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One-Step Synthesis of Multiphase Block Copolymers via Simultaneus Free Radical and Ring Opening Polymerization Using Poly(ethylene oxide) Possessing Azo Group

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Multiphase block copolymers having the structure of poly(ε-caprolacton-b-etyhlene glycol-b-styrene-b-ethylene glycol-b-ε-caprolacton) were synthesized from poly(ethylene oxide) possesing azo group in the main chain by the combination of free radical polymerization (FRP) of styrene (S) and ring opening polymerization (ROP) of ε-caprolacton (ε-CL) in one-step. The block copolymers were characterized ^{1}H-NMR and FT-IR spectroscopy and gel permeation chromatography (GPC). ^{1}H-NMR and FT-IR spectroscopy and GPC studies of the obtained polymers indicate that multiphase block copolymers easily formed as a result of combination FRP and ROP in one-step.

Keywords: multiphase block copolymers; ε-caprolacton; etyhlene glycol; styrene; ring opening polymerization; and one-step

1 Introduction

Block copolymers have been extensively studied and have industrial applications in many fields such as adhesives, surfactants and compatibilization agents in polymer blends. The different techniques of the synthesis of block copolymers are reviewed by several authors (1–6). In general, in the synthesis of block copolymers, combination of polymerization types such as anion to radical (7, 8), cation to radical (9) and anionic to cationic transformations (10) have been used. This route involves transformation reactions in which the mode of propogation of the first monomer is transformed into a different mode suited for the polymerization of the second monomer (11). In recent years, beside these various synthetic methods, one-step processes have been sucessfully used for the synthesis block copolymers. Mecerreyes et al. (12) proposed a new strategy for the one-step synthesis of block copolymers which involves the use of asymetric difunctional initiator that is capable of initiating the simultaneous polymerization of two monomers by different polymerization methods in such a way that this initiator remains attached to each type of growing chain. Aida and Takeuchi (13) studied the one-pot synthesis of the poly(oxetane-b-ε-caprolacton) block copolymer via sequential cationic and anionic polymerizations of oxetane and ε-caprolacton(ε-CL) using triftalate complexes of sterically hindered titanium bisphenolates. Chang et al. (14) proposed a new strategy for the one-step synthesis of block copolymers by using a combination of reverse atom transfer radical polymerization (ATRP) and ring opening polymerization (ROP). Poly(styrene-b-ε-caprolacton)/silicate nanocomposites were prepared via one-pot, one step *in situ* living polymerization from a silicate-anchored bifunctional initiator (15). Poly(styrene-r-maleic anhydride)-b-poly(-styrene) block copolymer was synthesized by the controlled radical polymerization of a 9:1 mixture of styrene and maleic anhydride at 120°C in the presence of 2,2,6,6-tetramethyl-piperidinyloxy (TEMPO) as the initiator (16). Synthetic parameters for the chemoenzymatic cascade synthesis of block copolymers combining enzymatic ROP and ATRP in one pot were investigated by Heise et al. (17). One-pot polymerization of hexylisocyanate with styrene (S) was investigated using different alkali metal counterions such as Li^+, Na^+, and K^+ with naphtalene in the presence of $NaBPh_4$ to give the rod-coil-rod triblock copolymer (18). Well-defined block copolymers were obtained from 4-hydroxy-butyl-2-bromoisobutyrate dual initiator, combining ATRP of t-butylmethacrylate and ROP of ε-CL in a one-step process (19). Amphilic poly(styrene-b-N-isopropylacrylamide) was prepared by a one-step interfacial-initiated microemulsion polymerization (20).

In this paper, we report the one-step synthesis of a multi block copolymers by using a dual initiator able to initiate polymerization of ε-CL and S.

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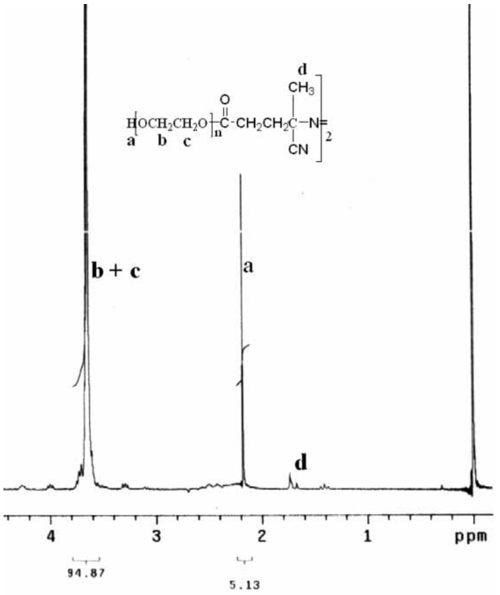


Fig. 1. ^{1}H-NMR spectrum of the PAE-3000.

2 Experimental

2.1 *Materials*

Poly(ethylene glycol) with molecular weights of 3000 (PEG-3000), dibutyltin dilaurate (DBTDL) was used as supplied. Styrene (99% Aldrich) and ε-CL (98% Merck) were purified by conventional methods. All other reagents were purchased from Aldrich or Fluka and used without further purification. 4,4′-azobis(4-cyano pentanoyl chloride) (ACPC) was obtained by the reaction of 4,4′-azobis(4-cyano pentanoic acid) (ACPA) with PCl_5 and recrystallized from chloroform solution. Polyethylene glycol azoester (PAE-3000) was synthesized by the reaction of ACPC and PEG-3000 in the presence of triethylamine in benzene at room temperature as follows: Into a flask equipped with magnetic stirrer and addition funnel were placed 300 ml of benzene, 6.44 g (18.4 mmol) ACPC, 3.72 g (36.8 mmol) triethylamine and 110.4 g (36.8 mmol) PEG-3000. The mixture was kept overnight at ambient temperature. The evaporation of the solvent, flask content was precipitated into cold diethyl ether. The yield was found as 64.6 g. ^{1}H-NMR (Figure 1) δ (ppm) 3,6-37 (-OC$\underline{H}_2$), 2,2 (-C$\underline{H}_3$), 1,7 (-O$\underline{H}$). IR (Figure 2) (Cm^{-1}) 3432 (-O$\underline{H}$), 2871(-C$\underline{H}_2$), 1736 (-$\underline{C}$=O). GPC (M_n: 4480 g/mol).

2.2 *One-step Polymerization*

The general procedure for one-step polymerization of S and ε-CL is as follows: to a Sclenck tube equipped with magnetic stirring bar, initiator (PAE-3000), solvent (DMF), degassed monomers (S and ε-CL), DBTDL were added. The tube was degassed by flushing pure argon and placed in a thermostated silicon-oil bath at given temperature. Block

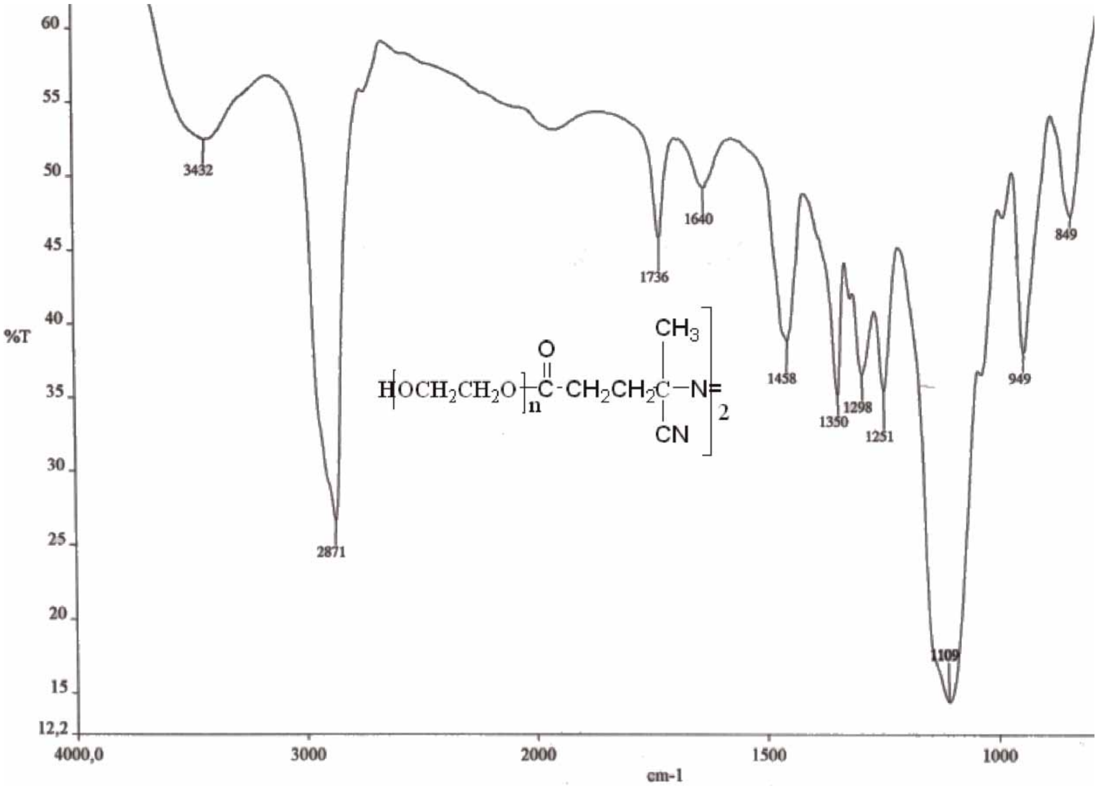


Fig. 2. FT-IR spectrum of the PAE-3000.

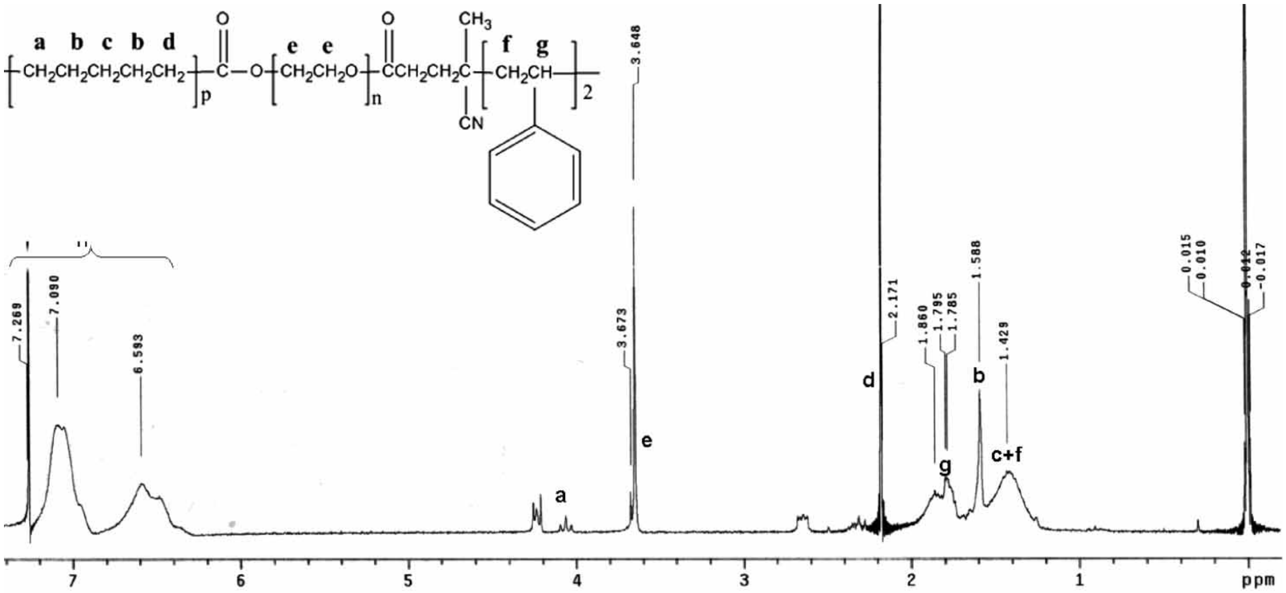
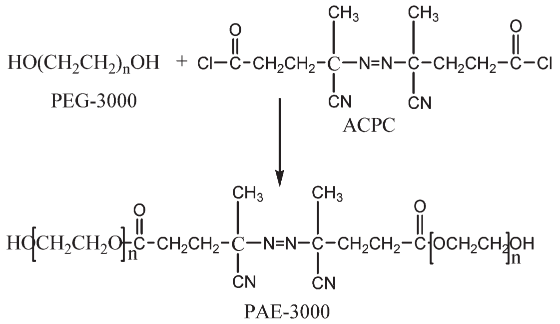


Fig. 3. ^{1}H-NMR spectrum of poly(ε-caprolacton-b-etyhlene glycol-b-styrene-b-ethylene glycol-b-ε-caprolacton) multiphase block copolymer (Code: PA-6 in Table 1).

copolymers formed were precipitated in ten-fold excess methanol.

2.3 *Characterization*

The number average molecular weight (M_n) and polydispersities (M_w/M_n) of obtained polymers were measured by gel permeation chromatography(GPC). GPC was performed with a Waters 2414 refractive index dedector and Waters model 1515 isocratic pump at a flow rate of 1 ml/min trough a combination of Waters HR3, HR4E and HR4 styragel columns. Poly(styerene) (PS) (Shodex SM-105) standards were used to calibrate the columns. The analysis was undertaken at 40°C with HPLC grade THF as an eluent. Waters Breeze software was used for data analysis. The ^{1}H-NMR spectra of the products were obtained from $CDCl_3$ solution on a Bruker NMR Spectrometry (Figures 1 and 3). IR spectra were recorded with polymer films cast from benzene solution with a Perkin-Elmer 1600 spectrometer.



Sch. 1. Synthesis of poly(ethlene glycol) azoester(PAE-3000).

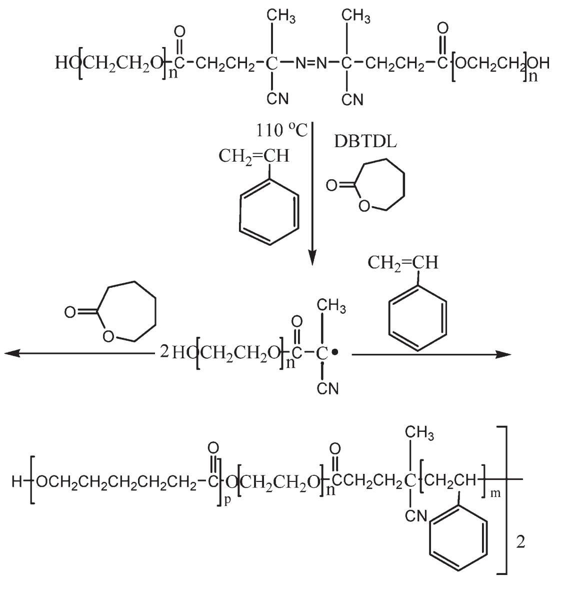
3 Results and Discussion

3.1 *Synthesis of PAE-3000*

The PAE-3000 macroinitiator was prepared according to the reaction sequence shown in Scheme 1, and was characterized by spectral (Figures 1 and 2) and GPC measurent.

3.2 *One-step Multi-block Copolymerizations*

Dual functional macroinitiator possessing two hydroxyl functions and azo group in the main chain initiates the ROP



Sch. 2. Synthesis of PCL-b-PEG-b-PS-PEG-PCL multiblock copolymers.

Table 1. The effect of the the amount of S on one-step block copolymerization of S and ε-CL

Code	PAE-3000 (g)	ε-CL (g)	S (g)	Yield of polymer (g)	$\overline{M_{n,GPC}}$	$\overline{M}_w/\overline{M}_n$
TA-1	0.1003	1.0141	0.5074	0.1790	75003	1.48
TA-3	0.1000	1.0163	1.5206	0.5390	89576	1.49
TA-4	0.1010	1.0018	2.0216	0.9176	116535	1.42
TA-5	0.1000	1.0032	2.5095	0.8835	120767	1.38
TA-6	0.1002	1.0521	3.0110	0.7160	107289	1.47

Polymerization time = 65 min, DBTDL = 1.0×10^{-6} mol, temperature: 110°C.

of ε-CL and FRP of S simultaneously. A monomer mixture of S and ε-CL that is initiated by the dual initiator in the presence of DBTDL as the ring opening catalyst gives the multiphase poly(ε-caprolacton-b-ethylene glycol-b-styrene-b-ethylene glycol-ε-caprolacton) block copolymer. Taking into account that PAE-3000 with two functional groups and termination of S, block copolymers should have the structure poly(ε-caprolacton-b-ethylene glycol-b-styrene-b-ethylene glycol-ε-caprolacton). The synthetic approach for the preparation of block copolymers is depicted in Scheme 2. Tables 1–3 give the results for several polymerizations using PAE-3000 as macroinitiator. The effect of the the amount of S on one-step block copolymerization is gathered in Table 1. The increasing amount of S caused an expected increase in the yield and molecular weights of the block copolymers. At higher amounts of S, a deviation from normal behavior was observed, which may be attributed to the increase in viscosity of the medium. The increased amount of macroinitiator (PAE-3000) in the reaction mixture leads to the formation of higher number of active centers. For this reason, more growing macro radicals are formed in the system, but they have shorter PS segments, which is confirmed by a decrease in molecular weights and an increase in polydispersities (1.48–2.29) of the multiphase block copolymers (Table 2). The increasing amount of ε-CL also caused an expected increase in the molecular weights of the multiphase block copolymers. At higher amounts of ε-CL, a deviation from normal behavior was observed, which may be attributed to increase in viscosity of the medium (Table 3).

3.3 Characterization of Block Copolymers

A series of multiphase block copolymers with poly(ε-caprolacton) (PCL), PEG and PS blocks various molecular weights were synthesized by the combination of FRP and ROP in one-step in the presence of PAE-3000 (M_n:4800 g/mol)with DBTDL as a catalyst. Multiphase block copolymers were characterized ^{1}H-NMR, FT-IR and

Table 2. The effect of the the amount of PAE-3000 one-step block copolymerization of S and ε-CL

Code	PAE-3000 (g)	ε-CL (g)	S (g)	Yield of polymer (g)	$\overline{M_{n,GPC}}$ (g/mol)	$\overline{M}_w/\overline{M}_n$
TB-1	0.0505	1.0008	1.0099	0.3270	100898	1.48
TB-2	0.1001	1.0176	1.0137	0.3588	80909	1.64
TB-3	0.1503	1.0034	1.0007	0.3891	77738	1.65
TB-4	0.2016	1.0149	1.0020	0.4094	64618	1.68
TB-5	0.2509	1.0029	1.0107	0.4596	55577	2.08
TB-6	0.3010	1.0394	1.0099	0.3908	45638	2.29

Time = 65 min, DBTDL = 1.0×10^{-6} mol, temperature: 110°C.

Table 3. The effect of the the amount of ε-CL one-step block copolymerization of S and ε-CL

Code	PAE-3000 (g)	ε-CL (g)	S (g)	Yield of polymer (g)	$\overline{M_{n,GPC}}$ (g/mol)	$\overline{M}_w/\overline{M}_n$
TC-1	0.1004	0.5155	1.0006	0.3334	70000	1.67
TC-3	0.1004	1.5245	1.0088	0.3980	72987	1.62
TC-5	0.1000	2.5307	1.0136	0.3453	87154	1.50
TC-6	0.1001	3.0094	1.0112	0.3475	68632	1.56

Time = 65 min, DBTDL = 1.0×10^{-6} mol, temperature: 110°C.

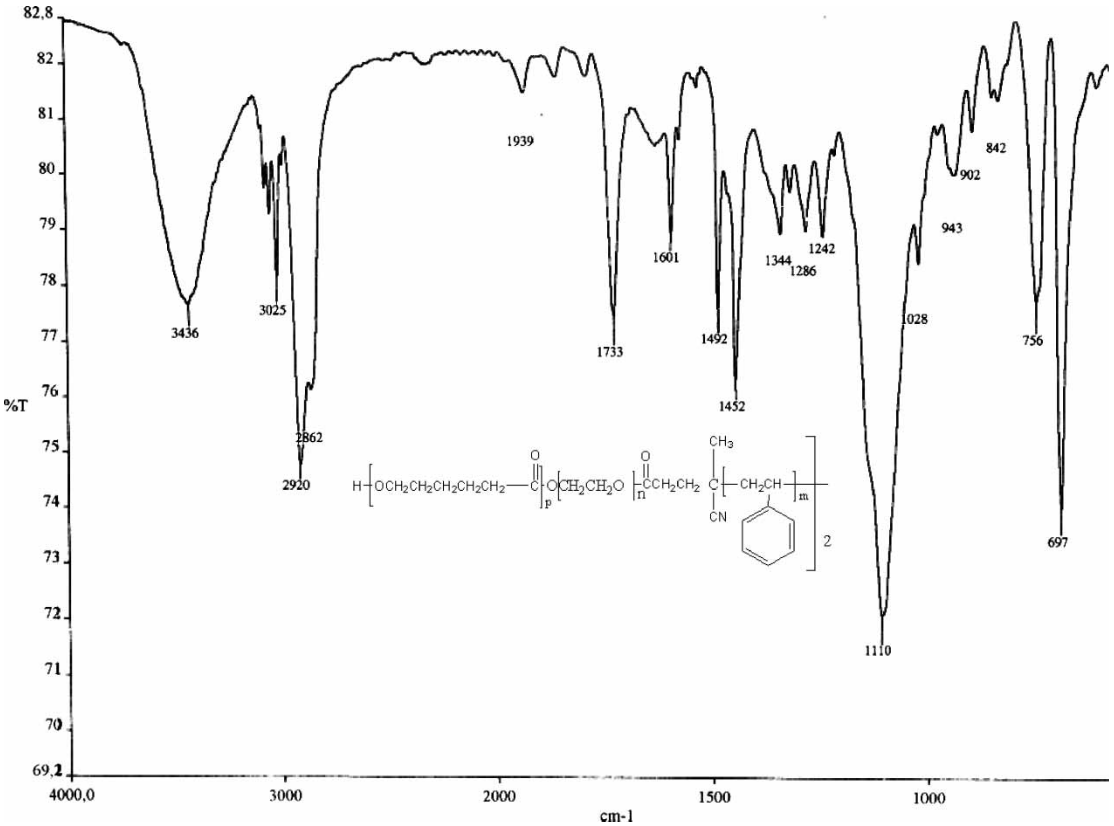


Fig. 4. FT-IR spectrum of poly(ε-caprolacton-b-etyhlene glycol-b-styrene-b-ethylene glycol-b-ε-caprolacton) multiphase block copolymer (Code: PA-6 in Table 1).

GPC measurements. Figure 3 shows the ^{1}H-NMR spectrum of PCL-b-PEG-b-PS-PEG-PCL multiphase block copolymer. The sharp doublet peak at 3.65 ppm can be attributed to the methylene protons of the PEG unit, the other four signals at 4.20, 2.17, 1.58 and 1.42 ppm can be assigned to the methylene protons of the PCL blocks as marked in Figure 3. The ^{1}H-NMR spectrum of PCL-b-PEG-b-PS-PEG-PCL multiphase block copolymer in Figure 3 shows also charecteristic signals at 7.27, 7.09 and 6.59 ppm aromatic protons of PS chain. The FT-IR spectrum of the PCL-b-PEG-b-PS-PEG-PCL multiphase block copolymer is shown in Figure 4. Each spectrum has the characteristic -OH group, aromatic -C-H, aliphatic -C-H, aromatic overtone, -C=O, phenyl -C-H and -C-O (ether linkage) bands at 3496, 3025, 2920, 1939, 1733, 1600 and 1110 cm^{-1}, respectively. Block copolymer formation was also evidenced by gel permeation chromatography as exemplified in Figure 5. These chromatograms indicate an increase in the molecular weight as a result of block copolymerization.

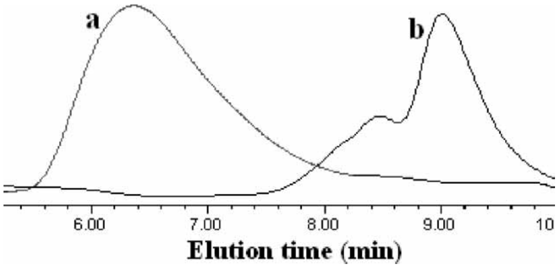


Fig. 5. GPC curves of (a) poly(ε-caprolacton-b-etyhlene glycol-b-styrene-b-ethylene glycol-b-ε-caprolacton) block copolymer (code PA-6 in Table 1), $M_n = 107289$ g/mol and (b) PAE-3000, $M_n = 4480$ g/mol.

4 Conclusions

In conclusion, A PAE-3000 macroazoinitiator can be used by the combination of FRP of S and ROP ε-CL in one-step to obtain PCL-b-PEG-b-PS-PEG-PCL multiphase block copolymers. The proposed procedures for the preparation of multiphase block copolymers by one-step polymerization are simple and efficient. Depending on the choice of monomer, a macroinitiator tailor-made block copolymer can be obtained, e.g. hard-soft, amphilic, etc. The block length can be adjusted by varying the monomer and initiator concentrations.

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