

Star Polymers by Photoinduced Copper-Catalyzed Azide–Alkyne Cycloaddition Click Chemistry

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ABSTRACT: Well-defined star polymers consisting of tri-, tetra-, or octa-arms have been prepared via coupling-onto strategy using photoinduced copper(I)-catalyzed 1,3-dipolar cycloaddition click reaction. An azide end-functionalized polystyrene and poly(methyl methacrylate), and an alkyne end-functionalized poly(ϵ -caprolactone) as the integrating arms of the star polymers are prepared by the combination of controlled polymerization and nucleophilic substitution reactions; whereas, multifunctional cores containing either azide or alkyne functionalities were synthesized in quantitatively via etherification and ring-opening reactions. By using photoinduced copper-catalyzed azide–alkyne cycloaddition (CuAAC) click reaction,

reactive linear polymers are simply attached onto multifunctional cores to form corresponding star polymers via coupling-onto methodology. The chromatographic, spectroscopic, and thermal analyses have clearly demonstrated that successful star formations can be obtained via photoinduced CuAAC click reaction. © 2015 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *00*, 000–000

KEYWORDS: click chemistry; copper-catalyzed azide-alkyne cycloaddition; core-first; metal-organic catalysts/organometallic catalysts; photochemistry; photoredox reactions; self-assembly; star polymers; synthesis

INTRODUCTION Star polymer is a typical nonlinear macromolecule consisting of several linear polymer chains connected at one central core.¹ Owing to its multiple functionality and compact spherical structure (smaller hydrodynamic volume and radius of gyration), star polymer has lower intrinsic viscosities and melting points than a linear polymer of similar composition and molecular weight. These unique properties generate several potential applications for star polymers, including drug delivery, cosmetics, coatings, membranes, lithography, viscosity modifiers, catalysis, separation media, thin films, and many other advanced materials. Depending on the formation sequence of cores and arms, there are three common methodologies namely, (i) “core-first,” (ii) “arm-first,” and (iii) “coupling-onto” that have been used to synthesize star polymers.² In the “core-first” strategy, a multifunctional initiator is employed to simultaneously initiate the polymerization of vinylic monomers, and thus forming the arms of the star polymer. With this strategy, controlled/living polymerization techniques have been successfully used to produce well-defined stars by the core-first method.³ This strategy also offers a more precise control over arm number by tailoring the number of functionalities of the multifunctional initiators. In the second strategy, a reaction of living polymeric chains with either a

difunctional monomer (crosslinker) or a multifunctional terminating agent has been applied to form a densely cross-linked core from which the arms radiate. This strategy also enables the synthesis of star polymers with a highly cross-linked core containing abundant reactive groups, which may potentially be employed for further encapsulation of the active materials such as drugs, metals, and catalysts.⁴ In the third strategy, a star polymer is synthesized by coupling of a preformed polymer chain containing reactive end-groups with a multifunctional core. Owing to the slow reaction rates, low efficiency, and selectivity of the coupling reactions, the variety of star polymers that can be synthesized is limited. But now, this trend has been changed after the discovery of highly efficient “click” chemistry reactions.⁵ The “click” chemistry reactions are very useful and versatile toolbox to construct star polymers because of their clean and efficient synthetic capacities and mild reaction conditions.⁶ In addition, they are considered orthogonal as the components react together in high yield and in the presence of many other functional groups. To illustrate these advantages, the synthesis of miktoarm star polymers bearing four or more different kinds of polymeric arms is often difficult or impossible owing to the complexity of the synthetic methodologies that must be implemented. The use of orthogonal click reactions

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allows in ready access to a large number of macromolecules as the individual building blocks can be covalently linked to one core, resulting in a desired miktoarm star polymers.^{7–9} For example, ABC-type miktoarm star polymers containing poly(ethylene glycol)-poly(ϵ -caprolactone)-polystyrene or poly(ethylene glycol)-poly(ϵ -caprolactone)-poly(*N*-butyl oxanorbornene imide) blocks were successfully prepared by coupling-onto methodology using orthogonal multiple click reactions. First, the clickable precursor polymers were synthesized by controlled/living polymerization and organic transformation reactions. Subsequently, these linear arms are simply attached via modular ligation reactions, Diels–Alder, copper-catalyzed azide–alkyne cycloaddition (CuAAC), and atom-transfer nitroxide radical coupling reactions onto an orthogonal multifunctional core containing anthracene, alkyne, and bromide moieties in a two-step reaction mode.¹⁰

Photochemical versions of these click reactions providing both temporal and spatial controls are recently introduced in synthetic polymer chemistry.^{11–13} For instance, a new strategy on the synthesis of ABC-type miktoarm star copolymers has been improved by employing a photoinduced thiol–ene click reaction, in combination with other techniques such as an atom-transfer radical polymerization and a heat-induced CuAAC.^{14–16} Photoinduced CuAAC click reaction is based on a reduction of an air-stable copper(II) complex to copper(I) via ligand metal charge transfer or using a variety of radical generators like photoinitiators.^{17–20} The nature of the photochemically generated radicals and the redox properties of the copper complex play vital role for the success of the generation of copper (I) species.^{21–34} Photoinduced CuAAC click reaction has been used to make, modify, and functionalize a number of soft materials, including synthetic polymers and biopolymers.^{17–19,35–42}

The goal of this study is to broaden the applicability of photoinduced CuAAC process for the macromolecular syntheses; herein, we report the preparation of tri-, tetra-, or octa-arm star polymers containing polystyrene, poly(methyl methacrylate) (PMMA) or poly(ϵ -caprolactone) (PCL). With this aim, an azide end-functionalized polystyrene (PSt- N_3) and PMMA- N_3 , and an alkyne end-functionalized PCL-alkyne as the integrating arms of the star polymers were prepared according to the well-known procedures. On the other hand, multifunctional cores, tri- and tetra-alkynyl compounds, and octa-azide polyhedral oligomeric silsesquioxane (POSS) were independently prepared by etherification and ring-opening reactions. Finally, clickable linear polymer chains were simply attached onto multifunctional cores to create corresponding star polymers via photoinduced CuAAC reactions.

EXPERIMENTAL

Materials

Styrene (St, 99%, Aldrich), methyl methacrylate (MMA, 99%, Aldrich), and ϵ -caprolactone (CL, >98%, Merck) were vacuum-distilled from calcium hydride just before use. *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA, \geq 98%, Merck) was distilled over NaOH before use. 1,1,1-*Tris*[4-(2-propynyloxy)phenyl]-ethane, propargyl bromide (80 wt % in toluene,

Aldrich), pentaerythritol (98%, Alfa Easer), propargyl alcohol (99%, Acros), 2,2-dimethoxy-2-phenyl acetophenone (DMPA, 99%, Aldrich), ethyl bromoisobutyrate (EBiB, 98%, Aldrich), and sodium azide (NaN_3 , 99%, Merck) were used as received. Octaglycidyl dimethylsilyl POSS (EP0435, viscous liquids at room temperature) was purchased from Hybrid Plastic (Hattiesburg, MS) and used as received. All other reagents were purchased from Merck and used as received. Commercial grade solvents were purified by conventional drying and distillation procedures.

Synthesis of 1,1,1-*Tris*[4-(2-propynyloxy) phenyl]-ethane

1,1,1-*Tris*[4-(2-propynyloxy) phenyl]-ethane was prepared according to the literature: 1,1,1-*tris*(4-hydroxyphenyl)-ethane (1.53 g, 5 mmol) was dissolved in dimethyl sulfoxide (6 mL) and propargyl bromide (80% in toluene; 1.3 mL, 18 mmol) was added in the mixture. Then, sodium hydroxide (2.4 g, 17.5 mmol) in water (3 mL) was added drop-wise via a dropping funnel to the flask over a 30-min period with vigorous stirring. The reaction mixture was stirred for 48 h at room temperature. After the reaction was completed, 50 mL of water was added and the mixture was extracted three times with diethyl ether. The combined organic phase was dried over Na_2SO_4 , filtered, and evaporated. The remaining product was purified by column chromatography over silica gel eluting with *n*-hexane/chloroform (1:1) to obtain pure product as white powder (yield, 90%).

¹H-NMR ($CDCl_3$, 500 MHz): δ = 2.1 (s, 3H, CH_3); 2.5 (s, 3H, $CH\equiv C$); 4.7 (t, 6H, $HC\equiv C-CH_2$); 6.8 (m, 6H, Ar-H); 7.1 (m, 6H, Ar-H).

FTIR (ATR, ν [cm^{-1}]): 3240 (C \equiv C–H); 3060 (C–H, Ar–H); 2920 (C–H, alkyl); 2850 (C–H, alkyl); 2120 (C \equiv C); 1460 (C–H).

Synthesis of Tetrakis(2-propynyloxymethyl) methane

Tetrakis(2-propynyloxymethyl) methane was prepared according to the literature: pentaerythritol (2 g, 15 mmol) was added in *N,N*-dimethylformamide (DMF; 50 mL) and the temperature was raised to 65 °C. Sodium hydride (2.16 g, 90.0 mmol) and propargyl bromide (8.2 mL, 90 mmol) were added. The reaction was stirred at 65 °C for overnight. Solvent was removed and the residue was purified by column chromatography over silica gel eluting with *n*-hexane/chloroform (4:1) to obtain pure product as a slightly yellow oil (yield, 76%).

¹H-NMR ($CDCl_3$, 500 MHz): δ = 2.4 (t, 4H, $CH\equiv C$); 3.5 (s, 8H, $C(CH_2)_4$); 4.1 (s, 8H, $HC\equiv C-CH_2$).

FTIR (ATR, ν [cm^{-1}]): 3290 (C \equiv C–H); 2920 (C–H, alkyl); 2860 (C–H, alkyl); 2120 (C \equiv C); 1460 (C–H, alkyl); 1090 (C–O–C).

Synthesis of Octakis{3-[(1-azido-2-hydroxy)propoxy]propyl dimethylsilyl} POSS

Octakis{3-[(1-azido-2-hydroxy)propoxy]propyl dimethylsilyl} POSS was prepared according to the literature⁴³: octaglycidyl dimethylsilyl POSS (4.1 g, 2.1 mmol) together with propan-2-ol (25 mL) was placed in a three-necked, round-

bottomed flask equipped with a thermometer, condenser, and a magnetic bar. A solution of NaN_3 (1.4 g, 21 mmol) in water (25 mL) was added and the pH was adjusted to 6 with acetic acid at room temperature. Then, the mixture was allowed to heat up to 60 °C and stirred for 24 h. After removing the solvent by rotary evaporation, the crude was dissolved in chloroform and washed three times with equal volume of water. The solvent was eliminated by rotary evaporation and the product was dried under vacuum for overnight (yield, 90%).

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): δ = 0.1 (s, 48H); 0.6 (m, 16H); 1.3–1.5 (m, 32H); 3.2–3.4 (m, 32H); 3.6 (m, 8H); 3.9 (m, 8H).

FTIR (ATR, ν [cm^{-1}]): 3375 (O–H); 2920 (C–H); 2095 (N_3); 1540 (C–C); 1250 (C–O–C), 1200–900 (Si–O–Si).

Synthesis of Intermediates and Precursor Polymers

ω -Azido-functional polystyrene⁴⁴ (PSt- N_3 ; $M_{n,\text{NMR}} = 1100 \text{ g mol}^{-1}$, $M_{n,\text{GPC}} = 1100 \text{ g mol}^{-1}$, and $M_w/M_n = 1.12$), ω -azido-functional PMMA- N_3 ⁴⁵ ($M_{n,\text{NMR}} = 2400 \text{ g mol}^{-1}$, $M_{n,\text{GPC}} = 2500 \text{ g mol}^{-1}$, and $M_w/M_n = 1.12$), and α -alkyne functional PCL⁴⁶ (alkyne-PCL; $M_{n,\text{NMR}} = 4700 \text{ g mol}^{-1}$, $M_{n,\text{GPC}} = 4800 \text{ g mol}^{-1}$, and $M_w/M_n = 1.31$) were prepared according to modified literature procedures.

$^1\text{H-NMR}$ (PSt- N_3 , CDCl_3 , 500 MHz): δ = 0.9 (t, 3H, CH_3 of EBiB); δ = 1.1 (t, 6H, $(\text{CH}_2)_2\text{-C}$ of EBiB); 1.2–2.2 (m, 27H, CH of PSt backbone); 3.9 (t, 1H, PSt- $\text{CH}_2\text{-CH}(\text{Ph})\text{-N}_3$); 4.5 (m, 2H, $-\text{CH}_2-$ of EBiB); 6.3–7.3 (s, 45H, Ar-H).

FTIR (PSt- N_3 , ATR, ν [cm^{-1}]): 3026 (C–H, Ar–H); 2920 (C–H, alkyl); 2850 (C–H, alkyl), 2090 (N_3).

$^1\text{H-NMR}$ (PMMA- N_3 , CDCl_3 , 500 MHz): δ = 0.7–1.2 (m, 69H, CH_3- of PMMA backbone and EBiB); 2.0–2.2 (m, 40H $-\text{CH}_2-$ of PMMA backbone); 3.6 (s, 60H, $\text{CH}_3\text{O}-$ of PMMA backbone); 4.4 (m, 2H, $-\text{CH}_2-$ of EBiB).

FTIR (PMMA- N_3 , ATR, ν [cm^{-1}]): 2990 (C–H, alkyl); 2950 (C–H, alkyl); 2100 (N_3), 1730 (C=O).

$^1\text{H-NMR}$ (PCL-alkyne, CDCl_3 , 500 MHz): δ = 1.4 (m, 90H, CH_2 on PCL backbone); 1.6 (m, 180H, CH_2 on PCL backbone); 2.3 (m, 90H, $\text{CH}_2\text{C=O}$ on PCL backbone); 2.5 (s, 1H, $\text{CH}_2\text{-C}\equiv\text{CH}$); 3.7 (t, 2H, CH_2OH); 4.0 (m, 88H, CH_2O on PCL backbone); 4.7 (s, 2H, $\text{CH}_2\text{-C}\equiv\text{CH}$).

FT-IR (PCL-alkyne, ATR, ν [cm^{-1}]): 3265 (C \equiv C–H); 2945 (C–H, alkyl); 2865 (C–H, alkyl); 2120 (C \equiv C); 1730 (C=O); 1460 (C–H, alkyl); 1245 ((C=O)–O); 1045 (C–O–C).

General Procedure for the Synthesis of Star Polymers via Photoinduced CuAAC

For tri-arm star polymer, tri-alkynyl:PMMA- N_3 : CuBr_2 :PMDETA:DMPA (molar ratios, 1:4:3:1:1), four-arm star polymer, tetra-alkynyl:PSt- N_3 : CuBr_2 :PMDETA:DMPA (molar ratios, 1:5:3:1:1), and eight-arm star polymer, octakis-azido-POSS:PCL-alkyne: CuBr_2 :PMDETA:DMPA (molar ratios, 1:8:6:2:2) were dissolved with DMF (2 mL) in a Pyrex

tube.³⁹ The solution was deaerated by bubbling nitrogen for 10 min and the mixture was irradiated for 24 h by a merry-go-round type reactor equipped with 16 Philips 8W/06 lamps emitting light at $\lambda > 350 \text{ nm}$ and a cooling system. At the end of this period, the mixture was precipitated into methanol, filtered, dried, and weighed.

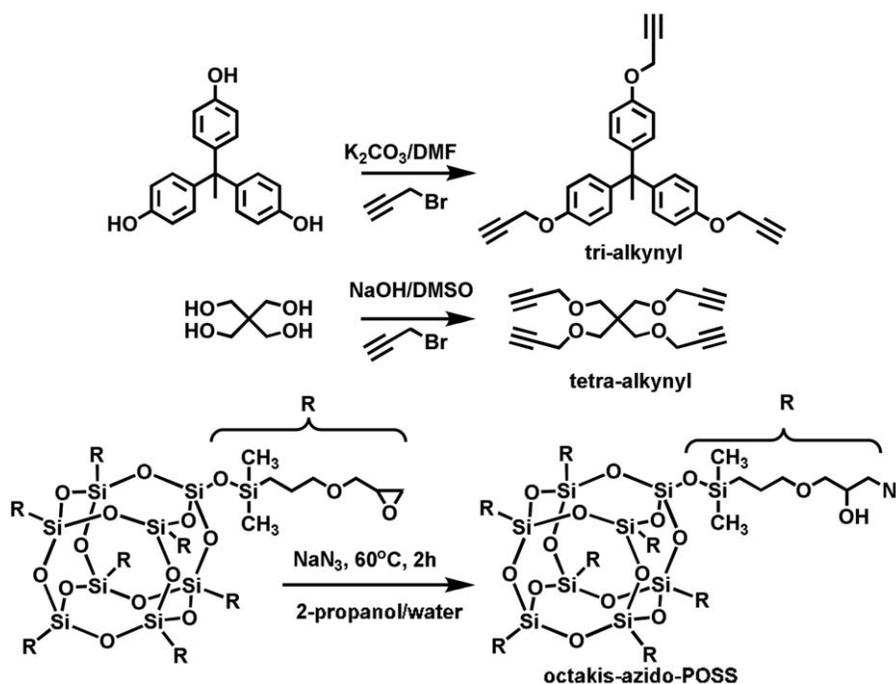
Characterization

All $^1\text{H-NMR}$ spectra were recorded on an Agilent NMR System VNMRS 500 spectrometer at room temperature in CDCl_3 with $\text{Si}(\text{CH}_3)_4$ as an internal standard. Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer FT-IR Spectrum One B spectrometer. Molecular weights were determined by a Viscotek GPCmax Autosampler system consisting of a pump module (GPCmax, Viscotek, Houston, TX), a combined light-scattering (Model 270 dual detector, Viscotek), and a refractive index (RI) detector (VE 3580, Viscotek). The light-scattering detector ($\lambda_0 = 670 \text{ nm}$) included two scattering angles: 7 and 90°. The RI detector was calibrated with polystyrene standards having narrow molecular weight distribution, and hence the quoted molecular weights of the polymers are expressed in terms of polystyrene equivalents. Two columns (7.8 \times 300 mm, LT5000L, Mixed, Medium Org and LT3000L, Mixed, Ultra-Low Org) with a guard column (4.6 \times 10 mm, Viscotek, TGuard) were used for the chloroform eluent at 35 °C (flow rate, 1 mL min^{-1}). Data were analyzed using Viscotek OmniSEC Omni-01 software. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Diamond DSC with a heating rate of 10 °C min^{-1} under nitrogen flow (10 mL min^{-1}).

RESULTS AND DISCUSSION

For the current methodology, several photochemically mediated click reactions have been developed and used for the synthesis and modification polymeric materials. These methods permit the spatial and temporal control of the click processes, which are not applicable for the other click reactions.^{13,47,48} A variety of photoinduced click reactions have been reported recently, photoinitiated thiol-ene/thiol-yne coupling,^{49–52} photoinduced CuAAC, photochemically generated nitrile imines,^{53–56} photoinduced ketene chemistry,^{57–60} “strain promoted” cycloaddition reaction of the photochemically generated cycloalkynes and azides,^{61–64} and photochemical uncaging of hydroquinone moieties.^{63–67} Owing to these prominent advantages of the photoinduced click reactions, this chemistry has been rapidly implemented in polymer synthesis and modification, biomaterial functionalization, and surface modification.¹¹

To broaden synthetic scope of photoinduced CuAAC reaction, here, different types of star polymers containing three-, four-, and eight-arms were synthesized and characterized by FTIR, $^1\text{H-NMR}$, gel permeation chromatography (GPC), and DSC analyses. For this purpose, tri-(1,1,1-*tris*[4-(2-propynyloxy)phenyl]-ethane), tetra-alkynyl (tetrakis(2-propynyloxy)methyl) methane) compounds, and octakis-azido-POSS (octakis{3-[(1-azido-2-hydroxy)propoxy] propyl dimethylsilyl} POSS) as multifunctional cores were synthesized via



SCHEME 1 The synthesis of multifunctional alkyne or azide cores.

etherification reactions between 1,1,1-*tris*(4-hydroxyphenyl)ethane⁶⁸ or pentaerythritol^{69,70} with propargyl bromide and ring-opening reaction of octaglycidyl dimethylsilyl POSS⁷¹ with sodium azide (Scheme 1).

In the ¹H-NMR spectra of multifunctional alkynes, it was evident that CH₂O protons of propargyl bromide at 3.9 were shifted to 4.7 and 4.1 ppm as a doublet signal of CH₂O for tri- and tetra-alkynyl molecules, indicating etherification reactions (Supporting Information Figs. S1 and S2). The disappearance of hydroxyl bands at 3350 and the FTIR spectra of multifunctional alkynes confirmed the nucleophilic displacement reaction and all hydroxyl groups were replaced to alkyne functionalities. The characteristic bands (C≡C–H and C≡C) of alkyne groups were also detected at 3265 and 2120 cm⁻¹, respectively (Experimental section). The structure of octakis-azido-POSS was also confirmed by ¹H-NMR and FTIR spectroscopy. The ¹H-NMR spectra of octaglycidyl dimethylsilyl POSS and octakis-azido-POSS with all the signal assignments are shown in Figure 1. After ring-opening reaction of octaglycidyl dimethylsilyl POSS, the signal for the protons (f at 2.8 ppm and g at 2.6 ppm) on epoxy rings were shifted to high-frequency regions (3.5 ppm) and low-frequency regions (1.3–1.5 ppm). The new peak corresponding to methine proton (h) of epoxy ring neighbors to azide functionality at 3.9 ppm. The FTIR spectrum of resulting octakis-azido-POSS showed characteristic hydroxyl (O–H at 3364 cm⁻¹), aliphatic alkyl (C–H, stretching at 2920 cm⁻¹), azide (N₃ stretching at 2095 cm⁻¹), and silicon–oxygen (Si–O asymmetric stretching at 990–1200 cm⁻¹) bands. Furthermore, the disappearance of asymmetric stretching vibration band of epoxy rings at 910 cm⁻¹ and the appearance of a new broad peak near the 3364 cm⁻¹ assigned to hydroxyl

groups confirmed that the epoxy rings of octaglycidyl dimethylsilyl POSS were clearly transformed to azide and hydroxyl functionalities (Supporting Information Fig. S3). These results indicated the successful formation of octakis{3-[(1-azido-2-hydroxy)propoxy]propyl dimethylsilyl} POSS via ring-opening reaction.

As a second step, PSt-N₃, PMMA-N₃,⁷² and PCL-Alkyne⁴⁶ were prepared by corresponding controlled polymerization

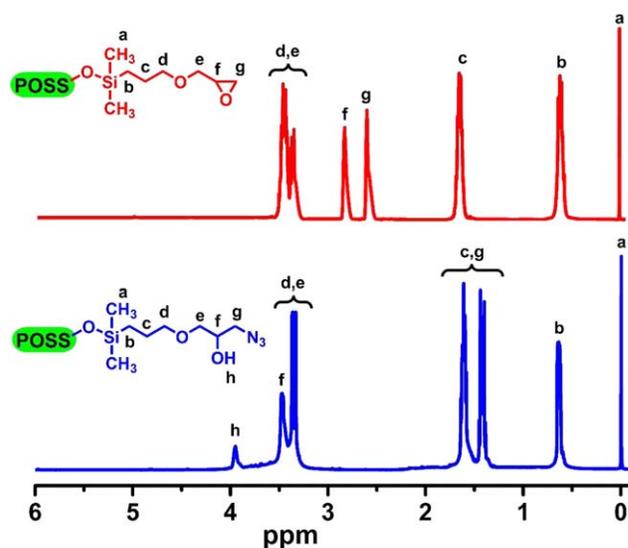


FIGURE 1 ¹H-NMR spectra of octakis{3-[(1-azido-2-hydroxy)propoxy]propyl dimethylsilyl} POSS and octaglycidyl dimethylsilyl POSS. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

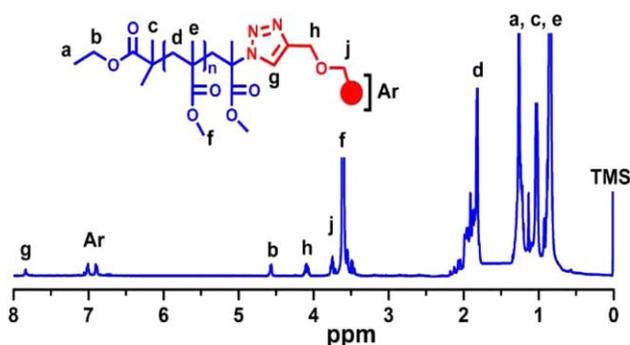


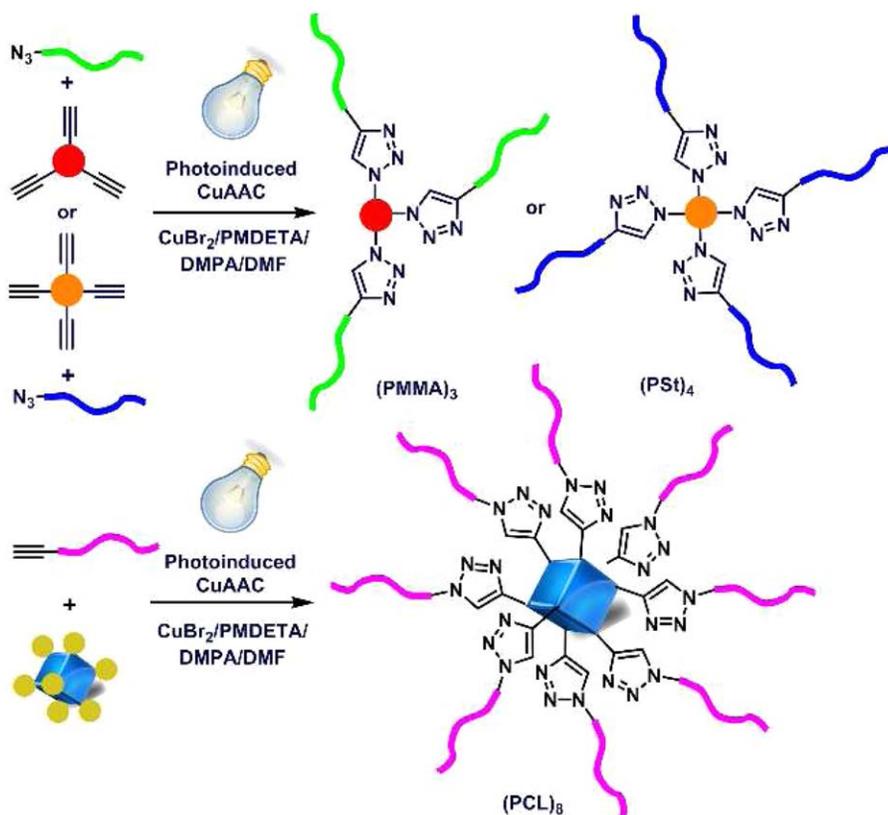
FIGURE 2 $^1\text{H-NMR}$ spectrum of $(\text{PMMA})_3$ star polymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

methods, namely atom-transfer radical polymerization of styrene and MMA followed by nucleophilic displacements using sodium azide and ring-opening polymerization of ε -CL initiated by propargyl alcohol with stannous octoate as catalyst. The azide end functionality of both PSt and PMMA was confirmed with $^1\text{H-NMR}$ spectroscopy. For PSt- N_3 , a signal at 4.2 ppm, assigned to $\text{CH}(\text{Ph})-\text{Br}$, was disappeared completely, and a new peak appeared at 3.9 ppm, representing the proton adjacent to the azide functionality. For PMMA- N_3 , although the nucleophilic substitution reaction of terminal bromide group to azide

could not be followed by $^1\text{H-NMR}$ spectroscopy, its structural characterization was accomplished by the combination of FTIR and $^1\text{H-NMR}$ techniques (Experimental section). The FTIR spectrum of azido-terminated PMMA had a signal at 2100 cm^{-1} assigned to the N_3 vibrations. On the other hand, the $^1\text{H NMR}$ spectrum of alkyne-PCL displayed the characteristic alkyne protons ($-\text{CH}_2-\text{C}\equiv\text{CH}$) at 4.7 and 2.5 ppm and repeating unit protons at 1.4, 1.6, 2.3, and 4.0 ppm, whereas the methylene protons of neighboring hydroxyl group $-\text{CH}_2-\text{OH}$ at 3.7 ppm were still observed. As a last step, star polymers consisting of different number of well-defined arms have been prepared via coupling-onto strategy using photoinduced CuAAC click reaction (Scheme 2).

For this reason, several experiments were performed using tri-, tetra-, or octa-functional cores in conjunction with corresponding azide- or alkyne-terminated polymers. Click reactions were carried out with small excess amount of precursor polymers (tri-alkynyl/PMMA- $\text{N}_3 = 1:4$, tetra-alkynyl/PSt- $\text{N}_3 = 1:5$ and octakis-azido-POSS:PCL-alkyne = 1:8) in DMF with $\text{CuBr}_2/\text{PMDETA}$ for 24 h under UV light emitting light at $\lambda > 350\text{ nm}$ and a cooling system. In our experiments, the reaction time was deliberately kept long so as to obtain the desired clicked product.

Star formations through the photoinduced CuAAC click reaction were confirmed by the measurements of $^1\text{H-NMR}$. From



SCHEME 2 The synthesis of $(\text{PMMA})_3$, $(\text{PSt})_4$, and $(\text{PCL})_8$ star polymers via photoinduced CuAAC click reaction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

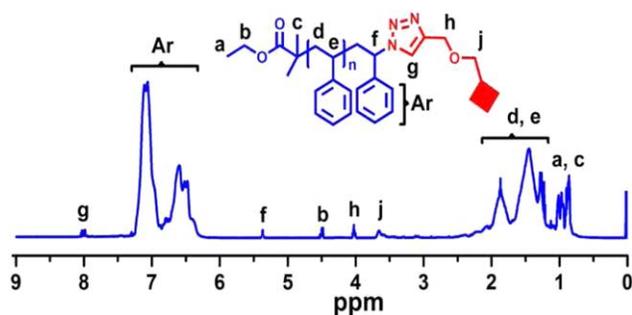


FIGURE 3 $^1\text{H-NMR}$ spectrum of $(\text{PSt})_4$ star polymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the spectrum of the $(\text{PMMA})_3$, it was confirmed that a quantitative conversion of the alkyne group of the core (characteristic bands of $\text{CH}\equiv\text{C}$ and $\text{HC}\equiv\text{C}-\text{CH}_2$ at 2.5 and 4.7 ppm were disappeared, respectively) to triazole and neighboring ether groups (characteristic bands of $\text{C}-\text{CH}-\text{N}$ and $\text{C}-\text{CH}_2-\text{O}$ were appeared at 7.8 (g), 4.6 (b), and 3.7 (j) ppm, respectively) in the star formation. Additionally, the aromatic protons of the core (Ar) and methylene protons of the ATRP initiator (b) were also observed with characteristic PMMA signals in the spectrum. Further evidence for the quantitative triazole ring formation was obtained from the FTIR analysis as the total disappearance of the azide peak at 2100 cm^{-1} was detected in the spectrum of $(\text{PMMA})_3$ after the click reaction (Experimental section) (Fig. 2).

In the $^1\text{H-NMR}$ spectrum of $(\text{PSt})_4$, methine group (CH) linked to the terminal azide functionality of PSt arm was shifted to upper field from 3.9 to 5.4 (f) ppm, whereas the triazole and ether protons were appeared at 8.1 (g), 4.2 (h), and 3.7 (j) ppm, respectively. In addition, the core (h and j)

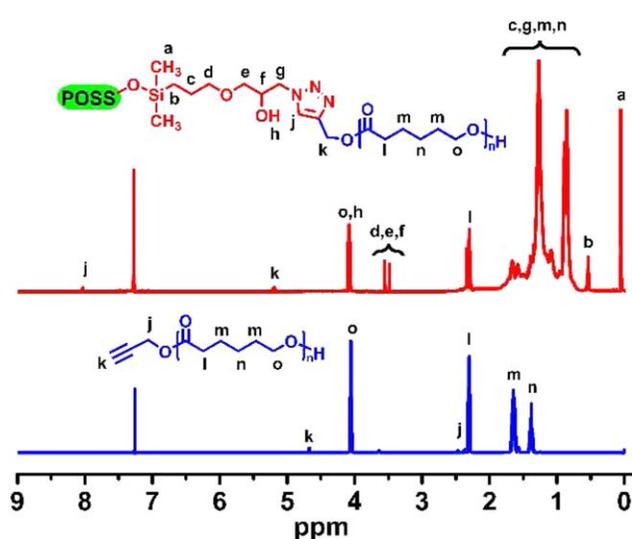


FIGURE 4 $^1\text{H-NMR}$ spectra of PCL-alkyne and $(\text{PCL})_8$ star polymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

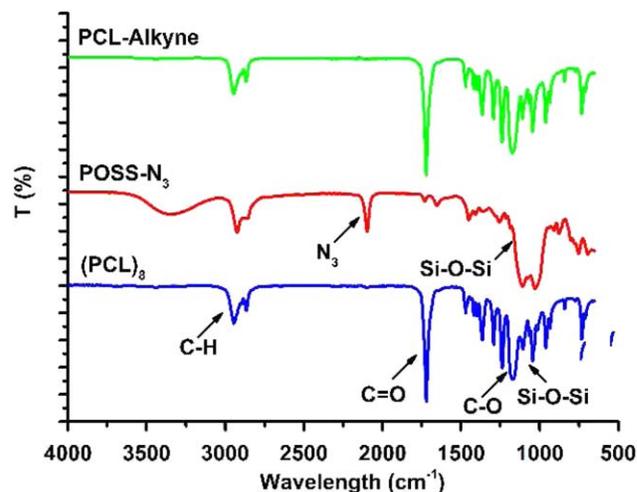


FIGURE 5 FTIR spectra of PCL-alkyne, octakis-azido-POSS, and $(\text{PCL})_8$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and ATRP initiator protons (a and b) were detected with the aromatic and aliphatic protons of polystyrene arms. It was also revealed from the FTIR analysis that the strong absorption peaks about 3290 , 2120 , and 2090 cm^{-1} assigned to the stretching vibrations of $\text{C}\equiv\text{C}-\text{H}$, $-\text{C}\equiv\text{C}$, and N_3 , respectively, disappeared, whereas new strong absorption peaks at 3060 cm^{-1} corresponding to the stretching vibration of $\text{C}=\text{C}-\text{H}$ of the triazole ring appeared (Fig. 3).

The $^1\text{H-NMR}$ spectra of the PCL-alkyne and $(\text{PCL})_8$ star polymer are shown in Figure 4. The disappearance of characteristic $\text{CH}_2-\text{C}\equiv\text{CH}$ proton (k) at 4.7 ppm and terminal $\text{CH}_2-\text{C}\equiv\text{CH}$ protons (j) at 2.5 ppm of the PCL precursor verified a successful click reaction while the appearance of triazole proton at 8.1 ppm was confirmed.⁷³ In addition, the peak at 0.1, 0.6, 1.1, and 5.5 ppm corresponding to methyl(CH_3), methylene (CH_2), and methine (CH) protons of the POSS core appeared, whereas no residual propargyl groups ($\sigma = 4.7$ and 2.5 ppm) were detected in $(\text{PCL})_8$ star polymer. In the FTIR spectrum (Fig. 5), the characteristic peaks at 3365 , 2945 , and 2865 cm^{-1} were assigned to the $\text{O}-\text{H}$ and $\text{C}-\text{H}$ stretching vibrations.

The peaks at 1730 and 1245 cm^{-1} were assigned to $\text{C}=\text{O}$ and $\text{C}-\text{O}-\text{C}$ stretching vibrations of the PCL arms. The broad absorption band in the region from 1150 to 1100 cm^{-1} was owing to $\text{Si}=\text{O}=\text{Si}$ stretching vibration of the POSS molecule. As shown in Figure 5, the peaks attributed to azide and propargyl groups disappeared, whereas the peak of the carbonyl and POSS group was maintained after the photoinduced CuAAC reaction, which further confirmed the successful synthesis of $(\text{PCL})_8$ star polymer.

The molecular weight and polydispersity index of star polymers were investigated by GPC and $^1\text{H-NMR}$ spectroscopy. The increase in molecular weights of star polymers confirmed the successful click reactions, which were detected by GPC as significant shifts in elution volume as well as the

TABLE 1 Conditions and Characterization Data of Precursor Polymers Together with the Resulting Star Polymers

Entry	$M_{n, \text{theo}}^a$ (g mol ⁻¹)	M_n , NMR ^b (g mol ⁻¹)	GPC ^c		DSC ^d	
			M_n (g mol ⁻¹)	M_w/M_n	T_g (°C)	T_m (°C)
PMMA-N ₃ ^e	2,300	2,400	2,500	1.12	106	n.d. ^f
PSt-N ₃ ^e	1,100	1,100	1,100	1.15	71	n.d.
PCL-Alk ^g	5,300	4,700	4,800	1.31	n.d.	47
(PMMA) ₃	7,200 ^h	6,600	7,000	1.25	114	n.d.
(PSt) ₄	4,400 ^h	4,200	4,500	1.20	83	n.d.
(PCL) ₈	37,600 ^h	34,500	36,000	1.48	n.d.	61

^a $M_{n, \text{theo}} = m_{\text{monomer}} \times [M]_0/[I]_0 \times \text{conversion}$.

^b Calculated according to the ¹H-NMR analysis.

^c Determined by GPC with linear polystyrene standards.

^d Determined by DSC with a heating rate of 10 °C min⁻¹ under nitrogen flow (10 mL min⁻¹).

^e Prepared by ATRP of MMA (yield, 46%) or St (yield, 21%) in bulk using ethyl-bromopropionate as an initiator and the molar ratio of [MMA]:[EBiB] = 50:1.

^f Not determined.

^g Prepared by ROP of CL (yield, 40%) in bulk using Sn(Oct)₂ as a catalyst and propargyl alcohol as an initiator and the molar ratio of [CL]:[propargyl alcohol] = 115:1.

^h The sum of $M_{n, \text{NMR}}$ of the precursor polymers.

hydrodynamic radius. In all cases, no residual remaining precursors were observed in GPC traces of the star polymers, implying complete transformations of the reactive precursors to the star polymers via photoinduced CuAAC reactions (Supporting Information Figs. S4–S6). In addition, it was noticed that the theoretical molecular weights of the tri- and octa-arm star polymers were deviated from the experimentally measured value. This could be explained by the reduced hydrodynamic volume of star polymers in relation to linear analogues of the same molecular weight. The conditions and characterization data of the star polymers and their precursors are summarized in Table 1. The measurements of DSC were carried out to determine the thermal transitions of star polymers and their linear counterparts to see the impact of chain architecture on these transitions. The PMMA-N₃ and PSt-N₃ are noncrystalline polymers and therefore do not exhibit any crystallization or melting transitions. The DSC curves of PMMA-N₃ and PSt-N₃ exhibited an endothermic peak approximately at 106 and 71 °C, corresponding to a glass transition temperature (T_g) of the polymers (Table 1). On the other hand, a melting temperature (T_m) of PCL segment was detected at 47 °C. Although it could be difficult to compare star polymers with their linear analogues, the obtained star polymers (PMMA)₃, (PSt)₄, and (PCL)₈ had higher T_g and T_m values than linear PMMA-N₃, PSt-N₃, and PCL-alkyne (Supporting Information Figs. S7–S9). The star polymers contain a core molecule that was comparatively rigid,⁷⁴ and the presence of this stiff unit would tend to increase the T_g or T_m values compared to linear precursors owing to the restricted segmental mobility in that region.⁷⁵

CONCLUSIONS

In conclusion, a facile photochemical method was developed for the synthesis of star polymers containing different numbers of well-defined arms. All the corresponding

precursors, PCL-alkyne, PMMA-N₃, and PSt-N₃, were easily synthesized by well-known procedures using the combination of controlled polymerization and nucleophilic substitution reactions. Spectroscopic and chromatographic investigations revealed that successful macromolecular syntheses have been achieved via photoinduced CuAAC click reaction. DSC data revealed slightly higher T_g and T_m of all (PMMA)₃, (PSt)₄, and (PCL)₈ star polymers as compared with their linear analogues. Because of the versatility of photoinduced CuAAC click reaction involving the capability to control the reaction in a way that is not offered by conventional CuAAC reactions, this process offers a facile and efficient route to exploring the many possibilities in polymer and material science.

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