

Synthesis of Molecular Brushes by “Grafting onto” Method: Combination of ATRP and Click Reactions

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Abstract: Molecular brushes (densely grafted polymers or bottle-brush macromolecules) were synthesized by the “grafting onto” method via combination of atom transfer radical polymerization (ATRP) and “click” reactions. Linear poly(2-hydroxyethyl methacrylate) (PHEMA) polymers were synthesized first by ATRP. After esterification reactions between pentynoic acid and the hydroxyl side groups, polymeric backbones with alkynyl side groups on essentially every monomer unit (PHEMA-alkyne) were obtained. Five kinds of azido-terminated polymeric side chains (SCs) with different chemical compositions and molecular weights were used, including poly(ethylene glycol)-N₃ (PEO-N₃), polystyrene-N₃, poly(*n*-butyl acrylate)-N₃, and poly(*n*-butyl acrylate)-*b*-polystyrene-N₃. All click coupling reactions between alkyne-containing polymeric backbones (PHEMA-alkyne) and azido-terminated polymeric SCs were completed within 3 h. The grafting density of the obtained molecular brushes was affected by several factors, including the molecular weights and the chemical structures of the linear SCs, as well as the initial molar ratio of linear chains to alkynyl groups. When linear polymers with “thinner” structure and lower molecular weight, e.g., PEO-N₃ with $M_n = 775$ g/mol, were reacted with PHEMA-alkyne (degree of polymerization = 210) at a high molar ratio of linear chains to alkynyl groups in the backbone, the brush copolymers with the highest grafting density were obtained ($Y_{\text{grafting}} = 88\%$). This result indicates that the average number of SCs was ca. 186 per brush molecule and the average molecular weight of the brush molecules was ca. 190 kg/mol.

Introduction

Molecular brushes are one-dimensional macromolecules, which contain a high density of side chains (SCs) connected to a linear backbone.^{1–3} Interest in molecular brushes comes from their compact structure and a persistent cylindrical shape. Depending on the nature of the backbone and SCs, molecular brushes can be potentially used as supersoft elastomers^{4,5} or templates for inorganic nanowires.^{6–8} Typically, brush polymers are synthesized by living polymerization techniques, such as living anionic polymerization^{9,10} and controlled/living radical polymerization (CRP).^{11–13} By using CRP methods, molecular brushes can be synthesized by one of three routes: “grafting

from”,^{14–16} “grafting through”,^{5,17,18} and “grafting onto”. Although the first two methods have been extensively studied for synthesis of various kinds of brush (co)polymers with different chemical compositions and chain sequence distributions, the synthesis of molecular brushes by CRP using the “grafting onto” method has not yet been reported. Due to steric congestion between reactive polymeric SCs and backbones, the grafting density of polymeric brushes (number-average ratio of brush SCs to backbone monomer units) prepared by the “grafting onto” method is usually low.² An excess of reactive SCs can be employed to increase the grafting density, although it is not easy to purify the final brush polymers by repeated fractionation to remove the unreacted linear chains. In order to increase the grafting density during the “grafting onto” synthesis, two factors should be considered. One is to use a reactive polymeric SC with a “thinner” structure, which can decrease the steric hindrance during grafting reactions. The other is to perform an organic reaction with high efficiency, which assures a fast coupling reaction between reactive SCs and backbones.

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Atom transfer radical polymerization (ATRP)^{19–21} is a particularly attractive CRP process for synthesis of linear polymers with a predetermined degree of polymerization (DP), narrow molecular weight distribution (low polydispersity, M_w/M_n), and high chain-end functionality.²² The polymers produced by ATRP preserve terminal halogen atom(s) that can be successfully converted into various desired functional chain-end groups through appropriate transformations, especially nucleophilic substitutions.

As a highly efficient organic reaction, the Cu(I)-catalyzed 1,3-dipolar cycloaddition reactions between an azide and an alkyne, i.e., “click reactions”, as termed by Sharpless et al.,²³ have gained a great deal of attention due to their high specificity and nearly quantitative yields in the presence of many functional groups. Click reactions^{24,25} have been widely used as a versatile method for synthesis of functional monomers,²⁶ functional polymers,^{27–37} bioconjugated polymers,^{38–40} and polymers with complex topologies.^{41–53} In recent publications, our group first reported the synthesis of 3-arm and 4-arm star polymers by combination of ATRP and click reactions, in which the yields

of 3-arm and 4-arm star polymers were above 90% and 83%, respectively.⁵¹ Poly(ϵ -caprolactone) (PCL) based star⁵⁴ and grafted copolymers^{55,56} were also synthesized by combination of ring opening polymerization and click reactions.

In this paper, we report for the first time the synthesis of molecular brushes by the “grafting onto” method via combination of ATRP and click reactions. Azido-terminated polymeric SCs with various chemical compositions and molecular weights were used to click with the alkyne-containing polymeric backbones and produced grafted copolymers, PA-g-PB, where PA and PB are the polymeric backbone and SC, respectively. The SCs were either homopolymers or block copolymers. The final grafting density of the brush polymers was determined by several parameters, such as the molecular weights and the chemical structures of the linear SCs and the initial molar ratio of SCs to alkynyl groups on backbones.

Results and Discussion

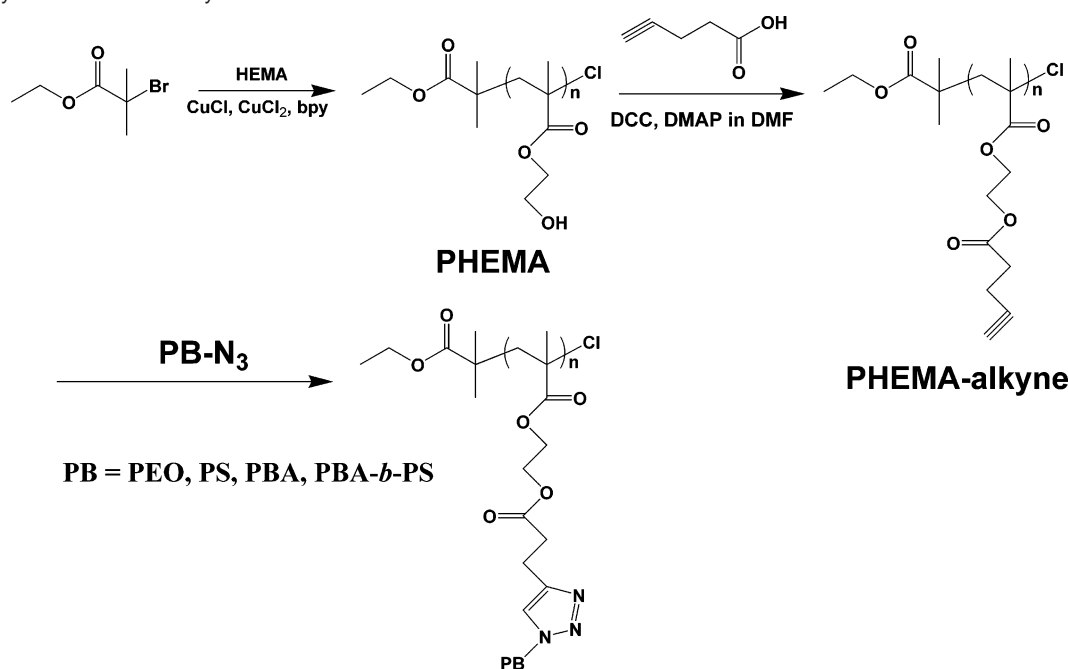
By using click reactions, molecular brushes can be synthesized by two strategies. One is to use an alkyne-containing polymeric backbone to react with azido-terminated polymeric SCs. The opposite approach is to react an azido-functionalized backbone with alkyne-terminated SCs. In this paper, the first strategy was applied to prove the feasibility of click reactions for synthesis of molecular brushes. The functional alkynyl side groups were introduced into the polymeric backbones by the esterification reactions between pentaerythric acid and the hydroxyl side groups on poly(2-hydroxyethyl methacrylate) (PHEMA). Then, the azido-terminated linear SCs with various chemical compositions and molecular weights were used to click coupling with the functional PHEMA-alkyne backbones and to form grafted copolymers, PHEMA-g-PB (Scheme 1).

Synthesis of PHEMA-alkyne. The linear PHEMA polymers were synthesized by ATRP of HEMA at 50 °C using ethyl 2-bromoisoobutyrate (EBiB) as initiator and CuCl/2,2'-bipyridine (bpy) as catalyst. The initial ratios of reagents were $[HEMA]_0/[EBiB]_0/[CuCl]_0/[CuCl_2]_0/[bpy]_0 = 500/1/0.8/0.2/2$, $[HEMA]_0 = 4.12$ M in solvent mixture of 2-butanone and methanol (3/2 by volume). During the polymerization, the first-order kinetic plot was linear (Figure 1A) and the GPC curves of PHEMA shifted smoothly toward a higher molecular weight range (Figure 1B), indicating a constant concentration of radicals and an efficient initiation. The polymerization was stopped at ca. 42% HEMA conversion in order to ensure a linear backbone structure. Determined by DMF GPC with linear PMMA standards, the apparent molecular weight of PHEMA polymer was around $M_{n,GPC} = 46.1$ kg/mol ($M_w/M_n = 1.22$), higher than the theoretical molecular weight ($M_{n,theor} = 27.5$ kg/mol), based on HEMA conversion (Figure 1C). The difference between the GPC molecular weight and theoretical molecular weight was previously reported and explained by the difference of hydrodynamic volumes between PHEMA and PMMA standards in DMF GPC.⁵⁷

Alkynyl side groups were introduced into the polymeric backbones by esterification reactions between the hydroxyl

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Scheme 1. Synthesis of Brush Polymers via Combination of ATRP and Click Reactions

groups on PHEMA and pentynoic acid. The obtained functional polymeric backbones, defined as PHEMA-alkyne, were analyzed by ^1H NMR spectroscopy using $\text{DMF-}d_7$ as solvent. In Figure 2A, no peak of the unreacted hydroxyl groups was detected in the NMR spectrum after esterification reactions, assuring the functionality of alkyne groups on the PHEMA-alkyne backbones was essentially 100%. The GPC traces in Figure 2B indicate that there was no change of apparent molecular weights between PHEMA and PHEMA-alkyne in DMF GPC measurements, although the theoretical molecular weight of PHEMA-alkyne increased from 27.5 kg/mol of PHEMA to 44.5 kg/mol after esterification reactions. The theoretical molecular weight of PHEMA-alkyne was similar to its apparent molecular weight ($M_{n,\text{GPC}} = 45.7$ kg/mol), and the molecular weight of one repeated unit in PHEMA-alkyne is 211 g/mol.

Synthesis of Azido-Terminated Polymeric SCs with Different Chemical Compositions and Molecular Weights. Five types of azido-terminated polymeric SCs were synthesized, and the relevant information was summarized in Table 1. Among these five linear SCs, three of them, polystyrene- N_3 (PS- N_3), poly(*n*-butyl acrylate)- N_3 (PBA- N_3), and PBA-*b*-PS- N_3 , were synthesized by chain-end modification of bromine-terminated linear polymers via nucleophilic substitution reactions with NaN_3 in DMF. The synthetic procedures have been reported previously^{43,51} and also briefly described in the Supporting Information.

For the synthesis of azido-terminated linear poly(ethylene glycol) chains (PEO- N_3) with different molecular weights ($M_n = 775$ and 2025 g/mol), hydroxyl-terminated PEO chains (PEO-OH) with different molecular weights were first converted to mesylate-terminated PEO (PEO-OSO₂CH₃) by reaction with methanesulfonyl chloride, followed by transformation of mesylate chain-end groups into azido groups via reaction with NaN_3 in DMF. The detailed synthetic procedures were described in the Supporting Information and illustrated in Figure 3A. The precise functionality of the obtained PEO- N_3 chains cannot be determined by ^1H NMR due to the overlapped peaks between

chain-end methylene protons (CH_2N_3) and the $(\text{CH}_2\text{CH}_2\text{O})_n$ protons in the backbone. Therefore, ^{13}C NMR was used to characterize the obtained polymers. The chain-end functionality of the product in each modification reaction was proved to be quantitative (nearly 100%), as evidenced by the disappearance of the CH_2OH peak in the PEO-OSO₂CH₃ spectrum and the disappearance of the -OSO₂CH₃ peak in the PEO- N_3 spectrum (Figure 3B).

The functionality of the synthesized PEO- N_3 775 chains was first evaluated by click coupling reactions with dialkyne-, trialkyne-, and tetraalkyne-containing coupling agents with stoichiometric ratios of azido to alkyne groups (Scheme 1S in the Supporting Information). By using $\text{CuBr}/\text{PMDETA}$ as catalyst and DMF as solvent,⁵⁸ the efficiency of click coupling reactions was nearly quantitative (essentially 100%) because the elution peak of unreacted PEO chains became undetectable in the GPC traces of the coupling products (Figures 1S, 2S and 3S in the Supporting Information). In our previous report, PS star polymers with different arm numbers were synthesized by click reactions between these alkyne-functionalized coupling agents and PS- N_3 linear chains ($M_n = 1400$ g/mol, DP = 14), in which the yields of 3-arm PS stars and 4-arm PS stars were 90% and 83%, respectively.⁵¹ Similar experimental conditions were applied for the coupling reactions with PEO- N_3 775 ($M_n = 775$ g/mol, DP = 16) chains, but the coupling efficiency of PEO stars was much higher. Such a difference in coupling efficiency could mainly be due to the lower steric congestion and "thinner" structure of PEO- N_3 , when compared to PS- N_3 chains.

Synthesis of Molecular Brushes by Click Reactions. Brush polymers were synthesized by coupling azido-terminated SCs and alkyne-containing polymeric backbones. The grafting density was affected by the chemical structures of polymer SCs and backbones and their molar ratio. Excess of SCs increases the grafting density, but an additional purification step is needed

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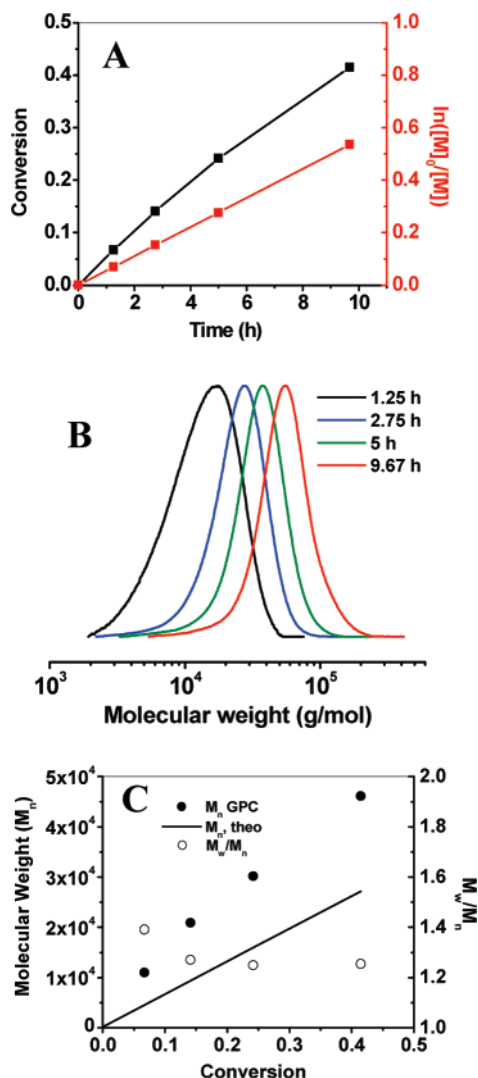


Figure 1. (A) Dependence of HEMA conversion and $\ln([M]_0/[M])$ on reaction time, (B) evolution of GPC traces, and (C) molecular weights and molecular weight distribution during synthesis of PHEMA homopolymer by ATRP. Experimental conditions: $[\text{HEMA}]_0/[\text{EBiB}]_0/[\text{CuCl}]_0/[\text{CuCl}_2]_0/[\text{bpy}]_0 = 500/1/0.8/0.2/2$; $[\text{HEMA}]_0 = 4.12 \text{ M}$; in 2-butanone/methanol (3/2 by volume) at 50°C ; linear PMMA standards were used for calibration of the DMF GPC.

to remove the unreacted linear polymers. To synthesize brush polymers, PEO- N_3 775 linear chains were first reacted with a PHEMA-alkyne backbone using the molar ratio of PEO- N_3 to alkynyl groups equal to 1.80/1 (Table 2, entry B1-1.80). By using CuBr/PMDTA as catalyst and DMF as solvent, the coupling reactions between PEO- N_3 775 and PHEMA-alkyne were completed within 3 h. The GPC traces in Figure 4 indicate that the coupling product had a higher apparent molecular weight than those of the PHEMA-alkyne precursors, determined by DMF GPC with linear PMMA as standards, indicating the formation of grafted copolymers, PHEMA-*g*-PEO.

During the coupling reactions, the conversion of PEO- N_3 SCs was determined by GPC using toluene as internal standard, which was preadded into the reaction system. Since toluene did not participate in the click coupling reactions, the percentage of reacted PEO- N_3 SCs could be calculated by comparing the peak areas of the PEO- N_3 and toluene in the DMF GPC chromatograms. When the initial molar ratio of PEO- N_3 775 SCs to alkynyl groups was 1.80/1, the percentage of reacted

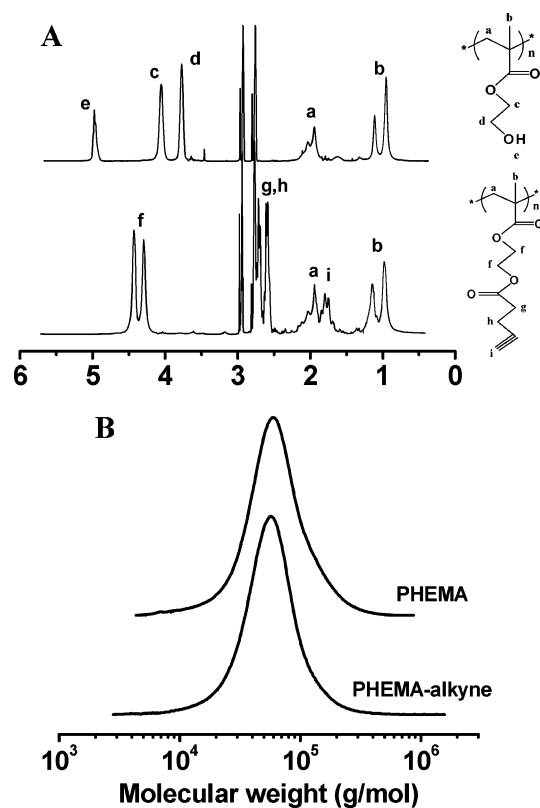


Figure 2. (A) ^1H NMR spectra and (B) DMF GPC chromatograms of PHEMA and PHEMA-alkyne. ^1H NMR conditions: 27°C , $\text{DMF-}d_7$ as solvent; linear PMMA standards were used for DMF GPC calibration.

Table 1. Summary of Azido-Terminated Polymeric SCs

entry	SCs	$M_{n,\text{theor}}^a$ (g/mol)	$M_{n,\text{NMR}}^b$ (g/mol)	$M_{n,\text{GPC}}^c$ (g/mol)	M_w/M_n^c
1	PEO- N_3	775	790	950	1.03
2	PEO- N_3	2025	2370	2810	1.02
3	PS- N_3	1380	1290	1250	1.04
4	PBA- N_3	2060	2100	2110	1.07
5	PBA- <i>b</i> -PS- N_3	3810	3870	3890	1.10

^a Theoretical molecular weight determined from monomer conversions or producer data. ^b Number-average molecular weight determined by ^1H NMR, 27°C , CDCl_3 as solvent. ^c Number-average molecular weight and polydispersity measured by THF GPC with RI detector, calibration with linear PMMA standards for PEO- N_3 , and linear PS standards for PS- N_3 , PBA- N_3 and PBA-*b*-PS- N_3 .

PEO- N_3 was ca. 34.7% and the grafting density (Y_{grafting}) of the obtained molecular brushes was ca. 62.5% (Figure 4S in the Supporting Information). This result indicates that, in the obtained PHEMA-*g*-PEO grafted copolymers, the mole fraction of reacted alkynyl groups was around 2 times larger than that of the unreacted alkynyl groups.

The ^1H NMR spectrum in Figure 5 clearly showed that after coupling reactions, new peaks (H_k , H_j , and H_f) appeared at ca. $\delta = 3.9$, 4.6, and 7.9 ppm, respectively. The peak H_j represented the methylene group next to the nitrogen of the triazole groups and the peak H_f represented the proton on the 1,2,3-triazole rings. Direct integration of peaks H_j and H_f was inaccurate because of the significant overlap of their baselines (dash line in Figure 5). Part of the broad peak H_f was beneath peaks H_j and H_k , underestimating the area of peak H_f . However, comparing the area of peaks of H_f and H_r indicates that the percentage of reacted PEO- N_3 was ca. 39% ($Y_{\text{grafting}} = 70\%$), which is similar to the result from the GPC measurement.

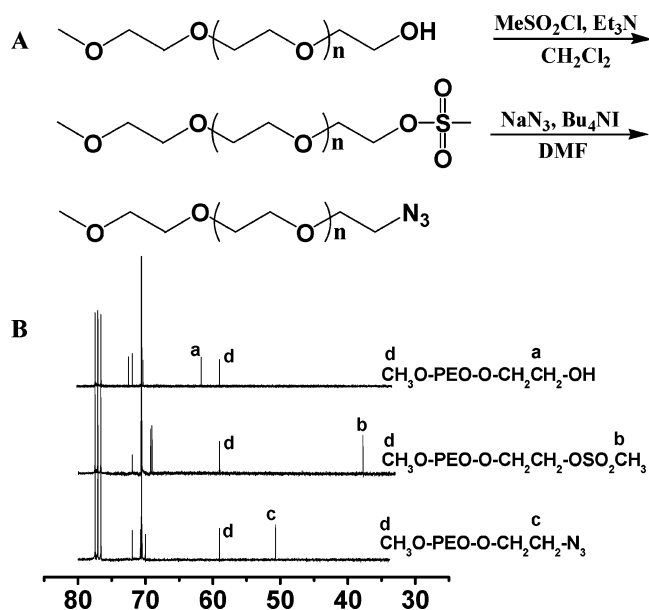


Figure 3. (A) Synthetic illustration and (B) ^{13}C NMR spectra of PEO-OH, PEO-OSO₂CH₃, and PEO-N₃ 775 ($M_n = 775$ g/mol) chains.

Table 2. Summary of PHEMA-*g*-PEO Grafted Copolymers^a

entry ^b	X	reacted PEO ^c	Y_{grafting}^d	$M_{n,\text{theor}}^e$ (kg/mol)	$M_{n,\text{GPC}}^f$ (kg/mol)	M_w/M_n^f
B1-0.65	0.65	49.1%	32.0%	96.0	81.2	1.35
B1-1.80	1.80	34.7%	62.5%	145.6	119.0	1.32
B1-3.65	3.65	23.6%	86.1%	184.0	141.9	1.34
B1-8.50	8.50	10.4%	88.4%	187.8	143.9	1.30

^a Experimental conditions: [PEO-N₃ 775]₀/[HEMA-alkyne]₀/[CuBr]₀/[PMDETA]₀ = $X/1/0.33/0.33$; [PEO-N₃ 775]₀ = 0.25 M; rt in DMF. ^b In entry code "Bn-X", "B" represents "brush" and "n" represents the entry number of SCs in Table 1. ^c Calculation was based on toluene internal standard during DMF GPC measurements. ^d $Y_{\text{grafting}} = X$ (in Bn-X) \times Reacted PEO (%). ^e $M_{n,\text{theor}} = M_n$ (PHEMA-alkyne) + $Y_{\text{grafting}} \times 210$ (DP of PHEMA-alkyne) \times 775 (M_n of PEO-N₃ 775). ^f Apparent number-average molecular weight and polydispersity, measured by DMF GPC with RI detector; PMMA standards were used for calibration.

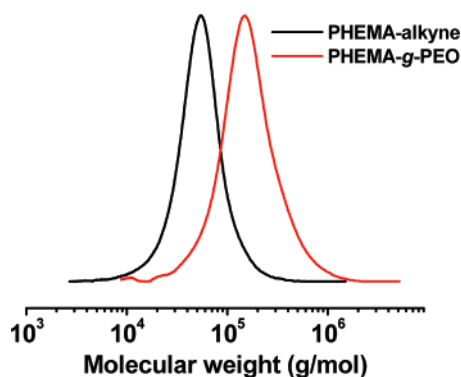


Figure 4. GPC traces of PHEMA-*g*-PEO grafted copolymers synthesized by the "grafting onto" method (Table 2, entry B1-1.80). Experimental conditions: [PEO-N₃ 775]₀/[HEMA-alkyne]₀/[CuBr]₀/[PMDETA]₀ = 1.80/1/0.33/0.33; [PEO-N₃ 775]₀ = 0.25 M, rt in DMF; linear PMMA standards for DMF GPC calibration.

To study the effect of initial molar ratio of SCs to alkynyl groups on the grafting density, different molar ratios of PEO-N₃ 775 versus HEMA-alkyne units were used for synthesis of PHEMA-*g*-PEO grafted copolymers. The results in Table 2 indicate that when more PEO-N₃ 775 SCs were used, the obtained brush polymers had higher apparent molecular weights ($M_{n,\text{GPC}}$) although these values are always smaller than the

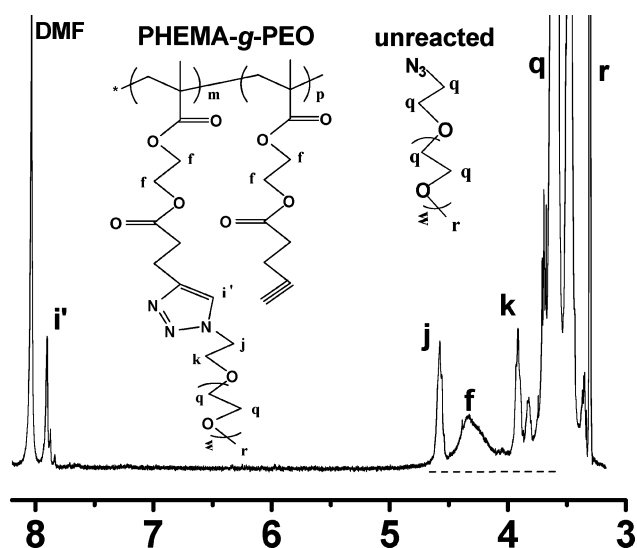


Figure 5. ^1H NMR spectrum of the reaction products between PHEMA-alkyne and PEO-N₃ 775 (Table 2, entry B1-1.80). NMR conditions: 27 °C, DMF-*d*₇ as solvent.

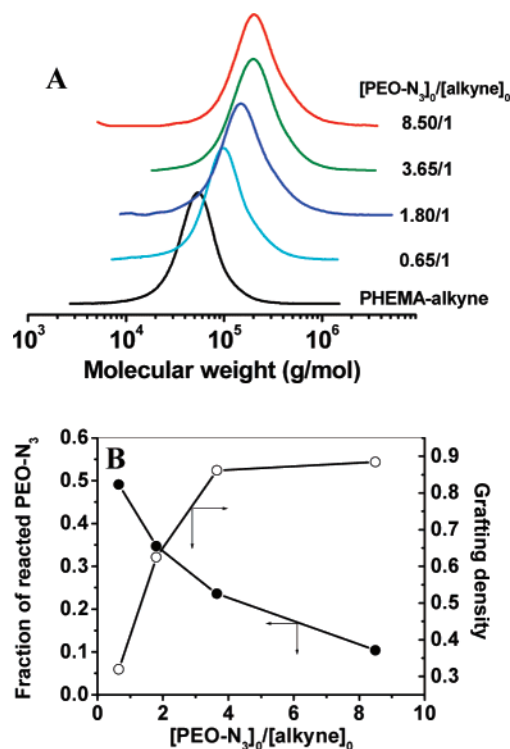


Figure 6. (A) GPC traces of PHEMA-*g*-PEO brush polymers and (B) fraction of reacted PEO-N₃ 775 SCs and grafting density of brush polymers at different molar ratios of $X = [\text{PEO-N}_3 \text{ 775}]_0/[\text{HEMA-alkyne}]_0$; experimental conditions in Table 2.

targeted values due to the compact structure of the grafted copolymers (Figure 6A). With an increase of the molar ratio of $X = [\text{PEO-N}_3 \text{ 775}]_0/[\text{HEMA-alkyne}]_0$, the grafting density of the brush polymers increased but the percentage of reacted SCs decreased (Table 2 and Figure 6B). The grafting density increased further when X was 3.65 and finally reached 88.4% when X was 8.50. Thus, due to steric congestion, the brush polymers synthesized by the "grafting onto" method had a grafting density less than 100% even when a large excess of PEO-N₃ was used. Recently, a similar result was observed during the synthesis of PCL-*g*-PEO brush polymers by click

Table 3. Synthesis of Grafted Copolymers by Click Reactions^a

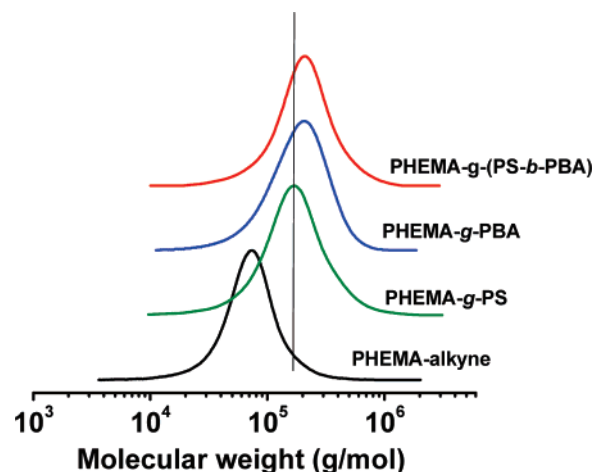
entry	SC ^b	reacted SCs ^c (%)	Y_{grafting}	$M_{n,\text{theor}}^d$ (kg/mol)	$M_{n,\text{GPC}}$ (kg/mol)	M_w/M_n
B1-1.80	PEO-N ₃ 775	34.7%	62.5%	145.6	119.0	1.32
B2-1.80	PEO-N ₃ 2025	26.5%	47.7%	246.7	206.9	1.28
B3-1.80	PS-N ₃ 1380	20.6%	37.1%	151.4	122.8	1.27
B4-1.80	PBA-N ₃ 2060	22.3%	40.1%	217.4	149.4	1.23
B5-1.80	PBA- <i>b</i> -PS-N ₃ 3810	11.3%	20.3%	206.3	150.9	1.26

^a Experimental conditions: $[\text{SC}]_0/[\text{HEMA-alkyne}]_0/[\text{CuBr}]_0/[\text{PMDETA}]_0 = 1.80/1/0.33/0.33$; rt in DMF; for B1-1.80 and B2-1.80, linear PMMA standards were used for DMF GPC calibration; for B3-1.80 to B5-1.80, linear PS standards were used for DMF GPC calibration. ^b The number represents the theoretical molecular weight of each SC. ^c Calculation was based on toluene internal standards during DMF GPC measurements. ^d $M_{n,\text{theor}} = M_n(\text{PHEMA-alkyne}) + Y_{\text{grafting}} \times 210$ (DP of PHEMA-alkyne) $\times M_n$ of SC.

coupling between azido-functionalized PCL and alkyne-terminated PEO.^{56,59} The effect of the molar ratio of reagents on grafting density suggests the progressively increased grafting density during click coupling reactions.

Synthesis of Brush Polymers with SCs Having Different Chemical Compositions and Molecular Weights. Different types of azido-terminated linear chains were used to react with PHEMA-alkyne for synthesis of brush polymers with different SCs. With the fixed initial molar ratio of SCs to alkynyl groups as 1.80/1, the grafting density of the polymer brushes was significantly influenced by the structure of the SCs. When the azido-terminated linear chains had a bulky structure and higher molecular weight, the steric hindrance and chain-end group concentration effect decreased the grafting efficiency and brush polymers with lower grafting densities were obtained. Table 3 summarizes the results of grafting copolymers with different SCs. When PEO-N₃ 775 was used for SCs, the brush polymers had the highest grafting density ($Y_{\text{grafting}} = 62.5\%$), which decreased when the molecular weight of PEO chains increased (Table 3, entries B1-1.80 and B2-1.80). When other polymers, such as PS-N₃, PBA-N₃, and PBA-*b*-PS-N₃, were reacted with PHEMA-alkyne, the grafting densities of the brush polymers were lower than that of PHEMA-*g*-PEO polymers, because of the more bulky structures of PS and PBA polymers than those of the PEO chains. It is worth noting that the PHEMA-*g*-(PS-*b*-PBA) grafted copolymers had the lowest grafting density when compared to other grafted copolymers. With the exception of the chain length effect, an additional possible reason could be the incomplete chain-end functionality in PBA-*b*-PS-Br and PBA-*b*-PS-N₃ chains, which is a common problem during the synthesis of block copolymers.⁶⁰

The GPC traces of the grafted copolymers with SCs having different chemical compositions and molecular weights are shown in Figure 7. All grafted copolymers had higher apparent molecular weights than the PHEMA-alkyne precursors, and the molecular weight distribution of the grafted copolymers remained as narrow as $M_w/M_n = 1.2-1.3$. As an example, the PHEMA-*g*-PBA brush polymer, soluble in THF, was characterized by THF GPC with a multiangle laser light scattering (MALLS) detector to determine its absolute molecular weight ($M_{w,\text{MALLS}} = 225.5$ kg/mol). This $M_{w,\text{MALLS}}$ value is similar to the theoretical one ($M_{n,\text{theor}} = 217.4$ kg/mol) and higher than the apparent molecular weight based on linear PS standards (Table 3, entry B4-1.80), indicating the compact structure of brush polymers. Based on the molecular weights of the PHEMA-alkyne precursor ($M_{w,\text{MALLS}} = 48.7$ kg/mol), PHEMA-*g*-PBA

**Figure 7.** GPC traces of molecular brushes with SCs of different chemical compositions and molecular weights.

brush polymers ($M_{w,\text{MALLS}} = 225.5$ kg/mol), and linear PBA-N₃ SC ($M_{n,\text{theor}} = 2.06$ kg/mol), the number of incorporated PBA SCs per brush polymer (Y_{grafting}) was determined to be 40.9% (DP of PHEMA-alkyne: 210), which is very similar to the result based on GPC measurement (40.1%).

These results indicate that azido-terminated linear polymeric chains with different chain lengths and chemical compositions successfully reacted with alkyne-containing polymer backbones, e.g., PHEMA-alkyne, and formed polymer brushes via click coupling reactions. The grafted copolymers had a grafting density as high as 88.4% and a narrow molecular weight distribution with M_w/M_n around 1.2–1.3.

Conclusions

Molecular brushes were successfully synthesized by the “grafting onto” method via combination of ATRP and click reactions. Alkyne-containing polymethacrylate backbones (PHEMA-alkyne) with an alkynyl group on every repeated monomer unit were used to react with azido-terminated polymeric SCs with various chemical compositions and molecular weights, such as PEO-N₃, PS-N₃, PBA-N₃, and PBA-*b*-PS-N₃. The alkyne functionality on backbones and azido functionality on polymeric SCs were very high. The click coupling reactions between PHEMA-alkyne and various azido-terminated linear chains were finished within 3 h and produced grafted copolymers. The grafting density of the obtained brush polymers was affected by three factors: the molecular weights and chemical structures of the reactive linear SCs, as well as the initial molar ratio of SCs to alkynyl groups. When bulkier linear (co)polymers, such as PS-N₃, PBA-N₃, and PBA-*b*-PS-N₃, were used to react with PHEMA-alkyne, the grafting densities of the molecular brushes

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were lower than 50%, due to the large steric congestion of grafted SCs restricting the incorporation of more linear chains into the grafted copolymers. When "thinner" PEO-N₃ linear chains with low molecular weights ($M_n = 775$ g/mol) were used to react with PHEMA-alkyne at a high molar ratio of PEO-N₃ to alkynyl groups, the grafting density of the polymer brushes reached 88.4%. Such a result indicates that for a PHEMA-alkyne backbone with DP = 210, the number of side chains per brush molecule was ca. 186 and the average molecular weight of the brush molecules was ca. 190 kg/mol.

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Supporting Information Available: Experimental part, GPC traces of PEO star polymers, and the calculation of grafting density by GPC method. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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