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Synthesis of an Amphiphilic Star Triblock Copolymer of Polystyrene, Poly(ethylene oxide), and Polyisoprene Using Lysine as Core Molecule

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ABSTRACT: A new amphiphilic ABC star triblock copolymer, with polystyrene (PS) and polyisoprene (PI) as hydrophobic segments and poly(ethylene oxide) (PEO) as hydrophilic segment, is successfully prepared using lysine as a core molecule. The mPEO with blocked methoxyl group at one end and hydroxyl at another end, PS, and PI with hydroxyl end groups are obtained by the anionic technique. The hydroxyl groups of mPEO-OH and PS-OH are converted into succinimidyl carbonate first and then coupled with ϵ and α amino groups of lysine, respectively, to yield an intermediate mPEO-PS-Lys-COOH. The PI-OH is also converted into PI carbonate (PI-SC) and then PI-NH_2 and reacted with a carboxyl group of lysine at the junction of PS and mPEO arms of mPEO-PS-Lys-COOH in the presence of *N,N′*-dicyclohexylcarbodiimide (DCC). The molecular weight distribution of the final product mPEO-PS-PI is rather narrow ($<$1.15). The structure of intermediates and final products was characterized by NMR, IR, UV, and SEC in detail. This method is promising for the synthesis of star copolymers with multiarms of different chain structure.

Introduction

Miktoarm star copolymers are a special class of nonlinear block copolymers in which the arms of different chemical nature and/or composition are linked to the same branch point.[1] Compared to the linear multiblock copolymers, ABC star triblocks can form more interesting morphologies due to the junction constraint of the center cores arose in the star block copolymer.[2−7]Some special morphologies such as a diamond prism shape IMDS (intermaterial dividing surface)[3] are observed. Theoretical study[8−11] also predicted a variety of complex morphologies such as lamella + sphere, perforated layer, lamella + cylinder, columnar piled disk, and lamella-in-sphere. Confirming these predicted complex morphologies through experiment is a challenging task for polymer scientists. The ABC star triblock copolymers are the simplest miktoarm star copolymers, which have been synthesized mainly by following methods: (1) The polymer chains are synthesized first by anionic polymerization, and then chlorosilane is used to couple with the polymeric carbanions; PI-PS-PBd[12] and PI-PS-PMMA[13] are obtained in this way. (2) Nonpolymerizable diphenylethylene is incorporated at the junction of two polymer blocks, and then a newly formed active species initiates the polymerization of third monomer to obtain the desired star copolymer. Some 3-arm star terpolymers such as the PS-PBd-PMMA,[14] PS-PBd-P2-VP,[7] PS-PtBuMA-PDMS,[15] PS-PEO-PCL, PS-PEO-PLL, PS-PMMA-PEO,[16] and PS-PEO-PtBuMA[17] are synthesized by this way. (3) The combination of different polymerization methods is suggested because the monomers suitable for anionic polymerization are limited. For example, PEO-PS-poly(methacrylic acid) star triblock copolymer is synthesized by combination of anionic polymerization with charge-transfer polymerization,[18] poly(tetrahydrofuran) (THF)/poly(1,3-dioxepane) (DOP)/PS triblock star copolymer is obtained by combination of cationic ring-opening polymerization (CROP) with atom transfer radical polymerization (ATRP),[19] and PCL-PMMA-PS is prepared by combination of ATRP with nitroxide-mediated radical polymerization (TEMPO).[20] It is obvious that greatly increased monomers are available by introduction of radical polymerization into the preparation of star triblock copolymers. However, the molecular weight distribution of these copolymers is generally rather wide.

In this article, a new method for preparing star triblock copolymers, using lysine as a core molecule, is presented. The coupling reaction is carried out between polymer chains with the high reactive succinimidyl carbonates and amino groups of lysine while the carboxylic group of lysine is activated as *N*-hydroxysuccinimide ester for another polymer binding. In this way a new star triblock copolymer composed of incompatible blocks of mPEO, PS, and PI is successfully prepared. This kind of copolymer may show the different morphologies and hydrodynamic properties comparing with its linear counterpart which have been studied systemically by Bates and co-workers.[21−24]

Experimental Section

Materials. Tetracyanoethylene (TCNE) (Acros, 98%), disuccinimidyl carbonate (DSC) (98%), 4-(dimethylamino)pyridine (DMAP) (99%), *N*-hydroxysuccinimide (NHS) (98%), *N,N′*-dicyclohexylcarbodiimide (DCC) (≥99.0%), lysine (99%), and silica gel (200−300 mesh, for column chromatography) are purchased from Sinopharm Chemical Reagent Co., Ltd. (SCR), all of them are used as received. Triethylamine (TEA) (99.7%) and ethylenediamine (99%) from SCR are dried over Na for 24 h and then distilled before use. Styrene (>99.5%), isoprene (>99%), and ethylene oxide (>99%) (SCR) were dried over CaH_2 for 24 h and then distilled before use. All other reagents (SCR) are purified by common purification procedures.

Measurements. ^{1}H NMR spectra were obtained at a DMX 500 MHz spectrometer with tetramethylsilane (TMS) as the internal standard and $CDCl_3$ as the solvent. Size-exclusion chromatography (SEC) was performed in tetrahydrofuran (THF) at 35 °C with an elution rate of 1.0 mL/min on an Agilent1100 with a G1310A pump, a G1362A refractive index

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detector, and a G1314A variable wavelength detector. One 5 μm LP gel column (500 Å, molecular range 500$-$2 $\times$ 10^4 g/mol) and two 5 μm LPgel mixed bed column (molecular range 200$-$3 $\times$ 10^6 g/mol) were calibrated vs polystyrene standard samples. For mPEO, SEC was performed in distilled water at 40 °C with an elution rate of 0.5 mL/min on an Agilent1100 with a G1310A pump, a G1362A refractive index detector, and a G1315A diode-array detector. Three TSK-gel PW columns are in series (bead size: 6, 13, 13 μm; pore size: 200 Å, greater than 1000 Å, less than 100$-$1000 Å; molecular range: 0$-$5 $\times$ 10^4, 5 $\times$ $10^4$$-$8 $\times$ 10^6, (5$-$8) $\times$ 10^6 g/mol, respectively) are calibrated by PEO standard samples. The injection volume is 20 μL, and the concentration is 5 mg/mL for SEC. UV spectra are taken on a 756 MC ultraviolet$-$visible light spectrophotometer (Shanghai Third Analytical Instrument Factory, China). IR spectra are obtained on a Magna-550 Fourier transform infrared spectrometer.

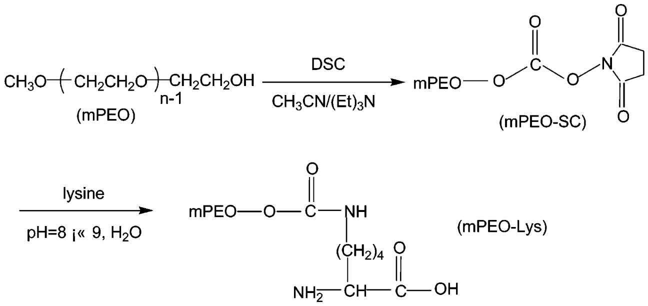
Preparation of mPEO-OH. 2-(2-Methoxyethoxy)ethanol (5.95 mL, 50 mmol) is added to 100 mL of dried THF, and then potassium (2.34 g, 60 mmol) with fresh surface is introduced. The reaction mixture is magnetically stirring for 12 h at 60 °C. After removing unreacted potassium; the obtained potassium 2-(2-methoxyethoxy)ethoxide solution is titrated by 0.1 M HCl, and the concentration is 0.48 mmol/mL. Ethylene oxide (20 mL, 404 mmol) is initiated by the solution of initiator (7 mL) in 100 mL of THF, and the calculated number-average molecular weight is 5000 g/mol. The reaction is kept at 30 °C for 12 h and is terminated with acidic methanol (1 vol % HCl). After purification of the crude product, the resultant mPEO-OH sample is characterized by ^{1}H NMR and SEC with refractive index detector. ^{1}H NMR (ppm) ($CDCl_3$): 3.38 (s, 3H, $C\mathbf{H_3}-O-PEO$), 3.60$-$3.70 (m, $-C\mathbf{H_2}CH_2O-$ of PEO main chain). $M_{n(SEC)} = 5034$ g/mol, $M_w/M_n = 1.07$, $M_{n(NMR)} = 5337$ g/mol (determined by ^{1}H NMR using the integrated area ratio of peaks at 3.60$-$3.70 and 3.38 ppm.)

Preparation of PS-OH and PI-OH. The anionic polymerization of styrene and isoprene and then end groups functionalization of polymeric anions are carried out according to the literature.[25] Lithium (2.08 g, 300 mmol) with fresh surface is added to 100 mL of dried petroleum ether (60$-$90 °C), and *n*-butyl chloride (15.1 mL, 144 mmol) is introduced dropwise. The reaction mixture is magnetically stirring for 12 h at 60 °C. After removing insoluble material, the solution of *n*-butyllithium (*n*-BuLi) is analyzed by the double-titration method,[26] and the concentration was 1.23 mmol/mL.

For polystyrene, styrene (10 mL, 86.7 mmol), cyclohexane (98 mL), and THF (2 mL) are placed in a 150 mL ampule, followed by the addition of *n*-BuLi solution (1.46 mL, 1.8 mmol), and the calculated number-average molecular weight was 5000 g/mol. After the reaction was kept at 30 °C for 8 h, ethylene oxide (4-fold excess, 0.36 mL, 7.2 mmol) dissolved in cyclohexane (5 mL) is added, and the red solution changed to faint yellow; the contents are left overnight at room temperature and terminated with acidic methanol (1 vol % HCl). After purification of the crude product, the dried sample is characterized by ^{1}H NMR and SEC with a refractive index detector. ^{1}H NMR (ppm) ($CDCl_3$): 1.3$-$2.3 (m, $C_6H_5-C\mathbf{H}C\mathbf{H_2}-$) and 6.20$-$7.20 (m, aromatic C**H**) for PS chain, 3.30 (m, methylene connected with hydroxyl group); $M_{n(SEC)} = 5290$ g/mol, $M_w/M_n = 1.03$, $M_{n(NMR)} = 5348$ g/mol (determined by ^{1}H NMR using the integrated area ratio of peaks at 6.20$-$7.20 and 3.30 ppm).

For polyisoprene, isoprene (10 mL, 99.8 mmol), cyclohexane (84 mL), and THF (16 mL) are placed in a predried 150 mL ampule, followed by the addition of *n*-BuLi solution (1.37 mL, 1.69 mmol); the calculated number-average molecular weight was 4000 g/mol. After the reaction was kept at 30 °C for 8 h, ethylene oxide (4-fold excess 0.34 mL, 6.76 mmol) dissolved in cyclohexane (5 mL) is added, and the yellow solution changed to faint yellow; the contents are left overnight at room temperature and terminated with acidic methanol (1 vol % HCl). After purification of the crude product, the dried sample is characterized by ^{1}H NMR and SEC with a refractive index detector. In this polymerization system, polar THF is used as solvent to provide reasonable polymerization rates and the microstructure of the products.[27,28] The microstructure composition of PI analyzed by ^{1}H NMR[29,30] is as follows: approximately 63% 3,4-addition, 27% 1,4-addition, and 10% 1,2-addition.^{1}H NMR (ppm) ($CDCl_3$): 5.70 ppm (m, $-C\mathbf{H}{=}CH_2-$ of 1,2-addition), 4.95 ppm (m, $-CH{=}C\mathbf{H_2}-$ of 1,2-addition), 5.08 ppm (m, $-C\mathbf{H}{=}C-$ of 1,4-addition), 4.63$-$4.69 ppm (m, $-C{=}C\mathbf{H_2}-$ of 3,4-addition), 0.9$-$2.21 ppm (all other protons in PI chain), 3.60 (b, methylene connected with hydroxyl group), the contents of 1,2-addition, 1,4-addition, and 3,4-addition in PI chains are calculated by the integrated area ratio of peaks at 5.70, 5.08, and 4.63$-$4.69 ppm. $M_{n(SEC)} = 5592$ g/mol, $M_w/M_n = 1.04$ (determined by SEC with standard polystyrene as calibration), $M_{n(NMR)} = 4052$ g/mol (determined by ^{1}H NMR using the integrated area ratio of peaks at 5.70, 5.08, 4.63$-$4.69, and 3.60 ppm.)

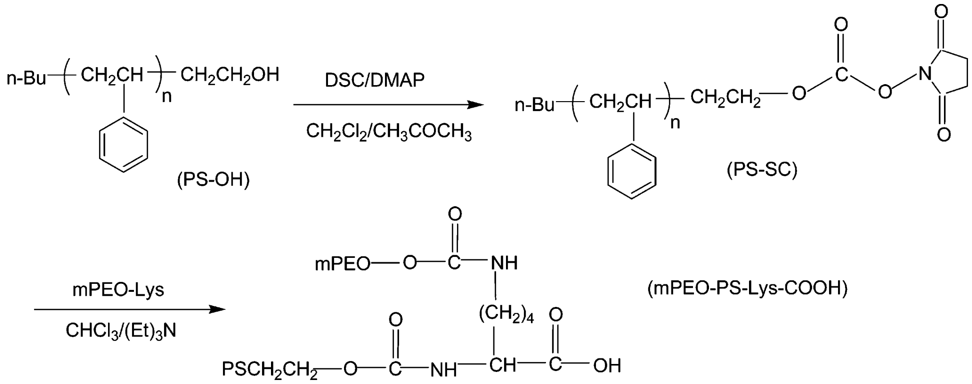
Scheme 1. Preparation of mPEO-Lys (DSC = Disuccinimidyl Carbonate)



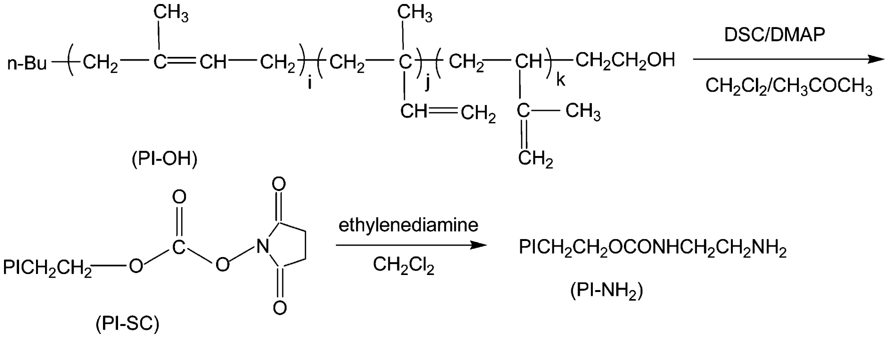
Preparation of mPEO-Lysine (mPEO-Lys). mPEO-Lys is prepared as described in Scheme 1. The mPEO with succinimidyl carbonate end group (mPEO-SC) is synthesized by the reaction of mPEO-OH with disuccinimidyl carbonate (DSC) according to the literature.[31,32] Dried mPEO-OH ($M_{n(SEC)} = 5034$, $M_w/M_n = 1.07$, 10 g, 2 mmol) is dissolved in 150 mL of dry CH_3CN, 3.07 g (12 mmol) of DSC, and 3.34 mL (24 mmol) of triethylamine (TEA) are added under stirring. After 12 h at room temperature, the solution is concentrated under vacuum to about 30 mL and precipitated into 300 mL of stirred diethyl ether. After filtration, the precipitate is resolved in 80 mL of toluene at 40 °C, and the insoluble excessive DSC is filtered quickly. The solution is concentrated to about $^1/_3$ of its original volume and precipitated in diethyl ether. The mPEO-SC is further purified by dissolution/precipitation with dichloromethane/ether twice in a yield of 82%. The SC contents of PEO-SC are calculated by *N*-hydroxysuccinimide absorption at 260 nm of UV spectra, which is produced by hydrolysis of PEO-SC;[33] the value is 98%. ^{1}H NMR ($CDCl_3$): 3.38 (s, 3H, $C\mathbf{H_3}-O-PEO$), 3.60$-$3.70 (b, $-C\mathbf{H_2}C\mathbf{H_2}O-$ of PEO main chain), 2.8 (m, 4H, $-OCC\mathbf{H_2}C\mathbf{H_2}CO-$), 3.9 (t, 2H, mPEO$-$$CH_2C\mathbf{H_2}OCO-$). It is confirmed by SEC that the molecular weight and molecular weight distribution of mPEO-OH before and after reaction are very close.

For the coupling of mPEO-SC with the ϵ amino group of lysine, lysine (0.73 g, 5 mmol) is dissolved in 150 mL of water at pH 8.0$-$8.3 first, and then to this solution the above product mPEO-SC (5.03 g, 1 mmol) is added in batches. To keep the pH 8.3 of the system, the solution is adjusted with 0.2 M NaOH. After being stirred overnight at room temperature, the solution is allowed to cool to 0 °C and the pH of the solution is adjusted to 3.0 with 1 M HCl. The solution is then extracted four times with chloroform and dried over $MgSO_4$. After filtration, the solution is concentrated to about $^1/_3$ of its original volume and added to diethyl ether dropwise; the precipitated product is dried to constant weight to give the product with a yield of 90%. ^{1}H NMR ($CDCl_3$): 3.38 ppm (s, 3H, $C\mathbf{H_3}-O-$ of mPEO), 3.60$-$3.70 ppm (b, $-C\mathbf{H_2}C\mathbf{H_2}O-$, mPEO main chain), 1.2$-$1.5 ppm (m, 6H, methylenes of lysine); 2.9 ppm (m, 2H, methylene of lysine connected with amide), 4.21 ppm (t, 2H, methylene, $CH_2C\mathbf{H_2}O$ of PEO connected with CONH$-$), 8.10 (t, 1H, mPEO$-$$OCON\mathbf{H}CH_2-$), 7.74 ppm (m, 3H, $N\mathbf{H_2}\cdot HCl$ of lysine). The new absorption at 1718 cm^{-1} for carbonyl of mPEO-O-CO-NH-lysine in the FTIR spectrum clearly confirms the formation of the product. SEC trace of the product gives single peak very close to that of starting homopolymer.

Scheme 2. Preparation of mPEO-PS-Lys-COOH (DSC = Disuccinimidyl Carbonate, DMAP = 4-(Dimethylamino)pyridine)



Scheme 3. Preparation of PI-NH$_2$ (DSC = Disuccinimidyl Carbonate; DMAP = 4-(Dimethylamino)pyridine)



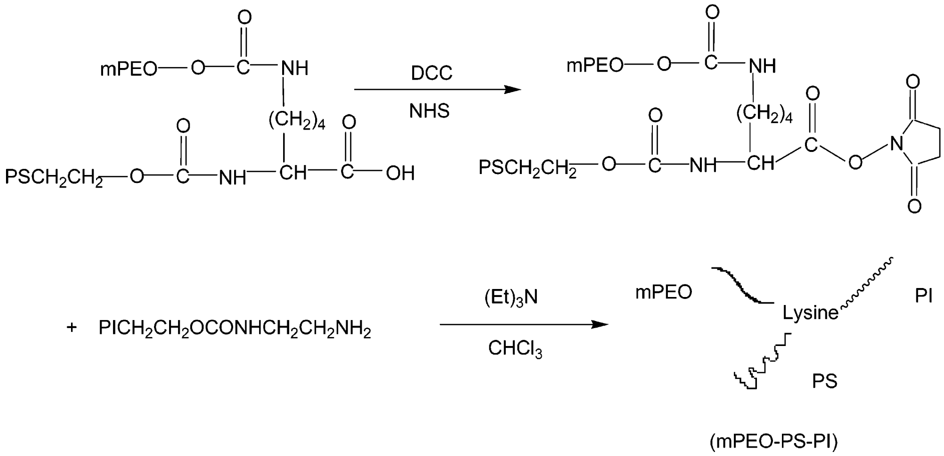
Preparation of mPEO-PS-Lys-COOH. The mPEO-PS-Lys-COOH is prepared by the following two steps as shown in Scheme 2: (1) PS−OH ($M_{n(SEC)} = 5290$, $M_w/M_n = 1.03$, 2.65 g, 0.5 mmol) and 4-(dimethylamino)pyridine (DMAP) (0.488 g, 4 mmol) are dissolved in 25 mL of dry dichloromethane, to which 60 mL of acetone containing *N,N′*-disuccinimidyl carbonate (DSC) (0.61 g, 2 mmol) is added under magnetic stirring. After 12 h of the reaction at room temperature, the solvent is distilled until the sticky solid is formed. To remove the excessive DSC, the sticky solid is redissolved in 100 mL of dry cyclohexane, and the insoluble DSC can be filtered. Repeating this process until a clear cyclohexane solution is obtained. The solution is then concentrated to $^1/_3$ of its original volume and then precipitated in dry CH_3CN with a yield of 86%. ^{1}H NMR (ppm) ($CDCl_3$): 1.3−2.3 (m, $C_6H_5-\mathbf{CHCH_2}-$), 6.20−7.20 (m, aromatic **CH**) for PS chain, 3.81−3.97 (m, 2H, methylene connected with oxygen atom of succinimidyl carbonate), and 2.8 ppm (m, 4H, succinimidyl ring). No noticeable change was found for the molecular weight and molecular weight distribution of the reactant and product. (2) mPEO-Lys (1.25 g, 0.25 mmol) obtained in the last paragraph is dissolved in 70 mL of anhydrous chloroform, in which triethylamine is added dropwise to adjust the solution to pH 9.0. To this solution, PS-SC synthesized by the first step (1.75 g, 0.33 mmol) is added over 1 h, and the system is maintained at pH 9.0 with TEA. After 10 h in room temperature under stirring, the reaction mixture is subsequently stirred for 3 days at 40 °C and then cooled to room temperature. The reaction solution is concentrated to $^1/_3$ of its original volume and precipitated in petroleum ether (30−60 °C); the residues after filtration are redissolved in toluene and extracted twice with water. The organic phase is separated and dried over $MgSO_4$ and then added dropwise to enough amount in petroleum ether (30−60 °C). The crude precipitated product is purified by column chromatography [silica gel (200−300 mesh)]. The progress of separation can be checked periodically by UV analysis. After front running of polystyrene eluted out of the column by pure CH_2Cl_2, the 10% methanol in CH_2Cl_2 is used to substitute the pure CH_2Cl_2 for washing out PS-PEO-Lys-COOH in the yield of 70%. ^{1}H NMR ($CDCl_3$): 1.3−2.3 (m, $C_6H_5-\mathbf{CHCH_2}-$), 6.20−7.20 (m, aromatic **CH**), 3.38 ppm (s, $\mathbf{CH_3}-O-PEO$), 3.60−3.70 ppm (b, $-\mathbf{CH_2CH_2}O-$ for PEO chain). $M_{n(SEC)} = 8655$ g/mol, $M_w/M_n = 1.09$, $M_{n(NMR)} = 10634$ g/mol (calculated from ^{1}H NMR spectrum based on the methoxyl protons at 3.38 ppm corresponding to end group of mPEO and the methyl protons at 3.60−3.70 ppm of PEO chain, and the aromatic protons 6.20−7.20 ppm of polystyrene.)

Preparation of PI-NH$_2$ and Coupling with mPEO-PS-Lys-COOH. The synthesis of PI-SC is the same as the PS-SC but PI-OH ($M_{n(SEC)} = 5592$, $M_w/M_n = 1.04$, $M_{n(NMR)} = 4052$) is used as precursor as shown in Scheme 3. The crude product is purified with a yield of 90%. ^{1}H NMR (ppm) ($CDCl_3$): 5.70 ppm (m, $-\mathbf{CH}{=}CH_2-$ of 1,2-addition), 4.95 ppm (m, $-CH{=}\mathbf{CH_2}-$ of 1,2-addition); 5.08 ppm (m, $-\mathbf{CH}{=}C-$ of 1,4-addition), 4.63−4.69 ppm (m, $-C{=}\mathbf{CH_2}-$ of 3,4-addition), 0.9−2.21 ppm (other protons in PI chain), 4.17−4.23 (b, 2H, methylene connected with oxygen atom of succinimidyl carbonate) and 2.8 ppm (m, 4H, succinimidyl ring). No obvious change is found for the molecular weight and molecular weight distribution of the reactant and product.

Then a solution of PI-SC (2.03 g, 0.5 mmol) in 30 mL of dichloromethane is added to 70 mL of dichloromethane containing ethylenediamine (0.668 mL, 10 mmol, 20 equiv) over 1 h and kept it overnight at room temperature. After that the mixture is concentrated to about $^1/_3$ of its original volume under reduced pressure and added dropwise into methanol with stirring. The precipitate is washed thoroughly with methanol until the constant concentration of amine determined by UV spectra was reached.[34,35] ^{1}H NMR: 5.70 ppm (m, $-\mathbf{CH}{=}CH_2-$ of 1,2-addition), 4.95 ppm (m, $-CH{=}\mathbf{CH_2}-$ of 1,2-addition), 5.08 ppm (m, $-\mathbf{CH}{=}C-$ of 1,4-addition), 4.63−4.69 ppm (m, $-C{=}\mathbf{CH_2}-$ of 3,4-addition), 4.11 ppm (t, 2H, $-\mathbf{CH_2}$-OCNH−), 3.1 (m, 2H, methylene, connected with amide, $OCNHC\mathbf{H_2}CH_2NH_2$), 2.8 (m, 2H, methylene, connected with amine, $CH_2\mathbf{CH_2}NH_2$), 7.18 (m, 2H, amine, $-CH_2CH_2N\mathbf{H_2}$), 7.24 (t, 1H, $PICH_2CH_2OCON\mathbf{H}CH_2-$), 0.9−2.21 ppm (other protons in PI chain).

For coupling of PI-NH$_2$ with mPEO-PS-Lys-COOH, the process is described as shown in Scheme 4: the dried mPEO-PS-Lys-COOH (1.06 g, 0.1 mmol) is dissolved in 70 mL of anhydrous chloroform containing *N*-hydroxysuccinimide (NHS) (0.034 g, 0.3 mmol), to which *N,N′*-dicyclohexylcarbodiimide

Scheme 4. Preparation of mPEO-PS-PI (DCC = *N,N′*-Dicyclohexylcarbodiimide; NHS = *N*-Hydroxysuccinimide)



(DCC) (0.082 g, 0.4 mmol) is added at 0 °C. After reacting overnight at room temperature, the solution is filtered to remove the formed solid dicyclohexylurea and then added to PI-NH_2 (0.65 g, 0.16 mmol) in 30 mL of chloroform, while pH is maintained at 9.0 with TEA.The reaction mixture is refluxed for 5 days, then cooled to the room temperature, and precipitated twice in petroleum ether (30−60 °C). The crude product is purified by column chromatography filled by silica gel (200−300 mesh). The progress of separation can be checked periodically by UV analysis. After front running of PI-NH_2 eluted out of the column by pure CH_2Cl_2, the 4% methanol in CH_2Cl_2 is used to substitute the pure CH_2Cl_2 for washing out pure product mPEO-PS-PI in the yield of 65%. ^1H NMR ($CDCl_3$): 0.9−2.3 (m, $C_6H_5-C\mathbf{H}C\mathbf{H_2}-$, protons in PI chain besides olefinic protons), 6.20−7.20 (m, aromatic C**H**), 3.38 ppm (s, $C\mathbf{H_3}-O-PEO$), 3.60−3.70 ppm (b, $-C\mathbf{H_2}C\mathbf{H_2}O-$ for PEO chain), 5.70 ppm (m, $-C\mathbf{H}{=}CH_2-$ of 1,2-addition), 4.95 ppm (m, $-CH{=}C\mathbf{H_2}-$ of 1,2-addition), 5.08 ppm(m, $-C\mathbf{H}{=}C-$ of 1,4-addition), 4.63−4.69 ppm (m, $-C{=}C\mathbf{H_2}-$ of 3,4-addition). $M_{n(SEC)} = 12851$ g/mol, $M_w/M_n = 1.12$, $M_{n(NMR)} = 15592$ g/mol (calculated from ^1H NMR spectrum based on the methoxyl protons at 3.38 ppm corresponding to end group of mPEO and the methyl protons at 3.60−3.70 ppm of PEO chain, the acromatic protons at 6.20−7.20 ppm of polystyrene, and the vinyl protons at 5.70, 5.08, 4.63−4.69 ppm of polyisoprene).

Results and Discussion

Characterization of Intermediates PS-SC and mPEO-PS-Lys-COOH. Figure 1 shows examples of the ^1H NMR spectra of PS-OH and PS-SC, the methylene connected with hydroxyl group at 3.30 ppm for PS-OH shown in Figure 1a disappeared, and new peaks at 3.81−3.97 (m, 2H, methylene connected with oxygen atom of succinimidyl carbonate) and 2.8 ppm (s, 4H, succinimidyl ring) shown in Figure 1b appeared. This is indicative of the formation of PS-SC by the functionalization of PS-OH with DSC. The SC contents in the PS-SC could be easily derived from the peaks area ratio of succinimidyl ring (2.8 ppm) and the aromatic hydrogens (6.20−7.20 ppm); the value is 96%.

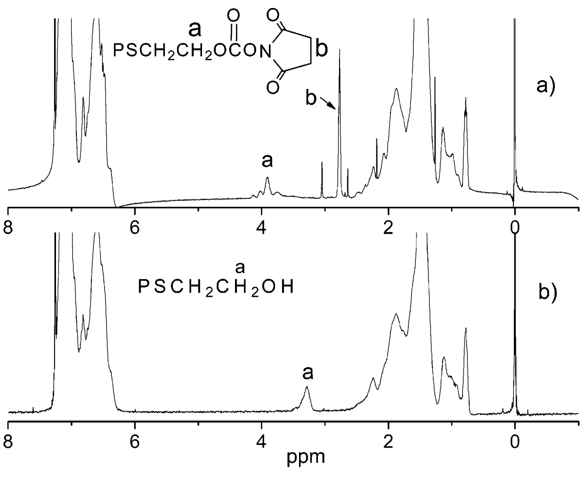


Figure 1. ^1H NMR ($CDCl_3$) spectra of (a) PS-SC and (b) PS-OH ($M_{n(SEC)} = 2032$ g/mol, $M_w/M_n = 1.04$, $M_{n(NMR)} = 2168$ g/mol).

Figure 2 shows the SEC diagram of the crude mPEO-PS-Lys-COOH, which is obtained by the reaction of mPEO-Lys with PS-SC in the presence of triethylamine. There are two peaks corresponding to the mPEO-PS-Lys-COOH with smaller retention volume and PS with larger retention volume.

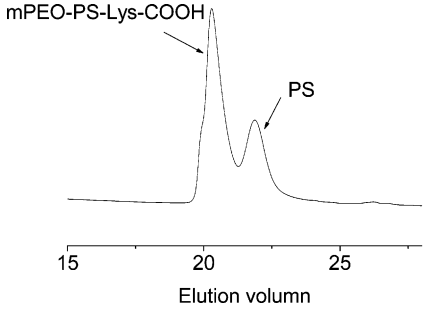


Figure 2. Size exclusion chromatograms with refractive index detector (SEC-RI) for crude product of mPEO-PS-Lys-COOH formed by reaction of mPEO-Lys ($M_{n(SEC)} = 5034$ g/mol, $M_w/M_n = 1.07$) with PS-SC ($M_{n(SEC)} = 5290$ g/mol, $M_w/M_n = 1.03$).

It is reported that when mPEO-SC is reacted with excessive lysine, the ϵ amino group of lysine is expected to consume first, whereas the α amino would almost remain unchanged because of higher activity of ϵ amino than α amino group.[36] We also find, as literature reported,[36] there are really triplet peaks at 8.10 ppm (t, 1H, mPEO-OCON**H**CH_2−) attributed to resulting carbamate via the reaction of mPEO-SC with the ϵ amino of lysine. Figure 3 shows the UV spectra of the mPEO-Lys (A), TCNE (B), the mixture of mPEO-Lys and TCNE (C), and the mixture of mPEO-PS-Lys-COOH and TCNE (D). When a compound with an amine group, an electron donor, mixed with TCNE, an electron acceptor, the red-shift peak due to the formation of charge-transfer complex (CTC) between them should appear. Figure 3 shows that before the reaction of mPEO-Lys with PS-SC the red-shift peak at 325 nm

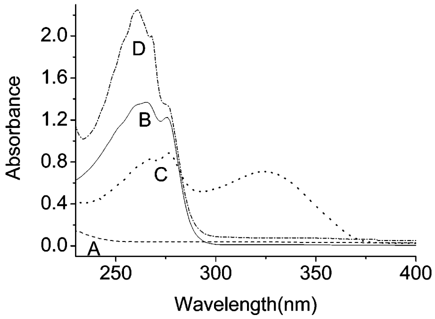


Figure 3. UV spectra of (A) mPEO-Lys (M_n = 5034 g/mol, M_w/M_n = 1.07, concentration 0.98 × 10^{-4} mol/L), (B) tetracyanoethylene (TCNE) (concentration 2.0 × 10^{-4} mol/L), (C) mixture of mPEO-Lys (concentration 0.98 × 10^{-4} mol/L) and TCNE (concentration 2.0 × 10^{-4} mol/L), (D) mixture of mPEO-PS-Lys-COOH (concentration 0.98 × 10^{-4} mol/L) and TCNE (concentration 2.0 × 10^{-4} mol/L) [solvent: CH_2Cl_2, mPEO-PS-Lys-COOH is the product of reaction of mPEO-Lys (M_n = 5034 g/mol, M_w/M_n = 1.07) with PS-SC (M_n = 5290 g/mol, M_w/M_n = 1.03)].

could be observed due to the formation of CTC composed of remaining α amino of mPEO-Lys and TCNE (curve C). After reaction of mPEO-Lys with PS-SC, the formed mPEO-PS-Lys-COOH is mixed again with TCNE; no red shift peak appeared at 325 nm as shown in Figure 3 (curve D), which means the α amino of mPEO-Lys is completely reacted with PS-SC.

As we mentioned in the Experimental Section, in the preparation of mPEO-PS-Lys-COOH, the excessive PS-SC is used, so the purification of the product is necessary. The column chromatography filled by silica gel (200−300 mesh) is used. When CH_2Cl_2 is used as the eluent, the PS-SC is well mobile, whereas mPEO-PS-Lys-COOH moves slowly. The UV spectrum of CH_2Cl_2 eluted solutions showed that the absorption at 254 nm corresponding to aromatic ring on the PS is observed, and the IR spectrum of CH_2Cl_2 eluted solutions also indicated that there are 700, 740, 840, 950, 1450, and 1600 cm^{-1}, corresponding to the aromatic ring, but no absorption at 1110 cm^{-1} for C−O−C of PEO segment appeared. It is clearly confirmed no mPEO-PS-Lys-COOH is eluted out in these conditions. After front running of PS-SC eluted out of the column (indicated by absence of UV absorption at 254 nm), the eluent is substituted by 10% methanol in CH_2Cl_2 for washing out mPEO-PS-Lys-COOH, and then UV absorption at 254 nm is detected again, which is attributed to the aromatic ring on the PS block of mPEO-PS-Lys-COOH. The IR spectrum of washed product shows absorption at 1718 cm^{-1} for carbonyl of −O−CO−NH-lysine besides characteristics bands of PS and PEO chains. The SEC of purified mPEO-PS-Lys-COOH shows the monomodal (the middle curve in Figure 7). Thus, it can reliably conclude that mPEO-PS-Lys-COOH is successfully isolated from PS-SC.

Figure 4 shows the ^{1}H NMR spectrum of purified mPEO-PS-Lys-COOH; all the peaks corresponding to the structure of mPEO-PS-Lys-COOH appeared, such as 1.3−2.3 ppm (m, $C_6H_5-\mathbf{CHCH_2}-$) and 6.20−7.20 (m, aromatic C**H)** for PS chain; 3.38 ppm (s, $\mathbf{CH_3}-O-PEO$) and 3.60−3.70 ppm (t, $-\mathbf{CH_2CH_2}O-$) for mPEO.

Characterization of PI-NH$_2$ and Star Triblock Copolymer mPEO-PS-PI. PI-NH$_2$ is obtained by the reaction of PI-SC with a large excess of ethylenediamine in order to prevent production of dimer, and the SEC trace of the product gives the single peak very close to that of starting homopolymer. The coupling of mPEO-PS-Lys-COOH with PI-NH$_2$ is performed in the presence of DCC (*N,N*′-dicyclohexylcarbodiimide). Two ways are used for this reaction: one is the coupling is directly carried out in the presence of DCC, and the other is the carboxyl of mPEO-PS-Lys-COOH is converted into succinimidyl ester in the presence of DCC first and then reacted with PI-NH$_2$; the coupling efficiency of the latter is much higher than the former. Figure 5 shows the SEC profile of crude product of mPEO-PS-PI, the peak at smaller elution volume is due to the star molecules, and the peak at larger elution volume is due to excess PI-NH$_2$.

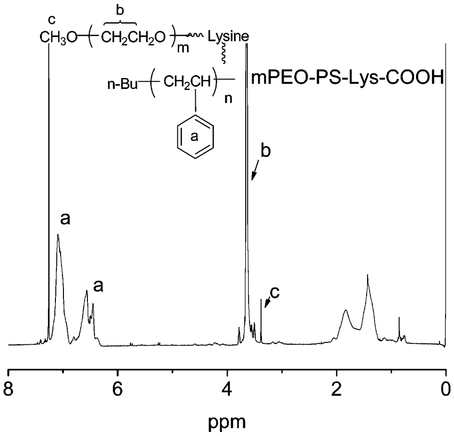


Figure 4. ^{1}H NMR ($CDCl_3$) spectra of copolymer mPEO-PS-Lys-COOH [no. 3 in Table 1, $M_{n(SEC)}$ = 8655 g/mol, M_w/M_n = 1.09, $M_{n(NMR)}$ = 10 634 g/mol].

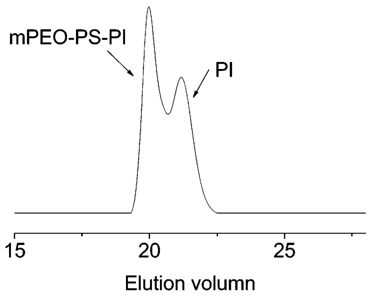


Figure 5. SEC-RI trace for crude product of mPEO-PS-PI formed by reaction of mPEO-PS-Lys-COOH ($M_{n(SEC)}$ = 8655 g/mol, M_w/M_n = 1.09, $M_{n(NMR)}$ = 10 634 g/mol) with PI-NH$_2$ ($M_{n(SEC)}$ = 5592 g/mol, M_w/M_n = 1.04, $M_{n(NMR)}$ = 4052 g/mol).

The purification of crude product of star mPEO-PS-PI is used the similar procedure as the case of diblock mPEO-PS-Lys-COOH, and the progress of separation for excessive PI-NH$_2$ is checked periodically by UV at 230 nm. After front running of unreacted homopolymer polyisoprene eluted out of the column by CH_2Cl_2, the eluent is substituted to 4% methanol in CH_2Cl_2, and the UV absorption at 254 nm can be detected, which is corresponding to aromatic ring on the polystyrene block of star mPEO-PS-PI. The IR spectrum of eluted product shows the appearance of new absorption at 1643 cm^{-1} for the −C=C− stretch of PI chains. Figure 7 (the left curve) also indicates the single peak appears for eluted product. Therefore, when the 4% methanol in CH_2Cl_2 is used as eluent, the resulting star mPEO-PS-PI could be successfully separated from the unreacted mPEO-PS-Lys-COOH. It is found, however, after front running of unreacted homopolymer polyisoprene eluted out of the column by CH_2Cl_2, the eluent is substituted to 10% methanol in CH_2Cl_2; then all remaining components

Table 1. Data (Number-Average Molecular Weight (M_n) and Polydispersity (PDI)) for ABC Miktoarm Star Copolymers mPEO-PS-PI and Intermediates mPEO-PS-Lys-COOH as Well as the Homopolymers of Monomethoxypoly(ethylene oxide) (mPEO-OH), Polystyrene (PS-OH), and Polyisoprene (PI-OH)

	mPEO-OH			PS-OH			PI-OH			mPEO-PS-Lys			mPEO-PS-PI		
no.	$M_n{}^a$ (SEC)	PDI[a]	$M_n{}^b$ (NMR)	$M_n{}^c$ (SEC)	PDI[c]	$M_n{}^d$ (NMR)	$M_n{}^c$ (SEC)	PDI[c]	$M_n{}^e$ (NMR)	$M_n{}^c$ (SEC)	PDI[c]	$M_n{}^f$ (NMR)	$M_n{}^c$ (SEC)	PDI[c]	$M_n{}^g$ (NMR)
1	2783	1.08	2891	2955	1.04	3073	3472	1.03	2346	6108	1.10	6237	8688	1.11	8201
2	2783	1.08	2891	2955	1.04	3073	4366	1.03	3241	6108	1.10	6237	10672	1.11	10139
3	5034	1.07	5337	5290	1.03	5348	5592	1.04	4052	8655	1.09	10634	12851	1.12	15592

[a] Determined by SEC-RI with water as solvent using PEO standards. [b] Calculated from ^{1}H NMR using two resonances at 3.60−3.70 and 3.38 ppm. $M_{n(NMR)} = (3I_{3.60-3.70}/4I_{3.38}) \times 44$. [c] Determined by SEC-RI with THF as solvent using PS standards. [d] Calculated from ^{1}H NMR using two resonances at 6.20−7.20 and 3.30 ppm. $M_{n(NMR)} = (2I_{6.20-7.20}/5I_{3.30}) \times 104$. [e] Calculated from ^{1}H NMR using resonances at 5.70, 5.08, 4.63−4.69, and 3.60 ppm. $M_{n(NMR)} = [(2I_{5.08}/I_{3.60}) + (2I_{5.70}/I_{3.60}) + (I_{4.69-4.63}/I_{3.60})] \times 68$. [f] Calculated from ^{1}H NMR spectrum based on the resonance at 3.38 ppm (CH_3O- of mPEO) as followed: $M_{n(NMR)} = M_{n(NMR)PS} + M_{n(NMR)mpeo} = (3I_{6.20-7.20}/5I_{3.38}) \times 104 + (3I_{3.60-3.70}/4I_{3.38}) \times 44$. [g] Calculated from ^{1}H NMR spectrum based on the resonance at 3.38 ppm (CH_3O- of mPEO) as follows: $M_{n(NMR)} = M_n(NMR)_{PS} + M_n(NMR)_{mpeo} + M_n(NMR)_{PI} = (3I_{6.20-7.20}/5I_{3.38}) \times 104 + (3I_{3.60-3.70}/4I_{3.38}) \times 44 + [(3I_{5.08}/I_{3.38}) + (3I_{5.70}/I_{3.38}) + (3I_{4.69-4.63}/2I_{3.38})] \times 68$. (Here $I_{6.20-7.20}$, $I_{3.38}$, $I_{3.60-3.70}$, $I_{5.08}$, $I_{5.70}$, and $I_{4.69-4.63}$ are the integral values of the peaks at 6.20−7.20, 3.38, 3.60−3.70, 5.08, 5.70, and 4.69−4.63 ppm, respectively.)

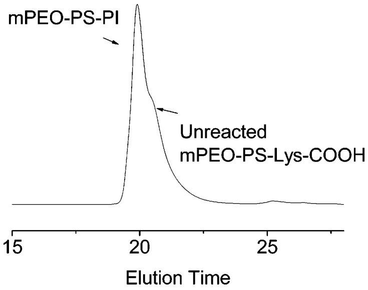


Figure 6. SEC-RI trace of the fraction eluted by 10% methanol in CH_2Cl_2 containing star terpolymer mPEO-PS-PI and unreacted mPEO-PS-Lys-COOH (no. 3 in Table 1).

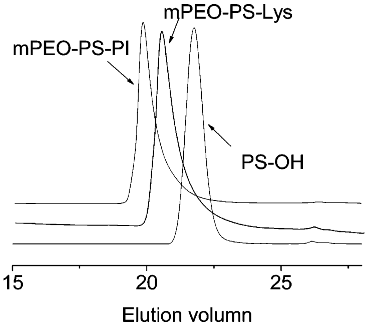


Figure 7. SEC-RI traces of PS-OH precursor ($M_{n(SEC)} = 5290$ g/mol, $M_w/M_n = 1.03$), purified mPEO-PS-Lys-COOH ($M_{n(SEC)} = 8655$ g/mol, $M_w/M_n = 1.09$, $M_{n(NMR)} = 10\,634$ g/mol), and purified star terpolymer mPEO-PS-PI ($M_{n(SEC)} = 12\,851$ g/mol, $M_w/M_n = 1.12$, $M_{n(NMR)} = 15\,592$ g/mol) from right to left (no. 3 in Table 1).

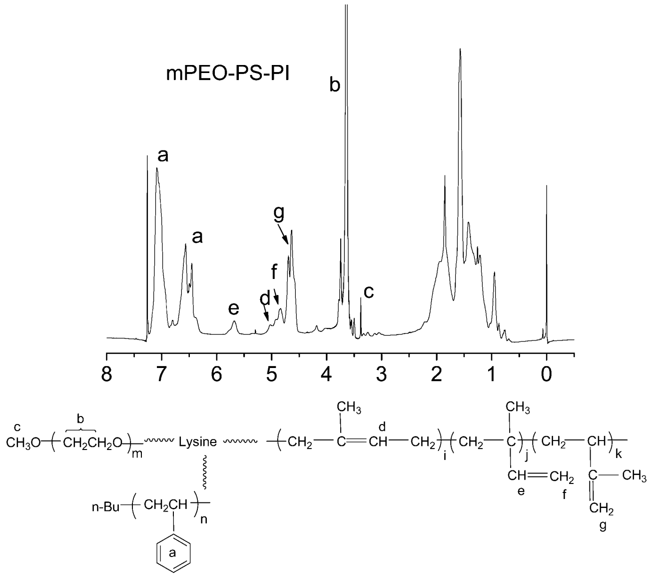


Figure 8. ^{1}H NMR ($CDCl_3$) spectra of star terpolymer PEO-PS-PI (no. 3 in Table 1) ($M_{n(SEC)} = 12\,851$ g/mol, $M_w/M_n = 1.12$, $M_{n(NMR)} = 15\,592$ g/mol).

composed of the resulting star mPEO-PS-PI and unreacted mPEO-PS-Lys-COOH are washed out. Figure 6 is a SEC diagram of washed product by 10% methanol in CH_2Cl_2, compared with the elution curve of Figure 5; a shoulder peak corresponds to unreacted mPEO-PS-Lys-COOH is still observed, except the main peak of star mPEO-PS-PI. It means that the mixture of resulting star mPEO-PS-PI and unreacted mPEO-PS-Lys-COOH cannot be effectively separated by 10% methanol in CH_2Cl_2 as eluent.

Figure 7 is the SEC diagram of purified PS-OH, mPEO-PS-Lys-COOH, and mPEO-PS-PI; no unreacted homopolymers are detected, so the method is successful.

Figure 8 is the ^{1}H NMR of purified object product; all the peaks corresponding to the chain structure of mPEO-PS-PI appeared, such as 1.3−2.3 ppm (m, $C_6H_5-\mathbf{CHCH_2}-$) and 6.20−7.20 ppm (m, benzene ring) for PS chain; 3.38 ppm (s, $C\mathbf{H_3}-O-PEO$) and 3.60−3.70 ppm (m, $-C\mathbf{H_2}C\mathbf{H_2}O-$) for mPEO; 4.63−4.69 ppm (m, $-C{=}C\mathbf{H_2}-$, 3,4-addition of PI), 4.95 ppm (m, $-CH{=}C\mathbf{H_2}-$, 1,2-addition of PI), 5.08 ppm (m, $-C\mathbf{H}{=}C-$, 1,4-addition of PI), and 5.70 ppm (m, $-C\mathbf{H}{=}CH_2-$, 1,2-addition of PI) for PI.

Table 1 summarizes the data of number-average molecular weight and molecular weight distribution of the object products mPEO-PS-PI and intermediates mPEO-PS-Lys-COOH as well as the homopolymers of mPEO-OH, PS-OH, and PI-OH; in each case three samples with different molecular weights are taken for analysis. For all of them the molecular weight distribution is rather narrow. Table 1 also showed that when the molecular weight of three arms is low, the values obtained by NMR and SEC are close each other; when the molecular weight of three arms is high, the sharp difference is found for the values derived from NMR and SEC because of the difference of the hydrodynamic volume of star triblock copolymer with linear polystyrene standards.

Conclusion

A new method is suggested to prepare the star triblock copolymers with incompatible polymer chains. By using lysine as core molecule, the hydrophobic PS, PI, and hydrophilic PEO blocks are successfully put together. The coupling reaction is performed smoothly at 40 °C and is easily monitored by size-exclusion chromatography.

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