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ARTICLE

Well-defined polyethylene-based graft terpolymers by combining nitroxide-mediated radical polymerization, polyhomologation and azide/alkyne “click” chemistry[†]

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Novel well-defined polyethylene-based graft terpolymers were synthesized *via* the “grafting onto” strategy by combining nitroxide-mediated radical polymerization (NMP), polyhomologation and copper (I)-catalyzed azide-alkyne cycloaddition (CuAAC) “click” chemistry. Three steps were involved in this approach: (i) synthesis of alkyne-terminated polyethylene-*b*-poly(ϵ -caprolactone) (PE-*b*-PCL-alkyne) block copolymers (branches) by esterification of PE-*b*-PCL-OH with 4-pentynoic acid; the PE-*b*-PCL-OH was obtained by polyhomologation of dimethylsulfoxonium methylide to afford PE-OH, followed by ring opening polymerization of ϵ -caprolactone using the PE-OH as macroinitiator, (ii) synthesis of random copolymers of styrene (St) and 4-chloromethylstyrene (4-CMS) with various CMS contents, by nitroxide-mediated radical copolymerization (NMP), and conversion of chloride to azide groups by reaction with sodium azide (NaN₃) (backbone) and (iii) “click” linking reaction to afford the PE-based graft terpolymers. All intermediates and final products were characterized by high-temperature size exclusion chromatography (HT-SEC), Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance spectroscopy (¹H NMR) and differential scanning calorimetry (DSC).

Introduction

In recent years, there has been an increase interest in graft copolymers because of their compact structure and potential applications.^{1–2} Based on the nature of their backbone and side chains they can be used, among other, as compatibilizers, polymeric emulsifier and thermoplastic elastomer.^{3–4} There are three general methods to obtain graft copolymers: (i) “grafting through” or “macromonomer strategy”, where the macromonomers are copolymerized with conventional monomers;⁵ (ii) “grafting from”, where the branches are produced by polymerization of monomers using backbone initiating sites;^{6–7} and (iii) “grafting onto”, where the branches are attached to the backbone through highly efficient coupling reactions.^{8–10}

Recently, a wide range of complex macromolecular architectures were prepared by post-polymerization modifications and “click” reactions.¹¹ The copper (I)-catalyzed azide-alkyne cycloaddition (CuAAC) is one of the most useful and widely employed coupling reactions in polymer chemistry since CuAAC is highly efficient, robust and orthogonal to most chemistries used in polymer synthesis.^{12–13} Up to now, various well-defined graft copolymers have been synthesized *via* “grafting onto” by combination of CuAAC with ring opening polymerization (ROP),^{14–15} atom transfer radical polymerization (ATRP),^{16–18} reversible addition-fragmentation chain transfer (RAFT)¹⁹ and nitroxide-mediated radical polymerization (NMP).^{20–21}

Polyethylene-based block copolymers with polystyrene (PSt), polycaprolactone (PCL) and polyacrylate, have attracted significant interest.^{22–23} Despite the fact that several well-defined grafts have been synthesized, there are only a very few reports so far dealing with polyethylene-based grafts due to the challenge to control molecular weight and functionality of PE.^{24–29} Recently, Shea developed a polymerization methodology leading to hydroxyl-terminated polyethylene (polyhomologation). The general reaction scheme

involves the formation of an organoboron zwitterionic complex between the dimethylsulfoxonium methylide and the trialkyl borane that breaks down by intramolecular 1,2-migration. As a consequence, the methylene group is randomly inserted one by one into the three branches of the trialkyl borane to give a 3-arm star having boron junction point. The resulting star is subsequently oxidized/hydrolyzed to afford hydroxyl-end-capped linear PEs.^{30–33} The hydroxyl-functionalized PE can be used directly as initiator for (ROP)^{34–35} of cyclic ethers/esters or indirectly, after chemical modification, for (ATRP),^{36–39} (RAFT)⁴⁰ and ring-opening metathesis polymerization (ROMP).^{41–43}

In this work, we report the synthesis of novel polyethylene-based graft terpolymers *via* the “grafting onto” strategy by combining NMP, polyhomologation and CuAAC “click” chemistry.

Experimental information

Materials

Styrene (St, 99%, Acros) and 4-chloromethyl styrene (4-CMS, 90%, Aldrich) were passed through basic alumina before use. ϵ -Caprolactone (99%, Alfa Aesar) was distilled over CaH₂. Sodium hydride (60% dispersion in mineral oil, Acros) was washed with hexane before use. DMF (99%, Fisher), methanol (99%, Fisher), dichloromethane (>99%, Fisher), hexane (99%, Fisher) were used as received. Tetrahydrofuran (99%, Fisher) and toluene (99.7%, Fluka) were distilled over Na and benzophenone. CuBr (98%, Aldrich) was purified by stirring with acetic acid and washing with methanol and then dried under vacuum. Calcium hydride (CaH₂, 95%, Aldrich), trimethylsulfoxonium iodide (98%, Alfa Aesar), benzyl tri-*n*-butylammonium chloride (98%, Alfa Aesar) and trimethylamine *N*-oxide dihydrate (TAO, >99%, Fluka), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 98%, Aldrich), benzoyl peroxide (BPO, 75%, Aldrich), NaN₃ (99%, Fisher), *N,N,N',N',N''*-

pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), 4-pentynoic acid (95%, Aldrich), triethyl borane (Et₃B, 95%, Aldrich), *N,N*-dimethylpyridin-4-amine (DMAP, 99%, Aldrich), *N,N'*-dicyclohexylcarbodiimide (DCC, 99%, Aldrich), *t*-BuP₂ (2.0 M in THF, Aldrich), Merrifield's resin (1% crosslinked chloromethylated PS, Aldrich) and 1-hexyne (97%, Aldrich) were used as received.

Instrumentation

High-temperature-size exclusion chromatography (HT-SEC) measurements were carried out with the Agilent PL-SEC 220 having one PLgel 10 μ m MIXED-B column. 1,2,4-Trichlorobenzene (TCB) was used as eluent at a flow rate of 1.0 mL/min at 150 °C. The system was calibrated with PSt standards. SEC measurements at 35 °C were recorded on a Viscotek TDA 305 instrument equipped with one PLgel 10 μ m mixed-C column (only used for (PSt)₃B) or two columns, Styragel HR2 (7.8 $\times$ 300 mm) and Styragel HR4 (7.8 $\times$ 300 mm). THF was used as eluent at the flow rate of 1 mL/min. The system was calibrated with PSt standards. ¹H NMR spectra were recorded on a Bruker AVANCE III-600 spectrometer. Fourier transform infrared spectra (FTIR) were obtained with a Nicolet Magna 6700 FT spectrometer. Differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC1/TC100 system in an inert nitrogen atmosphere. The second heating curve was used to determine the glass transition temperature (*T*_g), melting temperature (*T*_m), and degree of crystallinity.

Synthesis of hydroxyl terminated polyethylene (PE-OH)

Into a dried 100 mL round bottom flask equipped with a stirrer, a solution of dimethylsulfoxonium methylide in toluene (see ESI) (84 mL, 0.96 mmol/mL, 81 mmol) was introduced by syringe under argon and heated to 50 °C, followed by the addition of 0.26 mL of triethyl borane (1 M, 0.26 mmol). After 15 min a sample of the reaction mixture was taken and added to water to measure the pH of the solution. Since the pH was neutral, meaning that all methylide monomer was consumed, TAO (0.28 g) was added to the solution under argon. After 3 hours the solvent was removed under reduced pressure and the polymer was precipitated in methanol and dried under vacuum. (1.2 g, 100 % yield, *M*_{n, NMR} = 2030 g·mol⁻¹). ¹H NMR (600 MHz, toluene-*d*₈, 80 °C) values included 3.38 ppm (t, 2H, CH₂-OH, end-group of PE), 1.36 ppm (m, 2H, -CH₂-, the backbone of PE).

Synthesis of OH-terminated polyethylene-*b*-polycaprolactone (PE-*b*-PCL-OH)

0.71 g of the macroinitiator PE-OH (*M*_{n, NMR} = 2030 g·mol⁻¹, 0.35 mmol) was dissolved in 3 mL of hot toluene (80 °C) followed by addition of 4 mL of ϵ -caprolactone (35 mmol), and 0.1 mL of catalyst solution *t*-BuP₂ (2 M in THF, 0.35 mmol) to perform ROP under argon at 80 °C. The polymerization was kept at 80 °C for 15 h and quenched by acetic acid (0.5 mL). The obtained copolymer was precipitated in methanol and dried under vacuum (2.3 g, 47 % yield, *M*_{n, NMR} = 4800 g·mol⁻¹). ¹H NMR (600 MHz, toluene-*d*₈, 80 °C) values included 4.02 ppm (t, CH₂O- of PCL), 3.38 ppm (t, 2H, CH₂-OH, end-group of PCL), 2.23 ppm (t, C=OCH₂ of PCL), 1.61-1.26 ppm (m, CH₂ of PCL), 1.40 ppm (m, -CH₂- of the PE backbone).

Synthesis of alkyne-terminated polyethylene-*b*-polycaprolactone (PE-*b*-PCL-alkyne)

PE-*b*-PCL-alkyne was synthesized by reacting PE-*b*-PCL-OH with 4-pentynoic acid in the presence of DCC and DMAP. 2.2 g of PE-*b*-PCL-OH (*M*_{n, NMR} = 4800 g·mol⁻¹, 0.45 mmol) was dissolved in 15 mL

of freshly distilled toluene followed by addition of 4-pentynoic acid (0.45 g, 4.5 mmol), DCC (1.3 g, 4.5 mmol) and DMAP (0.1 g, 0.9 mmol). The reaction was kept under stirring at 80 °C for 24 h. The white solid formed during the esterification was removed by filtration. The filtrate was precipitated in methanol twice giving a white solid product. The resulted PE-*b*-PCL-alkyne (2.1 g, 95 % yield, *M*_{n, NMR} = 4900 g·mol⁻¹) was characterized by HT-SEC, ¹H NMR and FTIR. ¹H NMR (600 MHz, toluene-*d*₈, 80 °C) values included 4.02 ppm (t, CH₂O- of PCL), 2.30-2.25 ppm (alkyne-CH₂-CH₂-CO-O-), 2.20 ppm (t, C=OCH₂ of PCL), 1.61-1.26 ppm (m, CH₂ of PCL), 1.40 ppm (m, -CH₂- of PE backbone).

“Click” grafting of PE-*b*-PCL-alkyne chains onto the azide-containing polymeric backbone

The synthetic procedure of azide-containing copolymers poly (St-*co*-4-CMS) and poly (St-*co*-4-AMS), reported previously²⁰, is briefly described in the ESI. Poly (St-*co*-4-AMS)-25 and poly (St-*co*-4-AMS)-55 were reacted with PE-*b*-PCL-alkyne in the presence of CuBr and PMDETA in toluene at 80 °C. Typical “click” grafting reactions are as follows. The azido-functionalized backbone poly(St-*co*-4-AMS)-25 (0.05 g, 0.0043 mmol, 1equiv. of azide group), the ω -alkyne-functionalized branches PE-*b*-PCL-alkyne (0.4 g, 0.086 mmol, 20 equiv of alkyne group) and CuBr (0.012 g, 0.086 mmol) were added into a 100 mL Schlenk flask followed by addition of 6 mL of deoxygenated toluene. Then, deoxygenated PMDETA (15 μ L, 0.086 mmol) was added with an argon-purged syringe. In another experiment, deoxygenated PMDETA (17 μ L, 0.098 mmol) was introduced with an argon-purged syringe to the backbone solution poly(St-*co*-4-AMS)-55 (0.05 g, 0.0028 mmol, 1equiv of azide group), PE-*b*-PCL-alkyne (0.5 g, 0.098 mmol, 35 equiv of alkyne group) and CuBr (0.015 g, 0.098 mmol) in 6mL dry toluene. The two mixtures were degassed by three freeze-thaw-purge (FTP) cycles and stirred under argon at 80 °C for 6h. The unreacted azide units were reacted with 1-hexyne until the FTIR absorption of azide group completely disappeared. The obtained graft terpolymer solutions were passed through neutral alumina columns to remove the copper, then precipitated in methanol and dried under vacuum at room temperature. The obtained graft terpolymers were washed with acetone to remove unreacted polystyrene and successfully treated with Merrifield's resin-azide to remove unreacted PE-*b*-PCL-alkyne (see ESI). Graft terpolymers synthesized from the backbone with 25 units of azide groups (0.15 g, 33 % yield) are designated as PST-*g*-(PCL-*b*-PE)-1 and those from 55 units (0.2 g, 40 % yield) as PST-*g*-(PCL-*b*-PE)-2. A typical ¹H NMR spectrum (600 MHz, toluene-*d*₈, 80 °C) for graft terpolymers is giving the following results: 7.50 ppm (s, 1H, CH=C triazole ring), 6.5-7.3 ppm (m, 9H, ArH of PSt and P (4-CMS)), 5.14 ppm (s, 2H, Ph-CH₂-triazole), 4.02 ppm (t, CH₂O- of PCL), 3.86 ppm (t, 2H, -CH₂-OCO-, PCL-*b*-PE), 2.71 ppm (2H, -CH₂CH₂- triazole), 1.61-1.26 ppm (m, 2H, aliphatic protons CH₂ of PCL, PS and PE).

Results and discussion

Synthesis of PE-*b*-PCL-alkyne

The synthetic route for the alkyne-terminated PE-*b*-PCL-alkyne is illustrated in Scheme 1. Hydroxyl terminated polyethylene (PE-OH) was synthesized *via* polyhomologation of dimethylsulfoxonium methylide using triethyl borane as the initiator followed by oxidation with TAO. The PE-OH was then used as macroinitiator to polymerize ϵ -caprolactone in the presence of phosphazene base *t*-BuP₂ as a catalyst. Alkyne side groups were attached on the polymeric chain by esterification of the hydroxyl groups of PE-*b*-PCL-OH with 4-

pentynoic acid. The molecular characteristics of PE-OH, PE-*b*-PCL-OH and PE-*b*-PCL-alkyne are listed in Table 1.

Scheme 1. Synthetic route for PE-*b*-PCL-alkyne copolymers.

Table 1 Molecular characteristics of PE-OH, PE-*b*-PCL-OH and PE-*b*-PCL-alkyne copolymers

No.	Polymers	$M_{n, \text{SEC}}^a$ (g mol^{-1})	PDI ^a	$M_{n, \text{NMR}}$ (g mol^{-1})
1	PE-OH	2150	1.12	2030 ^b
2	PE- <i>b</i> -PCL-OH	3850	1.19	4800 ^c
3	PE- <i>b</i> -PCL-alkyne	4000	1.16	4900 ^c

^a High-temperature SEC, PSt standards. ^b $M_{n, \text{NMR}}$ of PE homopolymer = $14 \times DP_n$ of PE (integrated value of $-\text{CH}_2-$ at 1.40 ppm / integrated value of $-\text{CH}_2-\text{OH}$ at 3.40 ppm). ^c $M_{n, \text{NMR}}$ of copolymers were calculated from the ratio of integrated values of signals at $\delta = 1.20\text{--}1.40$ ppm to signal at $\delta = 4.02$ ppm.

As revealed by the HT-SEC traces (ESI, Figure S1[†]) PE-OH, PE-*b*-PCL-OH and PE-*b*-PCL-alkyne polymers showed monomodal and narrow distributions. The success of the different synthetic steps was confirmed by FTIR spectroscopy (Figure S2[†]). After the ROP of ϵ -caprolactone by using PE-OH (Figure S2(a)[†]) as macroinitiator the characteristic absorption peak of the ester groups of PCL at 1730 cm^{-1} was appeared (Figure 2S(b)[†]). In the case of PE-*b*-CL-alkyne (Figure S2(c)[†]), the broad band of hydroxyl group ($3200\text{--}3600 \text{ cm}^{-1}$) disappeared and the characteristic absorption peaks of alkyne group appeared at 3300 cm^{-1} . The successful synthesis of PE-OH and PE-*b*-PCL-OH was also confirmed by ^1H NMR (Figure 1(a) and 1(b)), where all characteristic fingerprints of PE-OH and PCL are present. The ^1H NMR spectrum of the resulting product PE-*b*-PCL-alkyne (Figure 1(c)) revealed that the esterification of PE-*b*-PCL-OH proceeded practically quantitatively as confirmed by the presence of the new peaks at $\delta = 2.24\text{--}2.28$ ppm corresponding to the two methylene groups close to alkyne end group (alkyne- $\text{CH}_2\text{--CH}_2\text{--CO--O-}$). The peak of the $-\text{OH}$ at $\delta = 3.38$ ppm of PE-*b*-PCL-OH (Figure 1(b)) completely disappeared and a new peak at $\delta = 3.90$ ppm (Figure 1(c)) corresponding to the ester group, overlapped by the peak of PCL at $\delta = 4.00$ ppm, appeared. The melting points were determined from the DSC traces (Figure S3[†]) to be 110.59°C (PE-OH) $^\circ\text{C}$ and 110.27 and 54.40°C corresponding to PE and PCL blocks of PE-*b*-PCL-OH.

Figure 1. ^1H NMR spectra (a) PE-OH, (b) PE-*b*-PCL-OH and (c) PE-*b*-PCL-alkyne in $\text{toluene-}d_8$ at 80°C (600 MHz).

Scheme 2. Synthetic route for PSt-*g*-(PCL-*b*-PE) graft terpolymers via CuAAC.

Synthesis of graft terpolymers PSt-*g*-(PCL-*b*-PE) by CuAAC “click” reaction

The graft terpolymers were synthesized by coupling the alkyne-terminal groups of PE-*b*-PCL-alkyne with the side azido-groups of the two backbones, poly(St-co-4-AMS)-25 and poly(St-co-4-AMS)-55, using the $\text{CuBr}/\text{PMDETA}$ catalytic system in toluene at 80°C . After 6 h, 1-hexyne was added to react with the unreacted azide group. The graft terpolymers were purified using Merrifield's resin-azide to remove unreacted PE-*b*-PCL-alkyne. As shown in Figure 2, the HT-SEC traces of graft terpolymers shifted to higher molecular weight compared to that of precursor polymers, PE-*b*-PCL-alkyne and poly(St-co-4-AMS), indicating the successful synthesis of grafted terpolymers.

Figure 2 HT-SEC (TCB at 150 °C, PSt standard) traces of PST-g-(PCL-b-PE)-1 and PST-g-(PCL-b-PE)-2.

Another proof of the successful synthesis of the graft terpolymers comes from the ^1H NMR spectroscopy. As shown in Figure 3, the appearance of the new peaks at $\delta = 7.50$ ppm are assigned to the proton of triazole ring and the peak at $\delta = 5.14$ ppm to the methylene protons between phenyl and triazole rings. Furthermore, all fingerprints of PE, PCL and PSt are present in ^1H NMR spectrum. The efficiency of CuAAC “click” reaction was calculated from ^1H NMR and it was found to be around 20 and 16% for PST-g-(PCL-b-PE)-1 and PST-g-(PCL-b-PE)-2, respectively. Therefore, it is reasonable to postulate that the click reaction efficiency of the “grafting onto” method was affected by steric hindrance. Similar behavior was observed in other “grafting onto” cases.^{16,20} The success of the “click” reaction to yield the PE-based graft terpolymers was also confirmed by the disappearance of the azide and alkyne peaks at 2104 and 3300 cm^{-1} in the FTIR spectra (Figure S6[†]).

Figure 3. ^1H NMR spectrum of PST-g-(PCL-b-PE) in toluene- d_8 at 80°C (600 MHz).

Table 2 Molecular characterization data of graft terpolymers PST-g-(PCL-b-PE)

no.	Polymers	$M_{n, \text{SEC}}^a$ ($\text{g}\cdot\text{mol}^{-1}$)	PDI ^a	$M_{n, \text{NMR}}^b$ ($\text{g}\cdot\text{mol}^{-1}$)	Y_{grafting}^c
1	PST-g-(PCL-b-PE)-1	55800	1.12	32900	5
2	PST-g-(PCL-b-PE)-2	73100	1.18	56600	9

^a High-temperature SEC, PSt standards. ^b $M_{n, \text{NMR}}$ of graft terpolymer was calculated from ^1H NMR spectrum using the area ratio of protons in PSt backbone to the ones on the side chains. ^c Number of branches (Y_{grafting}), was calculated from ^1H NMR by taking into account the $M_{n, \text{NMR}}$ of graft, the $M_{n, \text{NMR}}$ of backbone and the $M_{n, \text{NMR}}$ of branch.

Thermal properties of poly (St-co-4-CMS), poly (St-co-4-AMS) and PST-g-(PCL-b-PE)

The poly (St-co-4-CMS), poly (St-co-4-AMS) and PST-g-(PCL-b-PE) with different molecular weights were analyzed by DSC under a nitrogen atmosphere. As shown in Figure 4, the T_g of Poly (St-co-4-CMS) copolymers increases with functionality. It was noticed that the T_g values gradually decreased when azide groups increasing. The crystallinity of the PE-based grafts was also measured by DSC (Figure 4). After the CuAAC “click” reaction, the lack of chain movements, due to the PE, prevents the PCL chains to crystallize as indicated by the presence of only one melting points corresponding to PE. This behavior was also observed in the PE-based bilayered molecular combbrushes.⁴² The T_g of PSt block in PST-g-(PCL-b-PE)-1 was observed but not in the case of PST-g-(PCL-b-PE)-2 due to the increased graft concentration.

Figure 4 DSC curves of poly (St-co-4-CMS), poly (St-co-4-AMS) and PST-g-(PCL-b-PE) at various stages (N_2 atmosphere, 10 °C/ min, second heating cycle).

Conclusions

Novel well-defined polyethylene-based graft terpolymers were synthesized via the “grafting onto” strategy by combining nitroxide-mediated radical polymerization (NMP), polyhomologation and copper (I)-catalyzed azide-alkyne cycloaddition (CuAAC) “click” chemistry. The well-defined character has been proved by HT-SEC, IR and ^1H NMR characterization. This general strategy allows the synthesis of various PE-based graft polymers with different structures. DSC studies on the graft terpolymers shown that due to the presence

of PE the mobility of the attached PCL chains decreases resulting in the disappearing of PCL melting point.

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Notes and references

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