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-NH2 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. 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. Some special morphologies such as a diamond prism shape IMDS (intermaterial dividing surface) are observed. Theoretical study 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 carbionanions; PI-PS-PBd and PI-PS-PMMA 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, PS-PBd-P2-VP, PS-PtBuMA-PDMS, PS-PEO-PCL, PS-PEO-PLL, PS-PMMA-PEO, and PS-PEO-PtBuMA 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, 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), and PCL-PMMA-PS is prepared by combination of ATRP with nitroxide-mediated radical polymerization (TEMPO). 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 carboxyl 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.

Experimental Section

Materials. Tetracyanoethylene (TCNE) (Acros, 99%), 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 CaH2 for 24 h and then distilled before use. Styrene (>99.5%), isoprene (>99%), and ethylene oxide (>99%) (SCR) were dried over CaH2 for 24 h and then distilled before use. All other reagents (SCR) are purified by common purification procedures.

Measurements. 1H NMR spectra were obtained at a DMX 500 MHz spectrometer with tetramethylsilane (TMS) as the internal standard and CDCl3 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...
detector, and a G1314A variable wavelength detector. One 5 μm LP gel column (500 Å, molecular range 500–2 x 10^4 g/mol) and two 5 μm LP gel mixed bed column (molecular range 200–3 x 10^4 g/mol) were calibrated vs poly styrene 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 by dissolution/preparation: 200 Å, greater than 1000 Å, less than 1000 Å; molecular range: 0–5 x 10^4, 5 x 10^4–8 x 10^4, (5–8) x 10^4 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 dry 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. Ethylene oxide (20 mL, 404 mmol) is initiated by the solution of initiator (7 mL, 500 Å, molecular range 1000 Å, less than 1000 Å; molecular range: 0–5 x 10^4, 5 x 10^4–8 x 10^4, (5–8) x 10^4 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 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.27,28 The microstructure characterization by 1H 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 com

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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 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$_3$CN with a yield of $90\%$. $^1$H NMR (ppm) (CDCl$_3$): 5.70 ppm (m, aromatic $CH$, 5.08 ppm (m, $CH$ of 3,4-addition), 4.95 ppm (m, $CH$ of 1,2-addition)), 4.95 ppm (m, $-CH=CH-$ of 1,2-addition); 5.08 ppm (m, $-CH=CH-$ of 1,4-addition), 4.63–4.69 ppm (m, $-C=CH-$ of 3,4-addition), 0.9–2.21 ppm (other protons in PI chain), 4.17–4.23 ppm, 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$_2$Cl$_2$, the 10% methanol in CH$_2$Cl$_2$ is used to substitute the pure CH$_2$Cl$_2$ for washing out PS-PEO-Lys-COOH in the yield of $70\%$. $^1$H NMR (CDCl$_3$): 1.3–2.3 (m, $C_6H_5CH_2$), 6.20–7.20 (m, aromatic $CH$), 3.38 ppm (s, $CH_2O$–PEO), 3.60–3.70 ppm (b, $-CH_2CH_2O$– 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 a 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, $-CH=CH_2$– of 1,2-addition), 4.95 ppm (m, $-CH=CH_2$– of 1,2-addition)); 5.08 ppm (m, $-CH=CH_2$– of 1,4-addition), 4.63–4.69 ppm (m, $-C=CH_2$– of 3,4-addition), 0.9–2.21 ppm (other protons in PI chain), 4.17–4.23 ppm, 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 and then the constant concentration of amine determined by UV spectra was reached $^{34,35}$ by NMR. $^1$H NMR: 5.70 ppm (m, $-CH=CH_2$– of 1,2-addition), 4.95 ppm (m, $-CH=CH_2$– of 1,2-addition)), 5.08 ppm (m, $-CH=CH_2$– of 1,4-addition), 4.63–4.69 ppm (m, $-C=CH_2$– of 3,4-addition), 4.11 ppm (t, 2H, $-CH_2O$–), 3.1 ppm (m, 2H, methylene, connected with amide, OCNHCH$_2$CH$_2$NH$_2$), 2.8 ppm (m, 2H, methylene, connected with amine, CH$_2$CH$_2$NH$_2$), 7.18 ppm (m, 2H, amine, $-CH=CH_2$NH$_2$), 7.24 ppm (t, 1H, PICH$_2$CH$_2$OCONHCH$_2$–), 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-NH₂ (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-NH₂ eluted out of the column by pure CH₂Cl₂, the 4% methanol in CH₂Cl₂ is used to substitute the pure CH₂Cl₂ for washing out pure product mPEO-PS-PI in the yield of 65%. 1H NMR (CDCl₃): 0.9–2.3 (m, C₆H₅–CH₂–, protons in PI chain besides olefinic protons), 6.20–7.20 (m, aromatic C–H), 3.38 ppm (s, C₃H₃–O–PEO), 3.60–3.70 ppm (b, –C₆H₄CH₂– for PEO chain), 5.70 ppm (m, –CH=C=CH₂– of 1,2-addition), 5.08 ppm(m, –CH=–C– of 1,4-addition), 4.63–4.69 ppm (m, –CH–CH₂– of 1,2-addition), 5.08 ppm (m, –CH=–C– of 1,4-addition), 4.63–4.69 ppm (m, –C=CH₂– of 3,4-addition). Mₓ(SEC) = 12851 g/mol, Mₓ/Mₘ = 1.12, Mₓ(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 aromatic 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 (CDCl₃) spectra of (a) PS-SC and (b) PS-OH (Mₓ(SEC) = 2032 g/mol, Mₓ/Mₘ = 1.04, Mₓ(NMR) = 2168 g/mol).

Figure 1. 1H NMR (CDCl₃) spectra of (a) PS-SC and (b) PS-OH (Mₓ(SEC) = 2032 g/mol, Mₓ/Mₘ = 1.04, Mₓ(NMR) = 2168 g/mol).

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 at 2.8 ppm and the aromatic protons at 6.20–7.20 ppm; the value is 96%.

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.

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-OCONHCH₂–) 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...
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 CH2Cl2 is used as the eluent, the PS-SC is well mobile, whereas mPEO-PS-Lys-COOH moves slowly. The UV spectrum of CH2Cl2 eluted solutions showed that the absorption at 254 nm corresponding to aromatic ring on the PS is observed, and the IR spectrum of CH2Cl2 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 CH2Cl2 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 profile of crude product of star 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-NH2.

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-NH2 is checked periodically by UV at 230 nm. After front running of unreacted homopolymer polyisoprene eluted out of the column by CH2Cl2, the eluent is substituted to 4% methanol in CH2Cl2, 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 CH2Cl2 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 CH2Cl2, the eluent is substituted to 10% methanol in CH2Cl2, then all remaining components are 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 CH2Cl2, the eluent is substituted to 10% methanol in CH2Cl2; then all remaining components were removed by eluting with 10% methanol in CH2Cl2. After the purification, the SEC of purified mPEO-PS-Lys-COOH shows the monomodal profile of crude product of star 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-NH2.

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Table 1. Data (Number-Average Molecular Weight (Mn) 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)

<table>
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<tr>
<th></th>
<th>mPEO-OH</th>
<th>PS-OH</th>
<th>PI-OH</th>
<th>mPEO-PS-Lys</th>
<th>mPEO-PS-PI</th>
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<tr>
<td>M_n (g/mol)</td>
<td>M_w (g/mol)</td>
<td>M_β (g/mol)</td>
<td>M_f (g/mol)</td>
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<td>5592</td>
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</tbody>
</table>

\[ M_n = \frac{m}{N} \] where \( m \) is the molecular weight of the sample, and \( N \) is the number of monomers.

\[ M_w = \frac{\sum m_i n_i}{\sum n_i} \] where \( m_i \) is the molecular weight of the i-th sample, and \( n_i \) is the number of samples.

\[ M_f = \frac{\sum m_f n_f}{\sum n_f} \] where \( m_f \) is the molecular weight of the final sample, and \( n_f \) is the number of final samples.

Figure 6. SEC-RI trace of the fraction of methanol in CH2Cl2 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 = 5290 g/mol, M_w/M_n = 1.03), purified mPEO-PS-Lys-COOH (M_n = 8655 g/mol, M_w/M_n = 1.09, M_w/M_n = 10 634 g/mol), and purified star terpolymer mPEO-PS-PI (M_n = 12 851 g/mol, M_w/M_n = 1.12, M_w/M_n = 15 592 g/mol) from right to left (no. 3 in Table 1).

A new method is suggested to prepare the star triblock copolymers with incompatible polymer chains. By using lysine as core molecule, the hydrophobic PS, Polyethylene oxide (mPEO), Polyethylene (PEO), and Polyisoprene (PI-OH).
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.

References and Notes


ABC Star Triblock Copolymer of PS, PEO, and PI 1113

(20) He, T.; Li, D. J.; Zhao, B. Macromolecules 2004, 37, 3128–3135.

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