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Facile Functionalization of Polyethylene via Click Chemistry

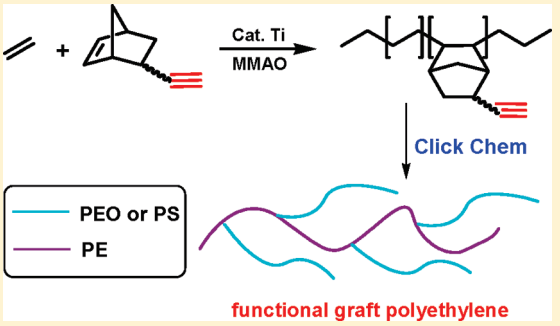
Miao Hong,[†,‡] Jing-Yu Liu,[†] Bai-Xiang Li,[†] and Yue-Sheng Li*[,†]

[†]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

[‡]Changchun Branch, Graduate School of the Chinese Academy of Sciences, Changchun 130022, China

Supporting Information

ABSTRACT: A series of well-defined functional polyethylene graft copolymers with high molecular weights have been conveniently synthesized via the combination of ethylene/5-norbornene-2-methyl propargyl ether (NMPE) copolymerization using bis(β-enaminoketonato)titanium catalysts and following click coupling reaction. Bis(β-enaminoketonato)titanium catalysts have been proved to be the potent catalysts for ethylene/NMPE copolymerization, producing high molecular weight copolymers with unimodal molecular weight distributions. ^{13}C NMR (dept) and ^{1}H NMR spectra reveal the copolymerization proceeds in a regioselective way with alkynyl group retained near the main chain. The following click coupling reactions between ethylene/NMPE copolymer and azido-terminated polymer (PEO−N_3, PS−N_3) have been achieved under mild conditions independent of the chemical structure and molecular weight of azido-terminated polymer, providing functional polyethylene with well-defined structure and high molecular weight.



INTRODUCTION

Despite commercial importance of polyethylene, the lack of functional groups in polyethylene has significantly limited many end uses, particularly those in which adhesion, dyeability, paintability, printability and compatibility with other polymers are paramount.[1] Thus, it has been a long scientific challenge in exploring the routes to functionalize polyethylene.[2,3]

"Click" chemistry has gained a great deal of attention due to high efficiency and nearly quantitative yield in the presence of many functional groups.[4] Especially, the Cu(I)-catalyzed 1,3-dipolar cycloaddition reaction between azide and alkyne has been extensively used in polymer chemistry to synthesize functional polymers,[5] bioconjugated polymers,[6] and polymers with complex topologies.[7] However, to date, the use of this type of click coupling reaction in functionalization of polyethylene has been limited.[8−10] Zhu and co-workers reported the synthesis of polyethylene-*b*-poly(ethylene oxide) diblock copolymer by click coupling reaction of azido-terminated polyethylene (PE-N_3) and alkynyl-terminated poly(ethylene oxide) (PEO−$CONHCH_2C{\equiv}CH$).[8] PE-N_3 was derived from tosylation and subsequent substitution by sodium azide of hydroxyl-terminated PE (PE−OH) which was prepared by chain shuttling ethylene polymerization with 2,6-bis[1-(2,6-dimethylphenyl)imino ethyl] pyridine iron(II) dichloride/methylaluminoxane/diethyl zinc and subsequent in situ oxidation with oxygen. Another example of click coupling reaction between PE-N_3 and propargyl acrylate or propargyl methacrylate was reported by D'Agosto et al. in which PE-N_3 was generated from substitution by sodium azide of end-halogenated PE (PE−I) that was synthesized by rapid and reversible chain transfer ethylene polymerization with $[(C_5Me_5)_2NdCl_2Li(OEt_2)_2]$/*n*-butyloctylmagnesium and subsequent in situ addition of iodine.[9] Nevertheless, a complete end-group functionalization (PE−OH or PE−I) is always difficult to achieve in these strategies and products with vinyl and saturated alkyl chain ends usually present due to undesirable chain transfer reaction, which make the purification after click coupling reaction complex. Moreover, the end-functionalized polyethylenes usually display low molecular weights (M_w < 5000 g/mol) since the chain transfer reaction to the main group metal center is no longer possible due to the dramatic decrease of chain mobility at high molecular weight. Most of all, to obtain PE−N_3, multiple functional group transformations are involved in these strategies. Therefore, more facile and straightforward synthesis of polyethylene containing azido or alkynyl group with high molecular weight for the following click coupling reaction is highly desired.

Recently, precise copolymerization of ethylene with reactive monomer has attracted wide attention because the retained reactive moiety can be converted into the functional group. *p*-Methylstyrene,[11] diene,[12−14] and an alkene-containing borane group[15] are the common reactive monomers and the copolymerization behaviors of ethylene with these reactive monomers have been widely investigated. Compared with these reactive monomers, alkene containing alkynyl group is a very promising and attractive monomer because the remaining alkynyl group can

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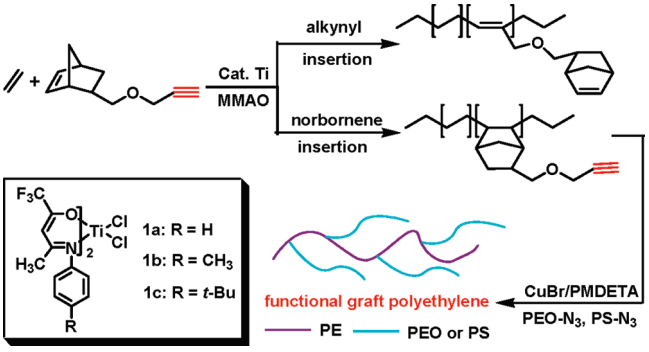
Scheme 1. Synthetic Route of Functional Polyethylene Graft Copolymer and the Structures of Catalysts Used in This Study



be utilized in click chemistry to prepare functional polyethylene. In contrast with previously reported functionalization of polyethylene via click coupling reactions, this strategy has a remarkable advantage in direct and convenient synthesis without requiring functional group transformation. However, the importance of alkene containing alkynyl group served as reactive monomer has not been realized and the copolymerization with ethylene has not been reported yet.

Herein, we report novel copolymerization of ethylene with 5-norbornene-2-methyl propargyl ether (NMPE) using bis(β-enaminoketonato)titanium catalysts (Scheme 1) which have the excellent ability to promote the copolymerization of ethylene with cyclic monomers.[14a,b,16] The obtained copolymer bearing alkynyl group can be directly utilized in Cu(I)-catalyzed 1,3-dipolar cycloaddition reactions with azido-terminated poly(ethylene oxide) (PEO−N_3) or polystyrene (PS−N_3) to provide functional polyethylene in a facile way.

EXPERIMENTAL SECTION

General Procedure and Materials. All work involving air- and/or moisture-sensitive compounds were carried out in MBraun glovebox or under an argon atmosphere by using standard Schlenk technique. The molecular weights and the molecular weight distributions of the polymer samples were determined at 150 °C by a PL-GPC 220 type high-temperature gel permeation chromatography. 1,2,4-trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min and the calibration was made by polystyrene standard Easi-Cal PS−1 (PL Ltd.). The FT-IR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer Pyris 1 DSC instrument under N_2 atmosphere. The samples were heated at a rate of 20 °C/min and cooled down at a rate of 20 °C/min. All ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity-400 MHz spectrometer (399.65 MHz for ^{1}H, 100.40 MHz for ^{13}C). The NMPE content of copolymer is determined by ^{1}H NMR spectra and calculated according to the formula: NMPE mol % = $[2I_{4.10\ ppm}/(I_{0.60-2.40\ ppm} - 3I_{4.10\ ppm})] \times 100\%$, where $I_{4.10\ ppm}$ is the peak area of proton at 4.10 ppm and $I_{0.6-2.4\ ppm}$ is the total peak area of protons at 0.60−2.40 ppm. PEO/PE (wt %/wt %) and PS/PE (wt %/wt %), which are the weight ratios of side chain to PE main chain in copolymer, are determined by ^{1}H NMR spectra and calculated according to the formulas: PEO wt % = $(44 \times I_{3.62\ ppm})/[44 \times I_{3.62\ ppm}+28 \times I_{1.36\ ppm}] \times 100\%$, PEO/PE (wt %/wt %) = PEO wt %/(100 − PEO wt %); PS wt % = $(416 \times I_{2.10\ ppm})/(416 \times I_{2.10\ ppm} + 28 \times I_{1.36\ ppm}) \times 100\%$, PS/PE (wt %/wt %) = PS wt %/(100 − PS wt %) ($I_{3.62\ ppm}$, $I_{1.36\ ppm}$, and $I_{2.10\ ppm}$ are the peak areas of protons at 3.62, 1.36, and 2.10 ppm, respectively). Molar percentage of alkynyl group which converts to the PS grafting chain is calculated according to the formula: Conv. (PS) = $I_{4.56\ ppm}/(I_{4.56\ ppm} + I_{4.10\ ppm}) \times 100\%$, where $I_{4.56\ ppm}$ and $I_{4.10\ ppm}$ are the peak areas of protons at 4.56 and 4.10 ppm.

Modified methylaluminoxane (MMAO, 7% aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc. and used without further purification. Anhydrous solvents used in this work were purified by Solvent Purification System purchased from Mbraun. 5-Norbornene-2-methanol and 3-bromo-1-propyne were purchased from Aldrich which were dried over molecular sieve for 3 days and distilled under reduced pressure before use. Two methoxypoly(ethylene glycol)s (PEO−OH) with different molecular weights (M_w = 1700 g/mol, PDI = 1.08; M_w = 6000 g/mol, PDI = 1.05) were purchased from Sigma and dried under vacuum at 60 °C for 24 h before use. Methanesulfonyl chloride, triethylamine, sodium azide, ethyl-2-bromoisobutyrate and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) were purchased from Aldrich and all were used as received. Styrene was purchased from Aldrich which were dried over calcium hydride for 3 days and distilled under reduced pressure before use. CuBr was purchased from Aldrich and purified according to the previous report.[5a] Catalysts **1a**−**c** were synthesized by the method described in the literature.[16]

Synthesis of 5-Norbornene-2-methyl Propargyl Ether (NMPE). A dry 500 mL three-necked flask was fitted with a dropping funnel, magnetic stirrer, and condenser. 5-Norbornene-2-methanol (11 g, 88.7 mmol) and dry hexane (30 mL) were added to the flask before vigorous stir. Sodium (2.04 g, 88.7 mmol) was added in batches quickly under N_2 atmosphere at room temperature. Then the reaction mixture was heated to 65 °C and kept stirring for about 10 h. After the sodium was reacted completely, the reaction mixture was cooled to 0 °C and the dropping funnel was charged with 3-bromo-1-propyne (100 mmol). When the slow addition of 3-bromo-1-propyne was completed, the reaction mixture was heated to 65 °C and kept stirring for about 7 h. During this period, the reaction mixture slowly turned orange, and white solid precipitated out. The ice water was slowly added to the reaction mixture and the organic layer is separated. The aqueous layer is extracted with three 50 mL portions of ether and the combined organic layers are washed with 50 mL of saturated aqueous Na_2CO_3 and NaCl in turn. The obtained solution was dried over with anhydrous $CaCl_2$ overnight, filtered and stripped of solvent on a rotary evaporator. Vacuum distillation of the residue yielded NMPE (yield: 75%).

Typical Copolymerization Procedure. Copolymerizations were carried out under atmospheric pressure in toluene in a 150 mL glass reactor equipped with a mechanical stirrer. The total volume of the solution was 50 mL. The reactor was charged with prescribed volume toluene and the described comonomer under argon atmosphere, and then the ethylene gas feed was started, followed by the addition of MMAO to the reactor. After equilibration at the desired polymerization temperature for 5 min, the polymerization was initiated by the toluene solution of the catalyst. After a desired period of time, the reactor was vented. The resulted copolymers were precipitated from hydrochloric acid/ethanol (2% by vol), filtered, washed three times with ethanol, then marinated in acetone for 12 h to remove the unreacted comonomer, and then dried in vacuo at room temperature to a constant weight.

Synthesis of Azido-Terminated Poly(ethylene oxide) (PEO−N_3). In a dry round-bottom flask, PEO−OH (M_w = 1700 g/mol, 10 g, 0.006 mol) was dissolved in dried methylene chloride (100 mL). The solution was cooled to 0 °C in an ice−water bath before triethylamine (1.67 mL, 0.012 mol) and methanesulfonyl chloride (0.93 mL, 0.012 mol) were added sequentially. The flask was then removed from the ice−water bath and the reaction was allowed to proceed for 24 h at room temperature. During this period, the reaction mixture slowly turned yellowish and some solid precipitated out. After filtration to remove the solid, the reaction mixture was washed successfully with 300 mL of 1 M HCl solution, 300 mL of 1 M NaOH solution and 200 mL of 1 M NaCl solution. The organic layer was dried over anhydrous $MgSO_4$ overnight

Table 1. Copolymerization of Ethylene and NMPE by Bis(β-enaminoketonato)titanium Catalysts [a]

entry	catalyst	comonomer (mmol)	yield (mg)	activity[b]	incorporation[c] (mol %)	M_w[d] (kg/mol)	M_w/M_n[d]	T_m[e] (°C)
1	**1a**	2.0	290	435	0.7	72	1.98	124.40
2	**1a**	3.0	170	255	1.5	58	2.23	118.63
3	**1b**	2.0	333	500	1.2	88	1.81	117.21
4	**1b**	3.0	200	300	3.0	64	1.95	109.17
5	**1b**	4.5	147	220	4.8	33	1.93	99.32
6[f]	**1b**	7.0	200	150	9.5	24	1.95	82.45
7	**1c**	2.0	350	525	1.0	90	1.78	125.06
8	**1c**	3.0	220	330	1.8	62	1.83	118.23

[a] Conditions: catalyst 8 μmol, ethylene 1 atm, V_{total} = 50 mL, temperature = 25 °C, time = 5 min, and Al/Ti = 2000, unless otherwise noted. [b] Catalytic activity: kg polymer/mol_{Ti}·h. [c] Comonomer incorporation (mol %) established by ^{1}H NMR spectra. [d] Weight-average molecular weights and polydispersity indices determined by GPC at 150 °C in 1,2,4-$C_6Cl_3H_3$ vs narrow polystyrene standards. [e] Melting temperatures were measured by DSC. [f] Catalyst 16 μmol; time = 10 min.

before the solvent was removed in vacuo, yielding a yellowish viscous liquid. The yield of the mesylate-terminated PEO (PEO−OSO_2CH_3) was 88%. Part of the PEO−OSO_2CH_3 (5.40 g, 0.003 mol) was dissolved in 40 mL of *N*,*N*-dimethylformamide (DMF) before sodium azide (0.40 g, 0.006 mol) and 0.15 g of tetrabutylammonium bromine were added sequentially. The reaction mixture was stirred magnetically at 50 °C for 24 h before removal of DMF by rotary evaporation. The solid was dissolved in methylene chloride and the undissolved solid was removed by filtration. The organic solution was washed twice by water before dried over anhydrous $MgSO_4$ overnight. After removal of the methylene chloride, PEO−N_3 was obtained with the yield of 87%. By using a similar procedure, azido-terminated PEO (M_w = 6000 g/mol) was also synthesized.

Synthesis of Azido-Terminated Polystyrene (PS−N_3). A mixture of styrene (10 mL, 87 mmol), CuBr (0.32 g, 2.2 mmol), ethyl-2-bromoisobutyrate (0.32 mL, 2.2 mmol), and toluene (1.1 mL) in a 25 mL Schlenk flask was subjected to three freeze−pump−thaw cycles. The flask was placed in an oil bath preheated to 90 °C, and PMDETA (0.46 mL, 2.2 mmol) was injected via nitrogen-purged syringe. After 75 min, the flask was removed from the heat, diluted with THF, and passed through a neutral alumina column to remove the catalyst. The absorbent in the column was washed with THF (30−40 mL) and the resulting polymer solution was concentrated by rotary evaporation. The polymer was precipitated in methanol and dried under vacuum (M_w = 2600 g/mol, M_w/M_n = 1.30). A fraction of the resulting polystyrene (2.0 g, 0.77 mmol) and NaN_3 (78 mg, 1.2 mmol) were dissolved in DMF (12 mL) in a sealed 50 mL round-bottomed flask. The mixture was stirred at room temperature for 4 h, and the resulting polymer was isolated by precipitation into methanol and drying under vacuum.

Synthesis of Graft Copolymer via Click Coupling Reaction. A typical procedure for synthesis of PE-*g*-PEO graft copolymers was started with the ratio of reagents [alkynyl]/[N_3]/[CuBr]/[PMDETA] = 0.155/0.28/0.136/0.426. Toluene (5 mL), chlorobenzene (2 mL), PEO−N_3 (1725 g/mol, 0.38 g, 0.22 mmol), and E/NMPE copolymer (9.5 mol %, 50 mg, 0.12 mmol alkynyl group) were introduced into a 50 mL Schlenk flask. The mixture was degassed with several cycles under vacuum and nitrogen. Before the click coupling reaction, the solution was stirred at 80 °C for 1 h to make the E/NMPE copolymer dissolved as possible. The click coupling reaction was carried out when CuBr (0.105 mmol) and PMDETA (0.33 mmol) were added. After the coupling reaction took place at 80 °C for 12 h, the reaction solution was poured into cold hexane in order to precipitate the crude product. The crude solid was extracted by Soxhlet extraction with acetone for 24 h to remove the unreacted PEO. After that, the polymer was dried under vacuum at 50 °C to a constant weight. PS-*g*-PE copolymer was prepared by similar procedure except for a longer reaction time (24 h).

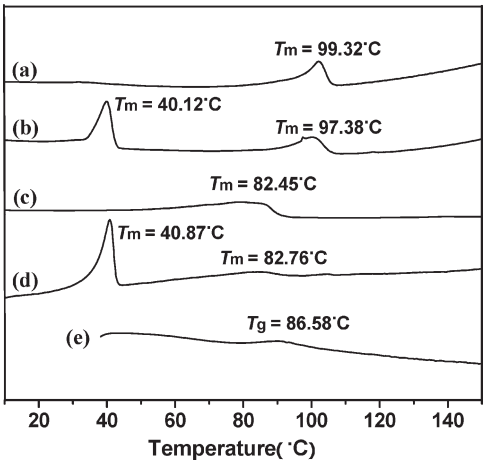


Figure 1. DSC curves: (a) ethylene/NMPE copolymer, NMPE mol % = 4.8 mol % (Table 1, entry 5); (b) PE-*g*-PEO, PEO/PE (w/w) = 56.0/44.0 (Table 2, entry 3); (c) ethylene/NMPE copolymer, NMPE mol % = 9.5 mol % (Table 1, entry 6); (d) PE-*g*-PEO, PEO/PE (w/w) = 72.4/27.6 (Table 2, entry 4); (e) PE-*g*-PS, PS/PE (w/w) = 78.8/21.2 (Table 2, entry 6).

RESULTS AND DISCUSSION

Ethylene/NMPE Copolymerization. The NMPE comonomer was synthesized in good yield (75%) by williamson reaction between 3-bromo-1-propyne and sodium 5-norbornene-2-methoxide which was prepared by in situ reaction of 5-norbornene-2-methanol and sodium. ^{1}H NMR spectrum of NMPE comonomer is provided in Figure S1 (see Supporting Information). The characteristic peaks ascribed to the protons of methylene near alkynyl group and the proton of alkynyl group are observed at 4.10−4.20 and 2.37 ppm, respectively, suggesting the successful synthesis of NMPE comonomer.

The copolymerization of ethylene with NMPE catalyzed by catalysts **1a**−**c** in the presence of MMAO is explored under different experimental conditions, and the obtained copolymers are fully characterized by ^{1}H and ^{13}C NMR (dept) spectra, GPC and DSC analyses. The typical copolymerization results are summarized in Table 1. Note that catalysts **1a**−**c** can copolymerize ethylene with NMPE and exhibit high catalytic activities. Compared with catalyst **1a**, catalysts **1b** and **1c** bearing electron-donating groups (Me and *t*-Bu) at the *para*-position of the *N*-aryl

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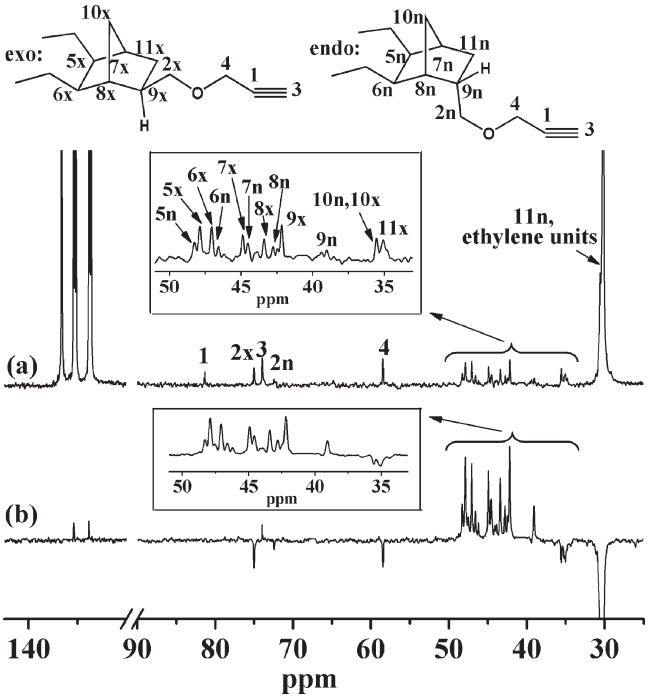

Figure 2. ^{13}C NMR (dept) spectra of ethylene/NMPE copolymer (NMPE mol % = 9.5 mol %, Table 1, entry 6) obtained by catalyst **1b** in *o*-$C_6D_4Cl_2$ at 125 °C.

moiety display higher activities (Table 1, entries 2, 4 and 8). The probable reason is that catalysts **1b,c** have less electrophilic Ti centers, generated by more electron-donating ligands, exhibiting higher tolerance to the polar atom (oxygen atom) and terminal alkyne which is known as mild acid, giving rise to an enhanced catalytic activity.[17] By varying the catalyst structure and the polymerization conditions, NMPE incorporation can be adjusted in the range of 0.7−9.5 mol %. The highest incorporation up to 9.5 mol % has been achieved by catalyst **1b** with activity of 1.5×10^5 g/mol$_{Ti}$·h (Table 1, entry 6). In addition, all the copolymers produced by catalysts **1a**−**c** display single melting temperatures (T_m) in the measurement of DSC, indicating the component of copolymer is homogeneous (typical second heating scans of DSC curves are provided in Figure 1a and 1c). With increasing comonomer incorporation, T_m values of copolymers decrease from 124.40 to 82.45 °C. Moreover, the copolymers have high molecular weights in the range of 24−90 kg/mol varied with catalyst structures and reaction conditions. As expected for a polymer generated from a chemically homogeneous catalyst, all the copolymers possess narrow molecular weight distributions (M_w/M_n = 1.8−2.3). As far as we know, the present catalyst system is the first example for successful copolymerization of ethylene with alkene bearing alkynyl group.

The microstructure of ethylene/NMPE copolymer is established by ^1H and ^{13}C NMR (dept) spectra. The typical ^{13}C NMR (dept) spectra for ethylene/NMPE copolymer are presented in Figure 2. The peak assignment was performed based on a comparison of ^{13}C NMR spectra with DEPT (135) spectra as well as the reference of the peak assignment of ethylene/5-norbornene-2-methanol copolymer reported previously.[18] Taking the chemical shift into account, the peaks at 81.37 and 74.00 ppm are assigned to quaternary and tertiary carbon in alkynyl group (marked as "1" and "3" in Figure 2), respectively. The carbon

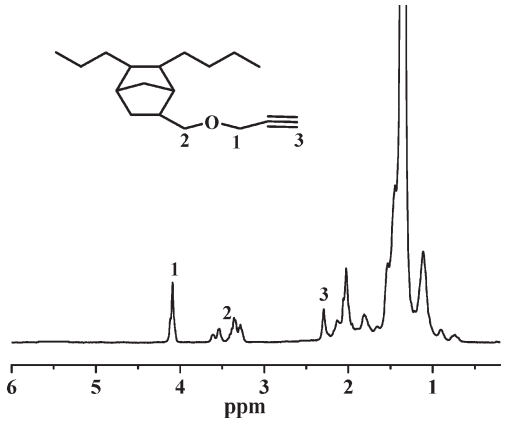

Figure 3. ^1H NMR spectrum of ethylene/NMPE copolymer (NMPE mol % = 9.5 mol %, Table 1, entry 6) obtained by catalyst **1b** in *o*-$C_6D_4Cl_2$ at 125 °C.

in methylene near the alkynyl group can also be observed at 58.48 ppm (marked as "4"). The peaks at 75.00 and 72.44 ppm (marked as "2x" and "2n") are attributed to the carbon in methylene between the norbornenyl moiety and oxygen atom corresponding to *exo* and *endo* enchainment, respectively. Those peaks in the region of 29.60−48.30 ppm are ascribed to the carbons in the norbornenyl moiety[18] and successive ethylene enchainment. It is noteworthy that the ethylene/NMPE copolymerizations by bis(β-enaminoketonato)titanium catalysts proceed through the enchainment of norbornene ring while the alkynyl insertion is absent (Scheme 1) because the peaks which are assigned to the vinyl double bond (126.6 and 131.5 ppm) and cyclic double bond (135.0 ppm) corresponding to alkynyl insertion are not observed in ^{13}C NMR spectra (Figure 2). This regioselective nature maintains under current reaction conditions. Moreover, the cross-linking is negligible as all ethylene/NMPE copolymers have excellent dissolvability in hot toluene. Consequently, the alkynyl groups are retained near the main chain, which can be directly utilized in the subsequent click coupling reaction. In addition, the regioselective copolymerization is further confirmed by ^1H NMR spectra (Figure 3) as the peaks ascribed to the protons of methylene near alkynyl group and the proton of alkynyl group are observed at 4.10 and 2.30 ppm while the peaks attributed to the double bonds corresponding to alkynyl insertion is absent (5−6 ppm).

Click Coupling Reactions between Ethylene/NMPE Copolymer and PEO−N_3 or PS−N_3. The obtained copolymer containing alkynyl group can be directly utilized in click coupling reaction with azide to provide functional polyethylene. In contrast with previously reported functionalization of polyethylene via click coupling reaction, this strategy has a remarkable advantage in direct and convenient synthesis without requiring functional group transformation.[8−10] In our study, two types of azido-terminated polymeric side chains (SCs), including azido-terminated poly(ethylene oxide) (PEO−N_3) and polystyrene (PS−N_3), with different molecular weights were chosen to react with ethylene/NMPE copolymer.

PEO−N_3 was synthesized in good yield according to previous report[7e] by using hydroxyl-terminated PEO (PEO−OH) which was first converted to mesylate-terminated PEO (PEO−OSO_2CH_3) by reaction with methanesulfonyl chloride, followed by the transformation of mesylate groups into azido groups via reaction with NaN_3. The chain-end functionality in each modification

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Table 2. Click Coupling Reactions between Ethylene/NMPE Copolymer and PEO−N_3 or PS−N_3.[a]

entry	NMPE[b] (mol %)	SC[c] (g/mol)	yield (mg)	SC/PE[d] (wt %/wt %)	convn[e] (%)	M_w[f] (kg/mol)	M_w/M_n[f]	T_m[g] (°C)	T_g[g] (°C)
1	4.8	1700	90	32.5/67.5	100	38	1.78	99.32	-
2	9.5	1700	175	42.5/57.5	100	29	1.91	80.01	-
3	4.8	6000	300	56.0/44.0	100	52	2.18	97.38, 40.12	-
4	9.5	6000	500	72.4/27.6	100	64	2.25	82.76, 40.87	-
5	4.8	2600	112	67.6/32.4	91	45	1.96	90.00[h]	-
6	9.5	2600	220	78.8/21.2	95	57	1.89	-	86.58

[a] Conditions: copolymer 50 mg, [alkynyl]/[N_3]/[CuBr]/[PMDETA] = 0.155/0.28/0.136/0.426. [b] Ethylene/NMPE copolymers with different contents of alkynyl groups (4.8 mol %, Table 1, entry 5; 9.5 mol %, Table 1, entry 6). [c] Weight-average molecular weight of side chain (SC) used in click coupling reaction. [d] Weight ratio of side chain to PE main chain established by ^{1}H NMR spectra. [e] Molar percentage of alkynyl group which converts to the grafting chain. [f] Weight-average molecular weights and polydispersity indices of graft copolymers determined by GPC at 150 °C in 1,2,4-$C_6Cl_3H_3$ vs narrow polystyrene standards. [g] Melting temperatures and glass transition temperatures were measured by DSC. [h] The melting temperature and glass transition temperature are overlapped at 90 °C.

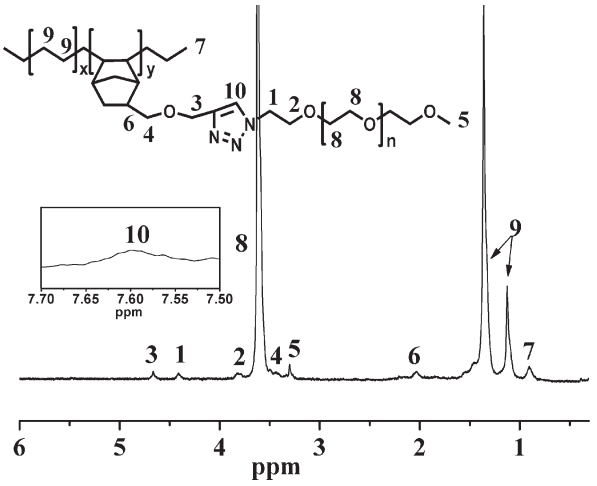

Figure 4. ^{1}H NMR spectrum of PE-*g*-PEO copolymer [PEO/PE (wt %/wt %) = 72.4/27.6, Table 2, entry 4] in *o*-$C_6D_4Cl_2$ at 125 °C.

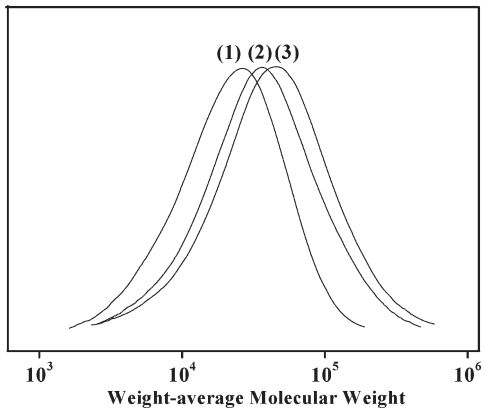

Figure 5. GPC profiles of PE-*g*-PEO copolymers: (1) M_w = 29 kg/mol, PDI = 1.91 (Table 2, entry 2); (2) M_w = 52 kg/mol, PDI = 2.18 (Table 2, entry 3); (3) M_w = 64 kg/mol, PDI = 2.25, (Table 2, entry 4).

reaction has been proved to be quantitative, as evidenced by complete disappearance of the CH_2OH peak (37.27 ppm) in ^{13}C NMR spectra of PEO−OSO_2CH_3 and the disappearance of the −OSO_2CH_3 peak (50.20 ppm) in PEO−N_3 spectra (Figure S2, see Supporting Information). A typical click coupling reaction between PEO−N_3 and ethylene/NMPE copolymer was performed successfully by using CuBr/PMDETA as the catalyst in toluene/chlorobenzene at 80 °C for 12 h. After the Soxhlet extraction with acetone for 24 h to remove unreacted PEO−N_3, the obtained PE-*g*-PEO copolymers are fully characterized by ^{1}H NMR spectra, IR spectra, GPC and DSC analyses, and the results are summarized in Table 2. By varying the content of alkynyl group in ethylene/NMPE copolymer and the molecular weight of PEO−N_3, the well-defined graft copolymers with different graft density and graft length have been prepared. PEO content of graft copolymer can be tuned in a wide range of 32.5−72.4 wt %. Higher content of alkynyl group and molecular weight of PEO−N_3 result in higher PEO content (Table 2, entry 1 vs 2, entry 1 vs 3).

The microstructure of PE-*g*-PEO copolymer is established by ^{1}H NMR spectra. As shown in Figure 4, the peaks corresponding to methylene protons adjacent to alkynyl group at 4.10 ppm and proton in alkynyl group at 2.30 ppm disappear completely after the click coupling reaction while the new peak at 7.60 ppm attributed to the proton of the newly formed five-membered trizole ring appears, indicating click coupling reaction has been achieved efficiently with the alkynyl groups fully converted to PEO graft chains. The complete reaction provides the advantage of convenient purification of the finally functional polyethylene, which needs not to remove unreacted ethylene/NMPE copolymer. Moreover, except both appearance of peaks corresponding to PE main chain [$(CH_2CH_2)_n$, 1.36 ppm] and PEO graft chain [$(CH_2CH_2O)_n$, 3.62 ppm], the characteristic peaks assigned to methylene adjacent to the five-membered trizole ring are also observed (marked as "1−3" in ^{1}H NMR spectrum).[7e,8] Further evidence of successful click coupling reaction can also be proved by FT-IR spectra (Figure S3, see Supporting Information) which display new absorption at 1105 cm^{-1} assigned to the stretching vibration of CH_2−O−CH_2 in PEO graft chain while the absorption at 3314 cm^{-1} attributed to the stretching vibration of alkynyl group disappears.

All the GPC curves of PE-*g*-PEO copolymers are unimodal without low molecular weight, indicating pure PE-*g*-PEO copolymer has been prepared after Soxhlet extraction (typical GPC profiles are provided in Figure 5). The molecular weight of PE-*g*-PEO copolymer is in the range of 29−64 kg/mol which is higher than the relevant ethylene/NMPE copolymer and PEO−N_3. The thermal transition temperatures of graft copolymers were examined by DSC analysis. PE-*g*-PEO copolymer with long graft length (M_w = 6000 g/mol) has two melting temperatures (T_m)

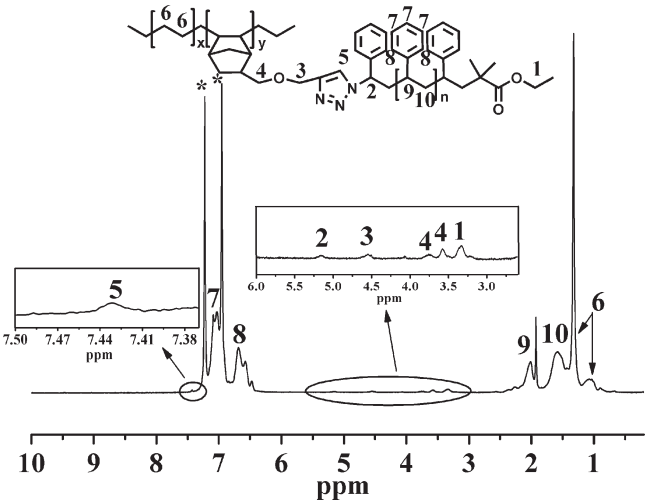

Figure 6. ^{1}H NMR spectrum of PE-*g*-PS copolymer [PS/PE (wt %/wt %) = 78.8/21.2, Table 2, entry 6] in *o*-$C_6D_4Cl_2$ at 125 °C.

(Table 2, entries 3 and 4). It is clear that the high temperature one (82−97 °C) is attributed to the T_m of PE main chain and the low temperature one at about 40 °C is attributed to the T_m of PEO graft chain (typical DSC curves are shown in Figure 1b and 1d). In contrast, PE-*g*-PEO copolymer with short graft length (M_w = 1700 g/mol) (Table 2, entries 1 and 2) only exhibits one melting temperature attributed to PE segments in the main chain while the melting temperature corresponding to PEO graft chain is indistinct probably due to low molecular weight of PEO limiting its crystallization.

PS−N_3 was synthesized according to previous literature[7i] by the reaction between NaN_3 and bromine-terminated PS (PS−Br, M_w = 2600 g/mol) which was prepared by ATRP using ethyl-2-bromoisobutyrate as initiator and CuBr/PMDETA as catalyst. The chain-end transformation reaction has been proved to be quantitative, as evidenced by complete disappearance of the proton peak of methine next to bromine at 4.41 ppm in ^{1}H NMR spectra of PS−Br and the appearance of the proton peak of methine next to azido group (3.92 ppm) in PS−N_3 spectra (Figure S4, see Supporting Information). A typical click coupling reaction between PS−N_3 and ethylene/NMPE copolymer was also carried out by similar procedure to the reaction of PEO−N_3 except for longer reaction time (24 h). Such a difference in coupling efficiency is mainly due to lower steric congestion and "thinner" structure of PEO−N_3. ^{1}H NMR spectra of PE-*g*-PS copolymer is shown in Figure 6. The new peak at 7.40 ppm attributed to the proton of newly formed five-membered trizole ring appears, indicating the click reaction has been achieved. Moreover, except both appearance of peaks corresponding to PE main chain [$(CH_2CH_2)_n$, 1.36 ppm] and PS graft chain [$(-CH_2-CH-Ph)_n$, 1.58−2.02 ppm; $(-CH_2-CH-Ph)_n$, 6.50−7.09 ppm], the characteristic peaks assigned to methylene (5.16 ppm) and methine (4.55 ppm) linked to the five-membered trizole ring (marked as "2" and "3" in ^{1}H NMR spectrum) are also observed,[7i] further confirming the successful click coupling reaction. However, about 5−9 mol % alkynyl groups still remain and do not convert to the grafting chains after reaction, which is different from the complete conversion in PEO click coupling reaction.

The PE-*g*-PS copolymers have high molecular weights in the range of 45−57 kg/mol with narrow molecular weight distributions as demonstrated by GPC analyses. The thermal transition temperatures of PE-*g*-PS copolymers were examined by DSC analysis (typical DSC curves are shown in Figure 1e). The PE-*g*-PS copolymer with low NMPE content (NMPE = 4.8%) has a transition temperature at 90 °C corresponding to the overlap of melting temperature and glass transition temperature (Table 2, entry 5). The PE-*g*-PS copolymer with high NMPE content (NMPE mol % = 9.5) exhibits glass transition temperature attributed to PS side chain at 86.58 °C (Table 2, entry 6) while the melting temperature attributed to PE main chain (about 80 °C) turn to be indistinct caused by high graft density of rigid PS side chain limiting the crystallization of PE main chain.

These results demonstrate that the click coupling reactions between ethylene/NMPE copolymers and azido-terminated polymers have been achieved under mild conditions independent of the chemical structure ("thinner" structure of PEO and "bulkier" structure of PS) and the molecular weight of azido-terminated polymeric side chains. Moreover, compared with low molecular weight of functional polyethylene (M_w < 10 kg/mol) reported previously via click coupling reaction,[8,9] it is noteworthy that the functional polyethylene produced in our work has much higher molecular weight which can be tuned in wide range.

CONCLUSIONS

Bis(β-enaminoketonato)titanium catalysts have been proved to be the potent catalysts for ethylene/NMPE copolymerization with good tolerance toward the terminal alkyne, producing high molecular weight copolymers with unimodal molecular weight distributions. ^{13}C NMR (dept) and ^{1}H NMR spectra reveal the copolymerization proceeds in a regioselective way with alkynyl group retained near the main chain. As far as we know, the present catalyst system is the first example for successful copolymerization of ethylene with alkene bearing alkynyl group. The retained alkynyl group in ethylene/NMPE copolymer can be directly utilized in click coupling reactions with azido-terminated polymer (PEO−N_3, PS−N_3). A series of well-defined functional polyethylene graft copolymers with high molecular weights have been successfully synthesized under mild conditions independent of chemical structure and molecular weight of azido-terminated polymer.

ASSOCIATED CONTENT

Supporting Information. ^{1}H NMR spectra for NMPE comonomer, ^{13}C NMR spectra for mesylate-terminated poly(ethylene oxide) and azido-terminated poly(ethylene oxide), FT-IR spectra for ethylene/NMPE copolymer and PE-*g*-PEO copolymer, and ^{1}H NMR spectra for bromine-terminated polystyrene and azido-terminated polystyrene. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Telephone: +86-431-85262124. Fax: +86-431-85262039. E-mail: ysli@ciac.jl.cn.

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