]	M_n=9800	M_n=13900	M_n=20600	M_n=23800
Copolymer composition obtained from feed	$PGLB_{11}$-PS_{60}-$PGLB_{11}$	$PGLB_{27}$-PS_{60}-$PGLB_{27}$	$PGLB_{41}$-PS_{60}-$PGLB_{41}$	$PGLB_{57}$-PS_{60}-$PGLB_{57}$
Copolymer composition obtained from ^{1}H NMR	$PGLB_{11}$-PS_{60}-$PGLB_{11}$	$PGLB_{23}$-PS_{60}-$PGLB_{23}$	$PGLB_{44}$-PS_{60}-$PGLB_{44}$	$PGLB_{63}$-PS_{60}-$PGLB_{63}$

Deprotection of hydroxyl groups in poly(1-ethoxyethyl glycidyl ether) units in copolymers was performed in the following way: 2.5 g of PGLB-PS-PGLB copolymer was dissolved in 8 ml of 1,4-dioxane and 10 ml of methanol was added dropwise until the mixture become slightly opaque. Then 50 mg of $AlCl_3 \cdot 6H_2O$ was added and the mixture was stirred at 40°C for 3h [3,4]. Copolymer solution was dialyzed against 10^{-2} mol/l HCl and subsequently against water using SERVA SpectraPor dialyzing tube with MWCO (molecular weight cut-off) 1000 g/mol. The final products were lyophilized and their ^{1}H NMR spectra in DMSO-d6 were recorded. The spectra of obtained copolymers are shown in Figures SI6 – SI9. Molar masses and copolymer compositions determined from the ^{1}H NMR spectra are given in Table 2 of the main text.

Characterization of PGL-PS-PGL copolymers

^{1}H NMR spectra

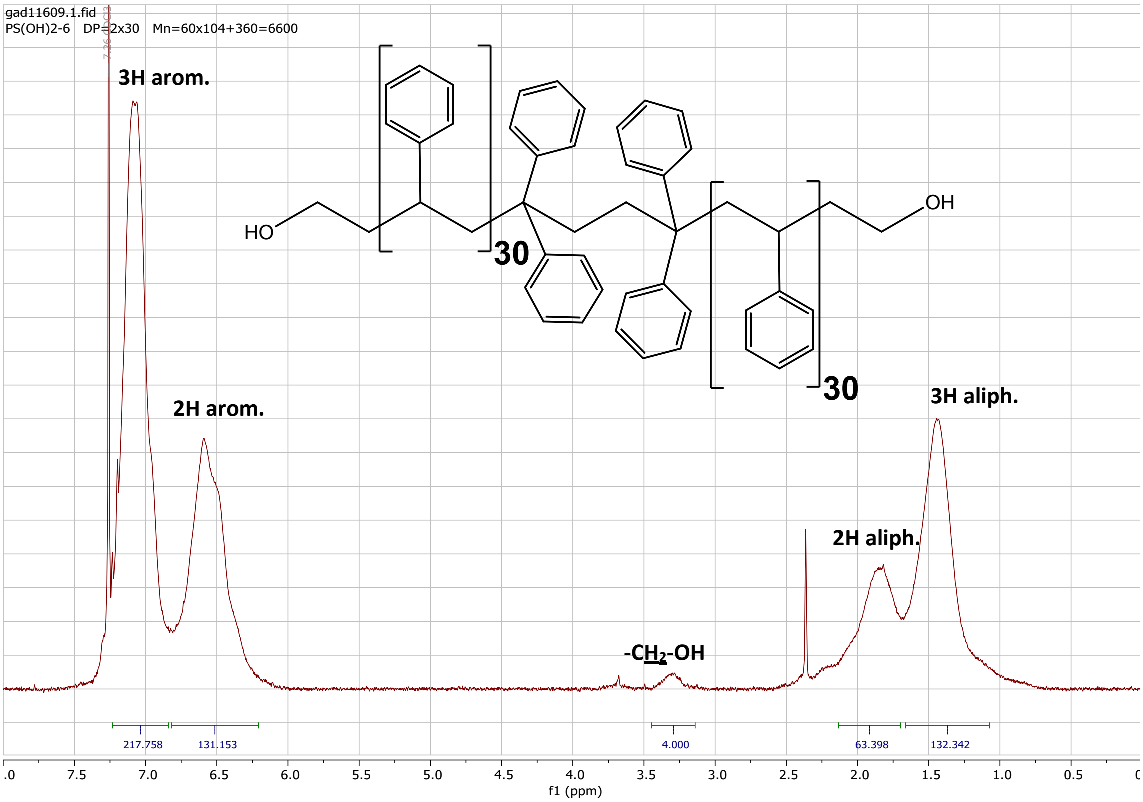

Figure SI1. 1H NMR spectrum of HO-PS-OH macroinitiator in CDCl$_3$.

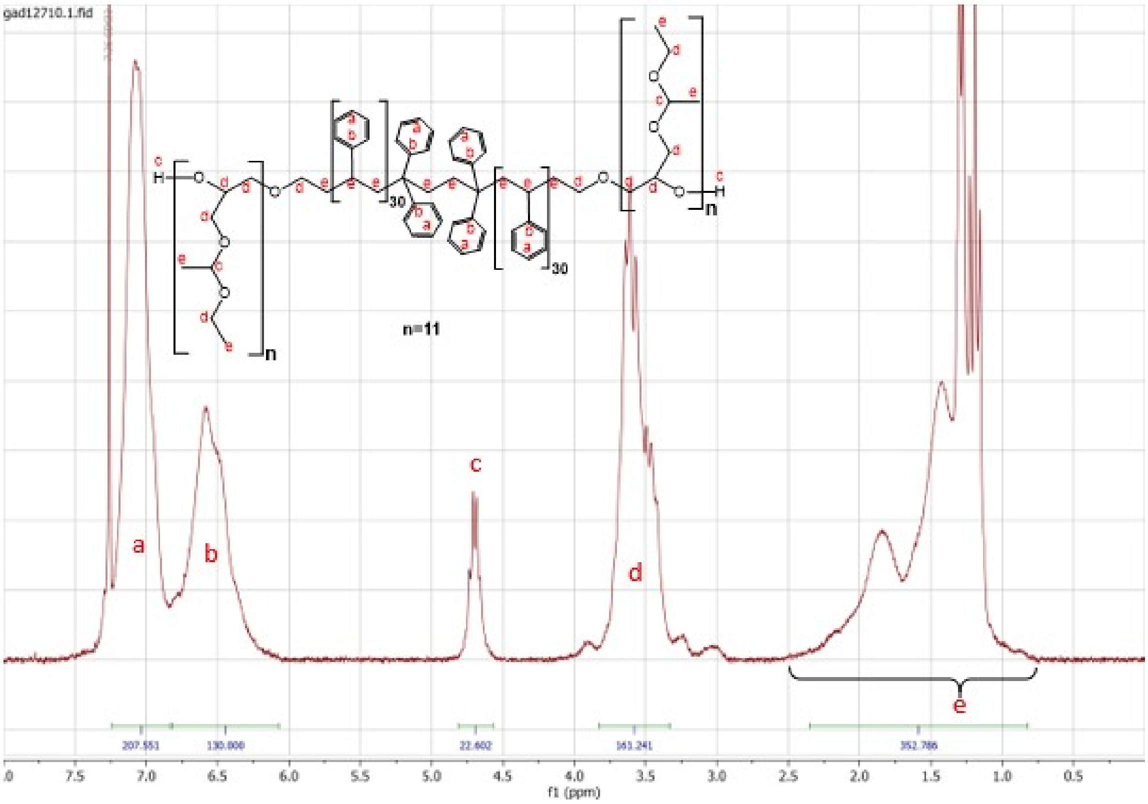

Figure SI2. 1H NMR spectrum of PGLB-PS-PGLB(1) in CDCl$_3$.

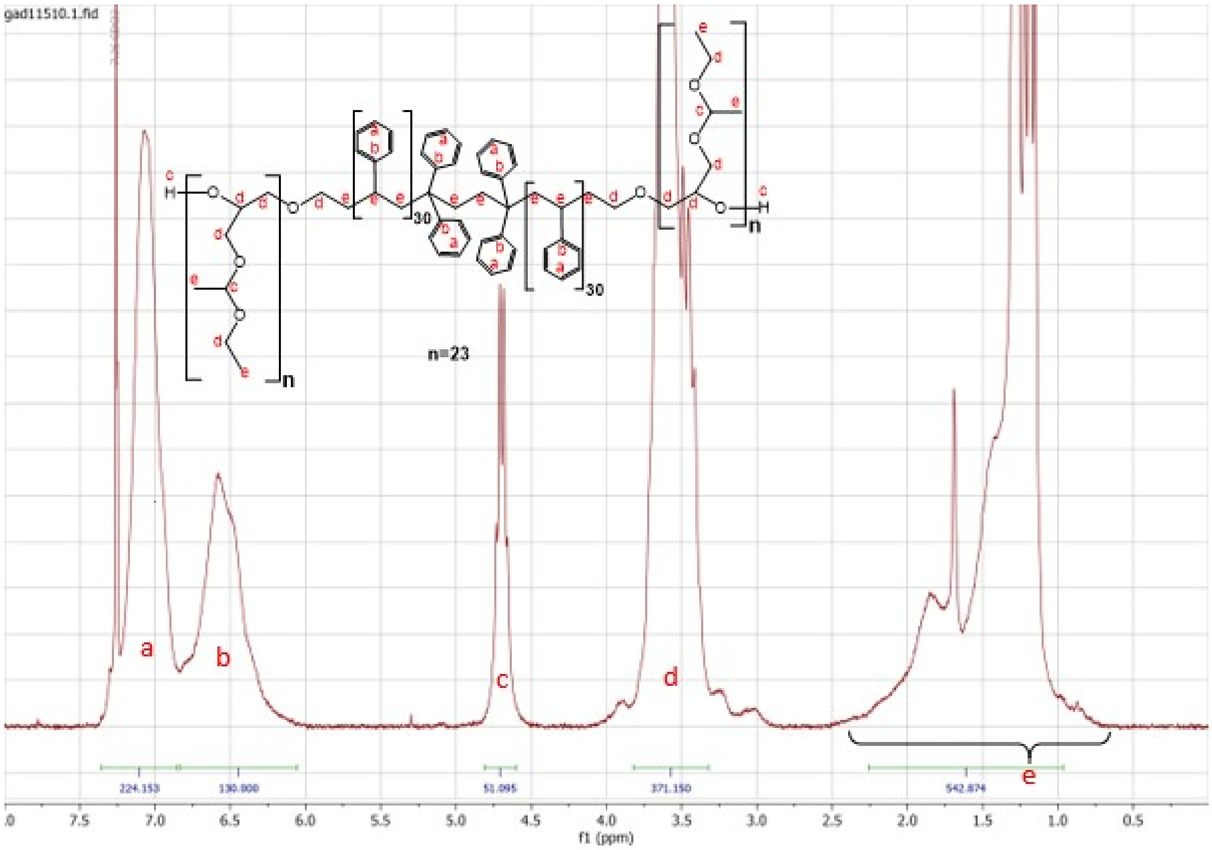

Figure SI3. ^{1}H NMR spectrum of PGLB-PS-PGLB(2) in CDCl$_3$.

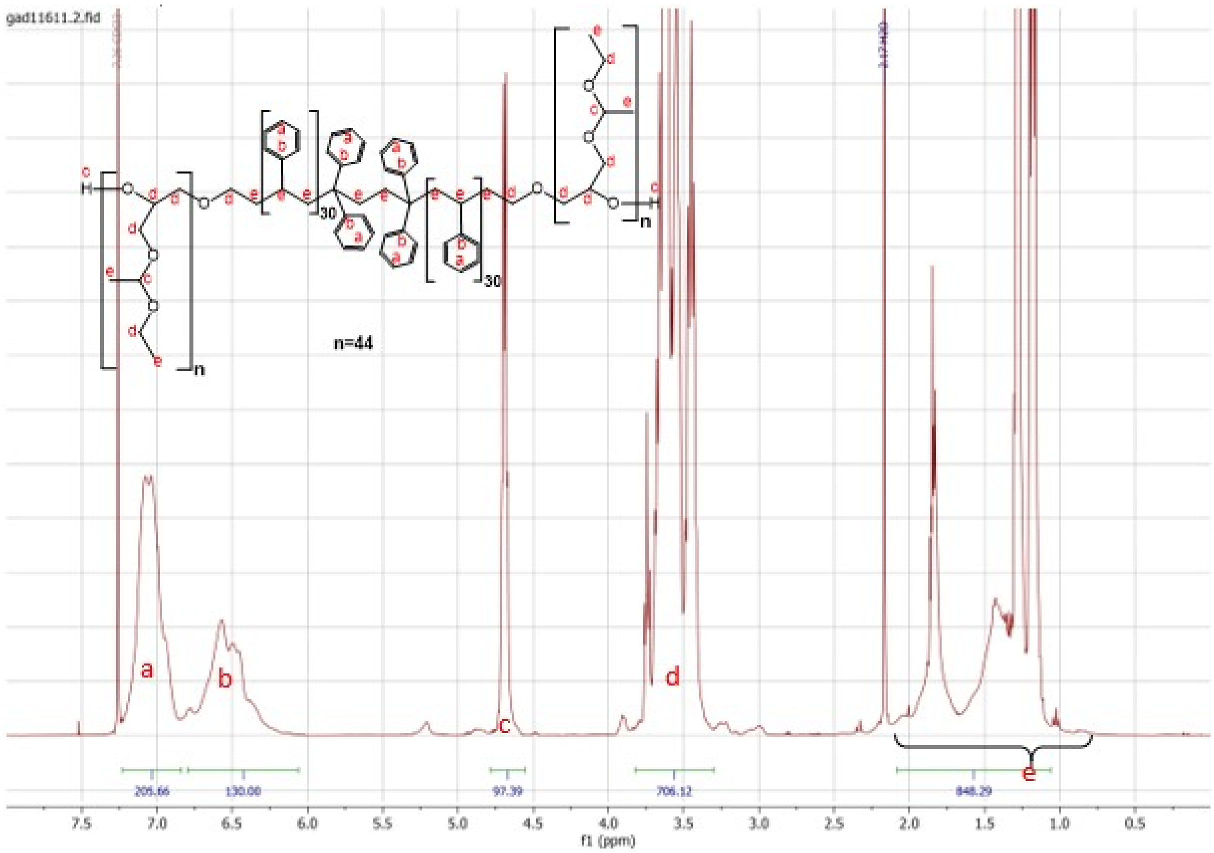

Figure SI4. ^{1}H NMR spectrum of PGLB-PS-PGLB(3) in CDCl$_3$.

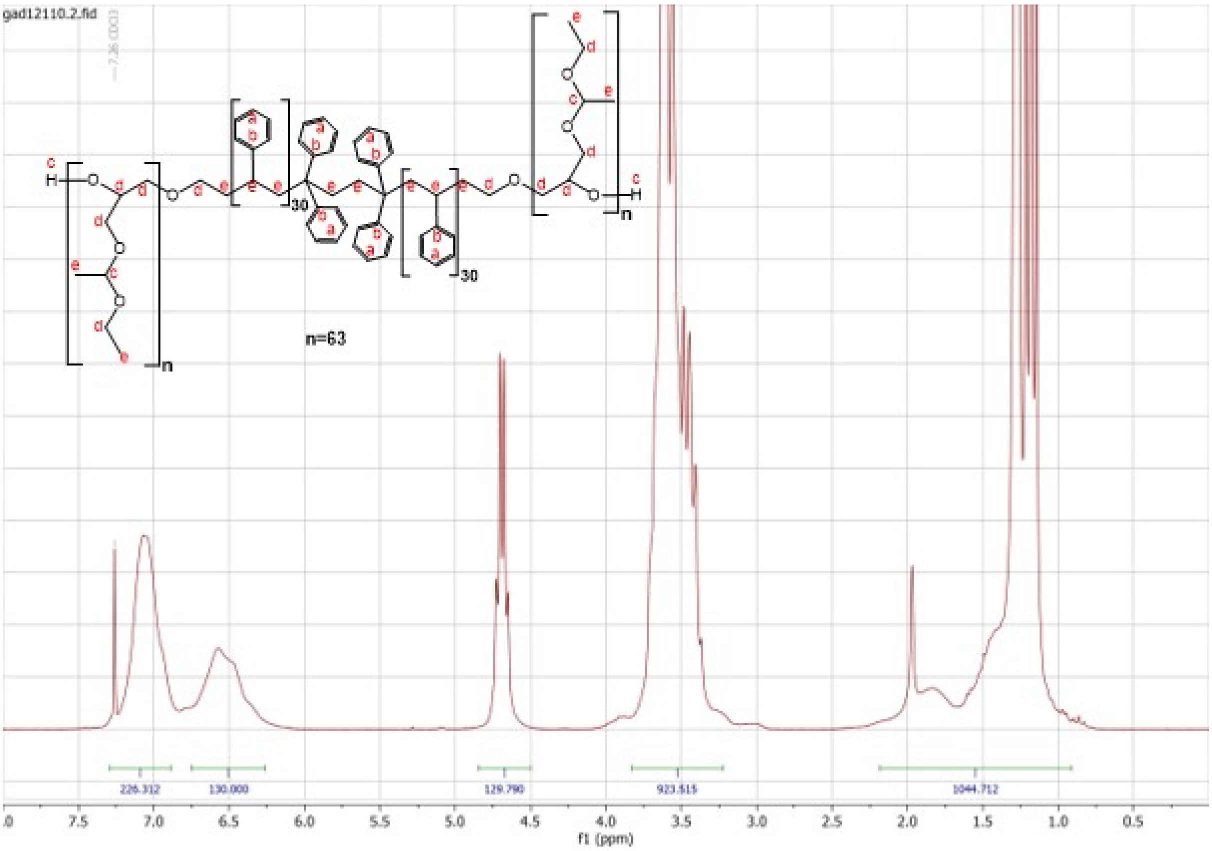

Figure SI5. ^{1}H NMR spectrum of PGLB-PS-PGLB(4) in CDCl$_3$.

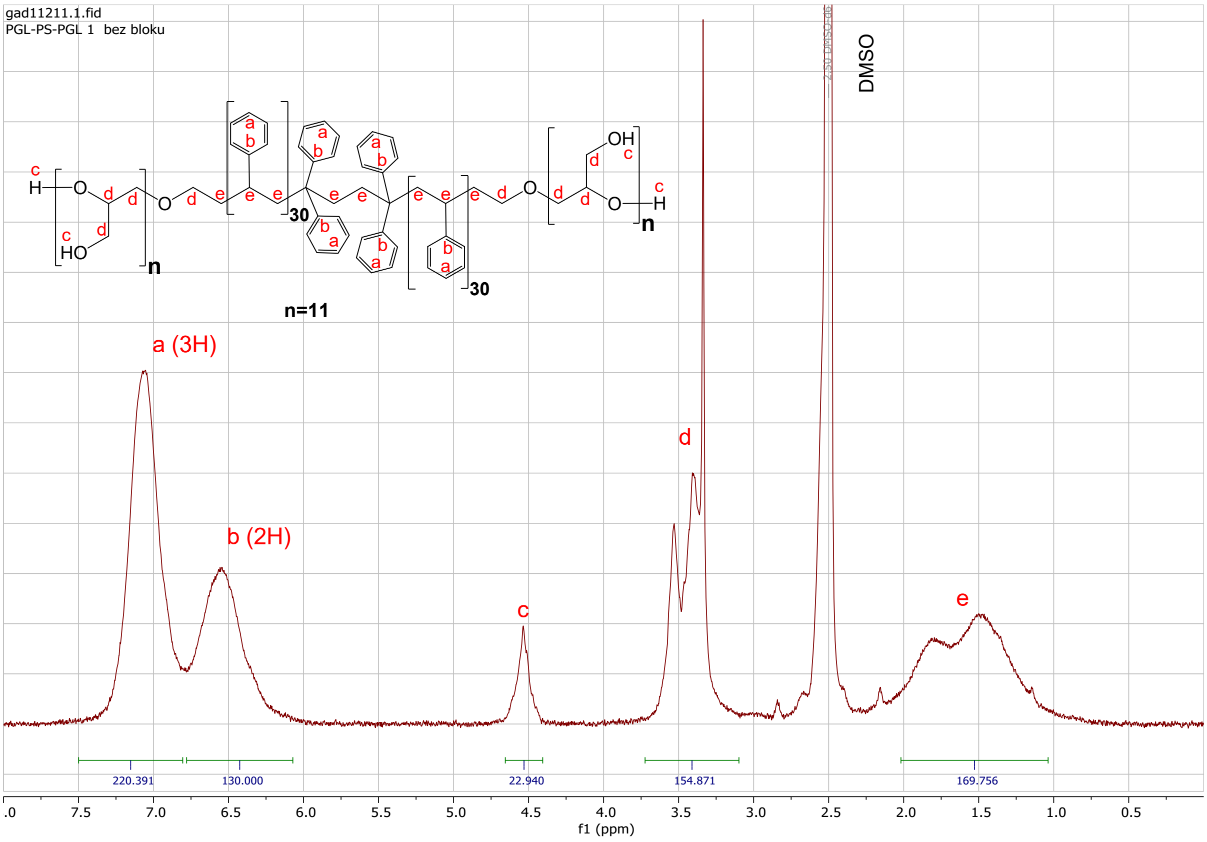

Figure SI6. ^{1}H NMR spectrum of PGL-PS-PGL(1) in DMSO-d6.

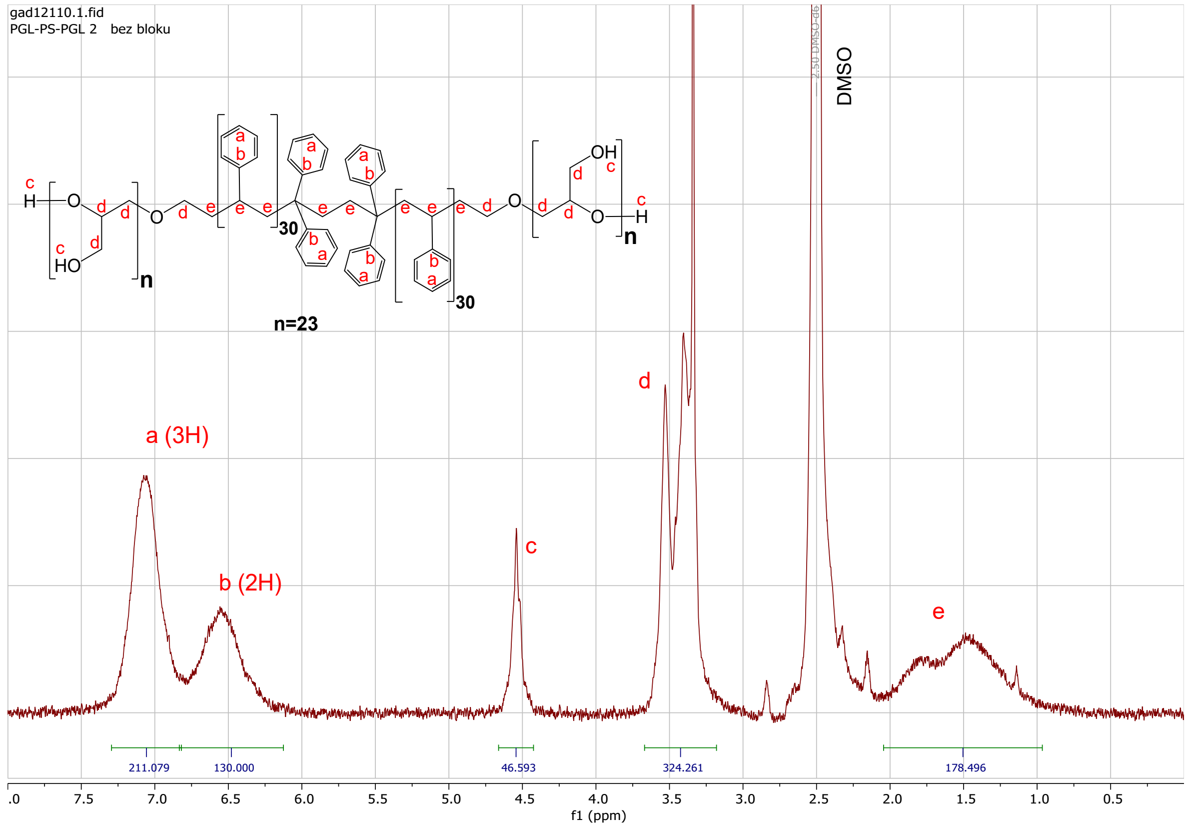

Figure SI7. ^{1}H NMR spectrum of PGL-PS-PGL(2) in DMSO-d6.

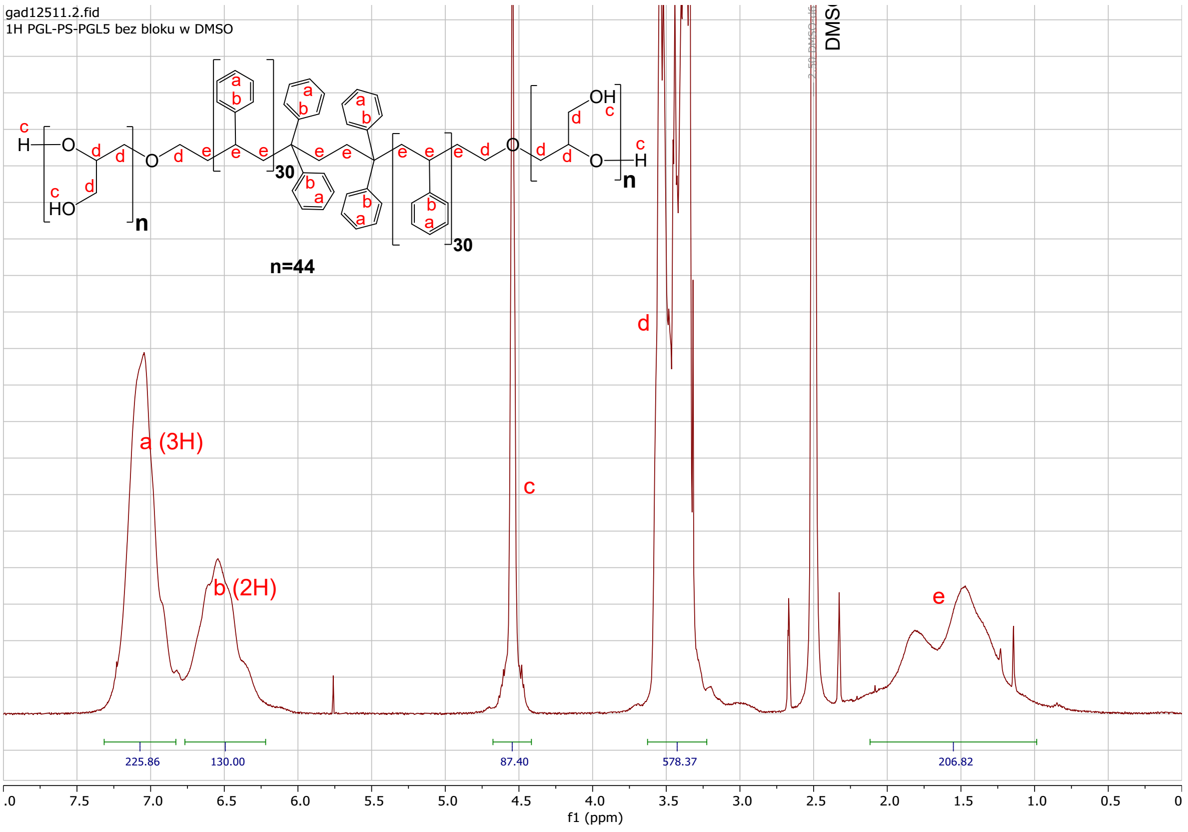

Figure SI8. ^{1}H NMR spectrum of PGL-PS-PGL(3) in DMSO-d6.

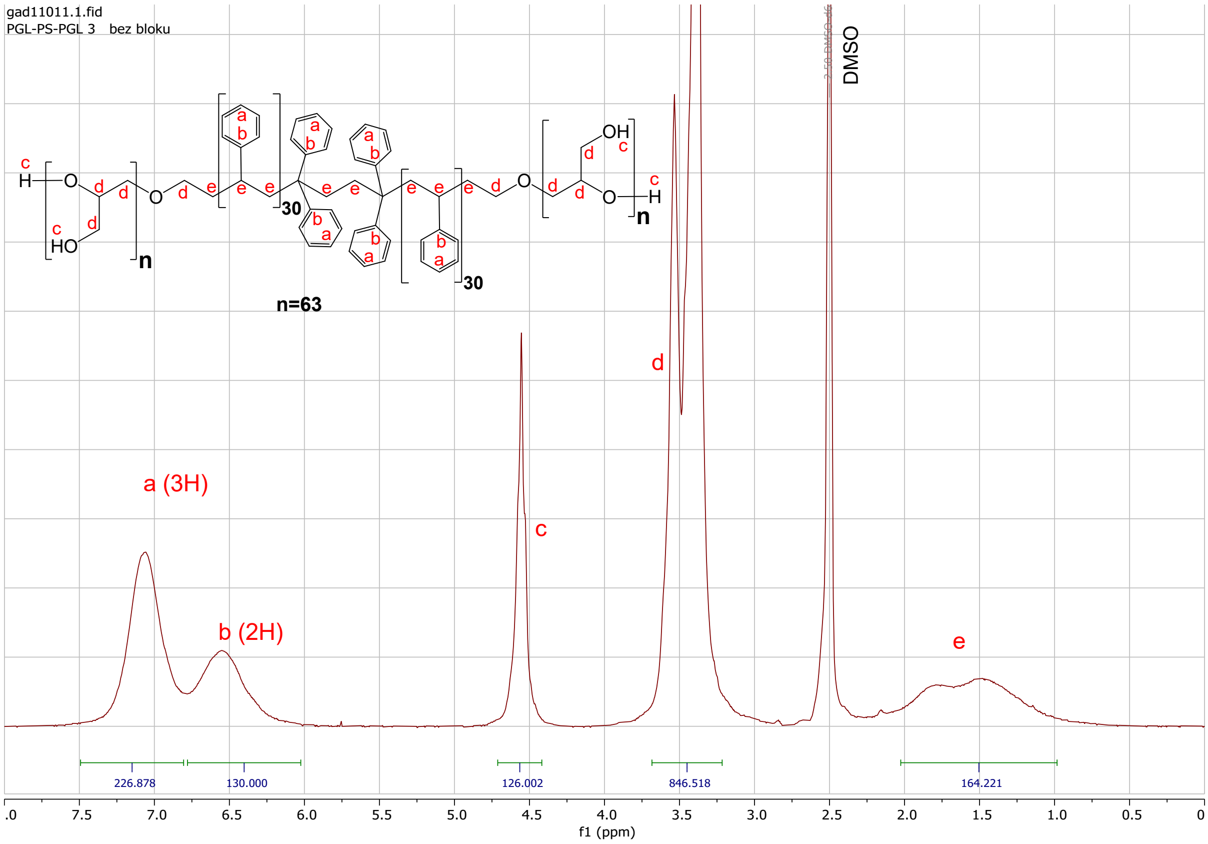

Figure SI9. ^{1}H NMR spectrum of PGL-PS-PGL(4) in DMSO-d6.

FTIR measurements

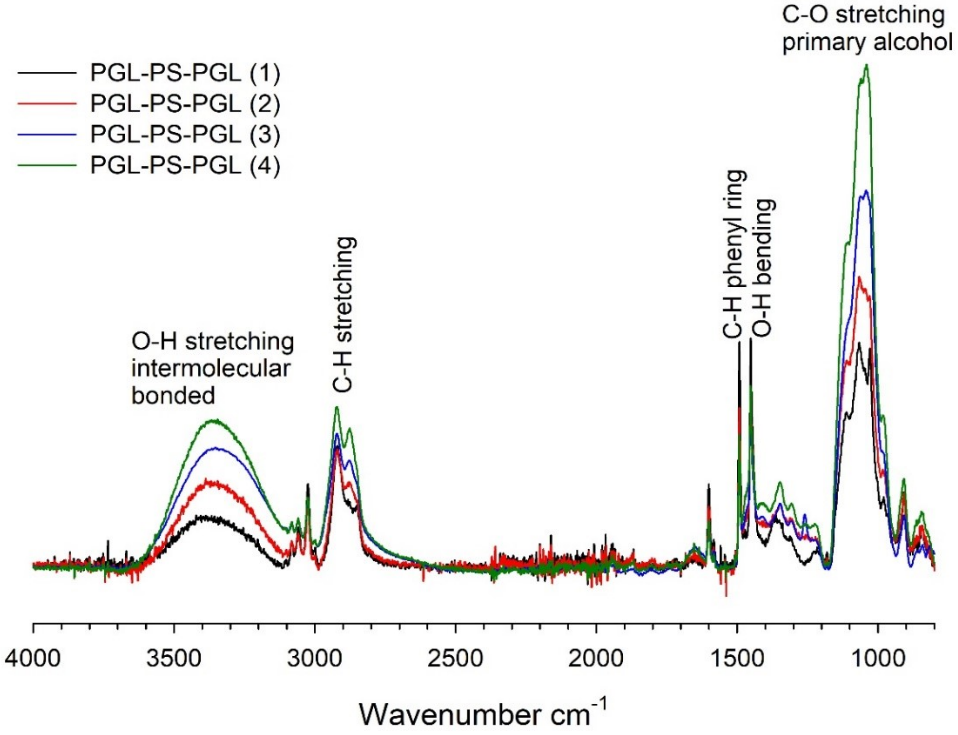

Figure SI10. FTIR spectra of PGL-PS-PGL copolymers

GPC of PGL-PS-PGL copolymers

In Fig. SI11 gel permeation chromatography of PS macroinitiator and PGL-PS-PGL triblock copolymers performed in DMF are shown.

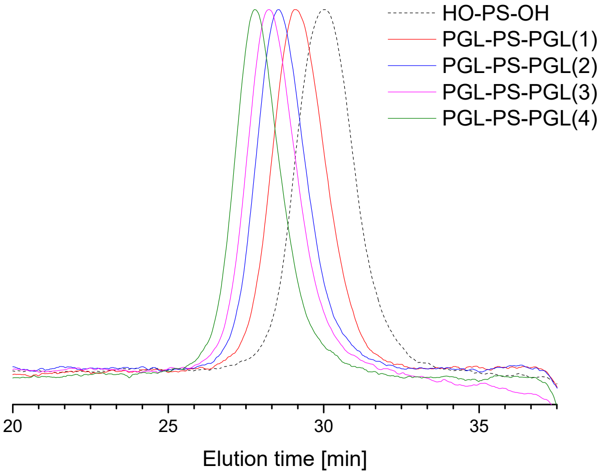

Figure SI11. Chromatograms (RI traces) of HO-PS-OH and PGL-PS-PGL copolymers

Surface characterization

Determination of PGL-PS-PGL film roughness was assessed as the root mean square (RMS) of a surface height variation, determined by atom force microscopy (Fig. SI12).

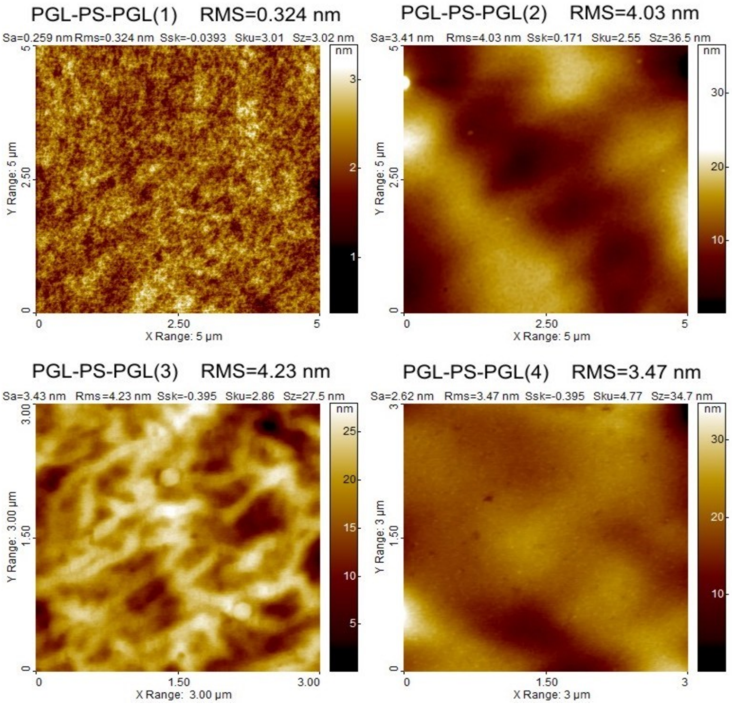

Figure SI12. AFM microphotographs of PGL-PS-PGL copolymer films used for determination of film roughness (RMS parameter).

Comparison of CMC for a set of PS-PGL and PGL-PS-PGL copolymers in H_2O.

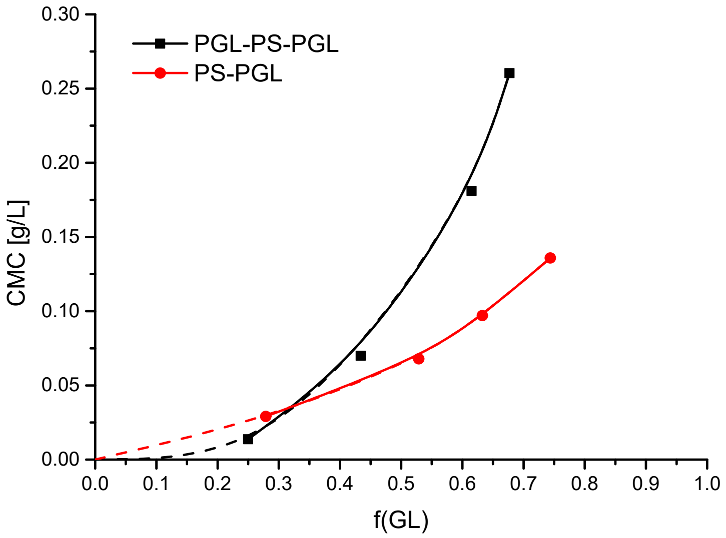

Figure SI13. Correlation between CMC obtained by DLS of PS/PGL copolymer vs. glycidol fraction in the chains. (Data for diblock copolymers were taken from [50]).

Stability of micelles

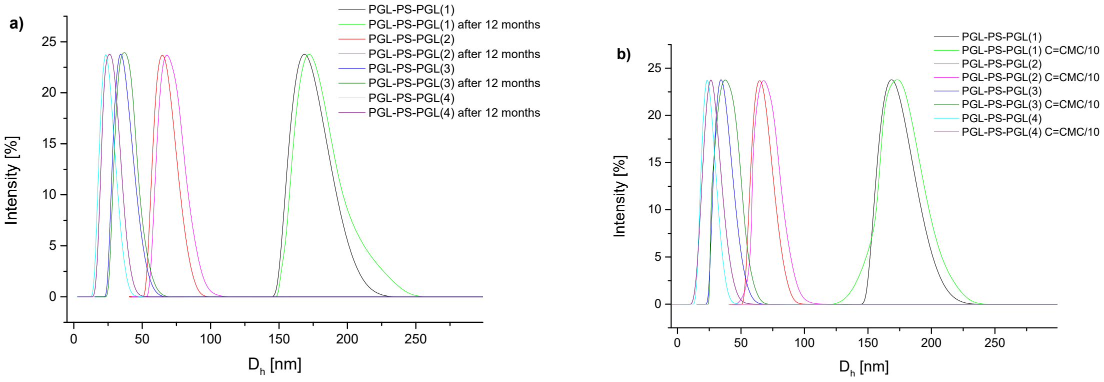

Figure SI14 a) Size distribution of PGL-PS-PGL particles after 12 months storage, b) size distributions of PGL-PS-PGL particles after dilution of their dispersion with water to concentration CMC/10.

Cryo-TEM images of PGL-PS-PGL copolymers

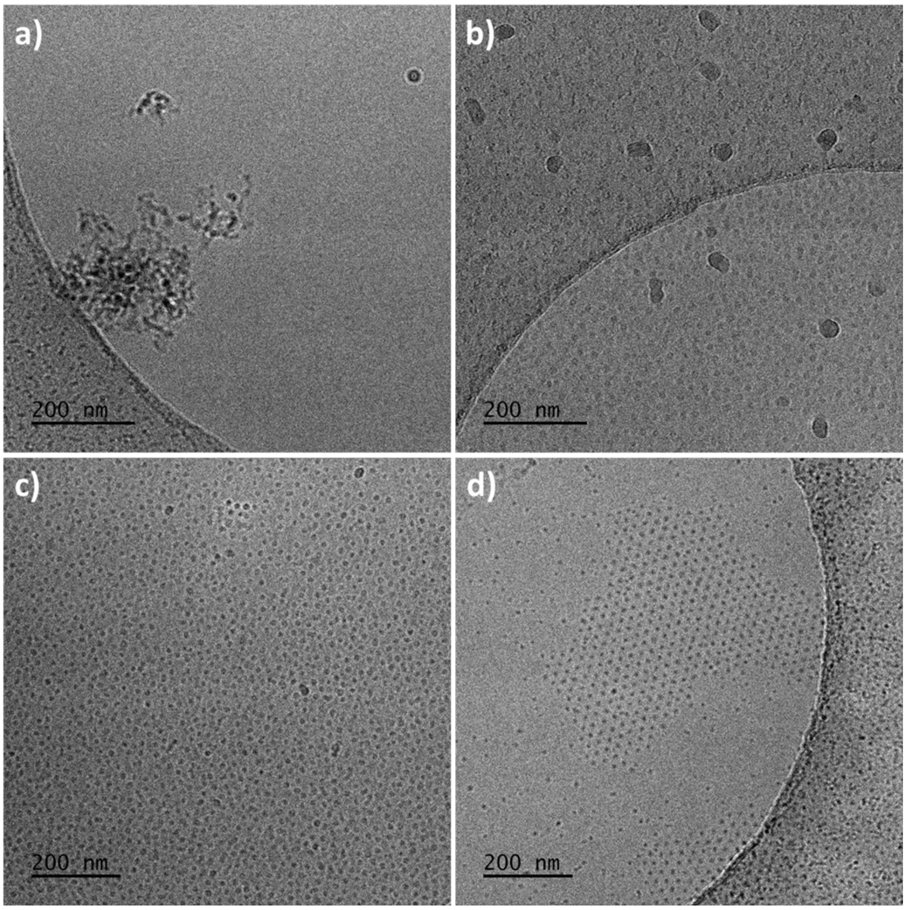

Figure SI15. Representative cryo-TEM images of the a) PGL-PS-PGL(1), b) PGL-PS-PGL(2), c) PGL-PS-PGL(3), d) PGL-PS-PGL(4) dispersions after 12 months of storage at room temperature.

Literature.

[1] Dimitrov, P.; Iyer, P.; Van Beylen M.; Hogen-Esch, T. 1,4-dilithio-1,1,4,4-tetraphenylbutane in diethyl ether: an effective initiator for the living anionic polymerization of dienes. J Polymer Sci: A: Polym Chem 2009, *47*, 2198-2206.

[2] Fitton, A.O.; Hill, J.; Jane, D.E.; Millar, R. Synthesis of simple oxetanes carrying reactive 2-substituents. Synthesis-Stuttgart 1987, *12*, 1140–1142.

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[4] Halacheva, S.; Rangelov, S.; Tsvetanov, C. Poly(glycidol)-based analogues to Pluronic based copolymers. Synthesis and aqueous solution properties. Macromolecules 2006, *39*, 6845–6852.