Synthesis of Dendrimer-Like Copolymers Based on the Star [Polystyrene-Poly(ethylene oxide)-Poly(ethoxyethyl glycidyl ether)] Terpolymers by Click Chemistry

GUOWEI WANG, XIAOLAN LUO, YANNAN ZHANG, JUNLIAN HUANG

Department of Macromolecular Science, The Key Laboratory of Molecular Engineering of Polymer, State Education Ministry of China, Fudan University, Shanghai 200433, China

ABSTRACT: The dendrimer-like copolymers [PEEGE-(PS/PEO)]$_n$ ($n \geq 2$) based on the star[Polystyrene-Poly(ethylene oxide)-Poly(ethoxyethyl glycidyl ether)] [star(PS-PEO-(PEEGE-OH))] terpolymers were synthesized by click chemistry. First, the star-shaped copolymers star[PS-PEO-(PEEGE-Alkyne)] (also termed as [PEEGE-(PS/PEO)]$_1$) were synthesized by the reaction of hydroxyl end group at PEEGE arm (on star[PS-PEO-(PEEGE-OH)]) with propargyl bromide. Then, the small molecule 1,4-diazidobutane (DAB) with two azide groups and pentaerythritol tetrakis (2-azidoisobutyrate) (PTAB) with four azide groups were synthesized and reacted with [PEEGE-(PS/PEO)]$_1$ by the click chemistry for dendrimer-like [PEEGE-(PS/PEO)]$_2$ and [PEEGE-(PS/PEO)]$_4$, respectively. However, in the latter case, only the [PEEGE-(PS/PEO)]$_3$ was formed as the main product because of the steric effect. The final dendrimer-like [PEEGE-(PS/PEO)]$_n$ copolymers were characterized by SEC and ^{1}H-NMR in detail. Comparing with the SEC of their precursor [PEEGE-(PS/PEO)]$_1$, the curves of [PEEGE-(PS/PEO)]$_2$ was shifted to the shorter elution time, while that of [PEEGE-(PS/PEO)]$_n$ ($n \geq 3$) was shifted to the longer elution time, which was attributed to the different hydrodynamic volume derived from their separate structures and compositions in THF solution. © 2009 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 47: 4800–4810, 2009
Keywords: click chemistry; dendrimer-like; poly(ethoxyethyl glycidyl ether) (PEEGE); poly(ethylene oxide) (PEO); polystyrene; star copolymer

INTRODUCTION

With the development of living/"controlled" polymerization techniques, such as the atom transfer radical polymerization (ATRP),[1] nitroxide-mediated radical polymerization (NMRP),[2] reversible addition fragmentation transfer polymerization (RAFT),[3] single electron transfer polymerization,[4] and living anionic polymerization, the copolymers with complicated structure and multiple composi-

tions were designed and synthesized. Meanwhile, the coupling strategies, such as the coupling reaction by chlorosilane agent, the atom transfer nitroxide radical coupling (ATNRC),[5] the atom transfer radical coupling (ATRC),[6] and the click chemistry[7] were also adopted to construct the copolymers with various structures.[8] Unlike the linear (co)polymer, the nonlinear copolymer such as comb-type,[9] hyperbranched,[10] cyclic,[11] dendritic,[12] and star-shaped copolymers[13] were always endowed with some promising properties and applications because of their intrinsic character.[14]

Typically, the dendrimer-like [A-A$_2$]$_2$, [A-B$_2$]$_2$, or [A-(B/C)]$_2$ (also termed as H-shaped) copolymers could be regarded as the connection of two

three-arm star-shaped copolymers with A segment as bridge (where A, B, and C represent the different compositions). Concerning their special structure, they might show unique morphologies and interesting rheological properties in the form of copolymer melts and solutions,[15] and they could be used as thermoplastic elastomers, compatibilizers of polymer blends and viscosity modifiers.[16] Using the single classical living anionic polymerization, H-shaped copolymers were prepared by several groups.[17,18] However, the limited monomers adapted for living anionic polymerization and the subsequent troublesome purification procedure restricted the application of this strategy.[18] Alternatively, the strategy using the combination of several polymerization mechanisms, such as ATRP, RAFT, and anionic ring-opening polymerization (ROP), could greatly enrich the copolymers construction. Gnanou and coworkers[19] prepared (Polystyrene)$_2$(PS$_2$)-Poly(ethylene oxide) (PEO)-(Polystyrene)$_2$(PS$_2$), Pan and coworkers reported the synthesis of(PS/PLLA)-PEO-(PS/PLLA),[20] (PS)$_2$-PEO-(PS)$_2$, and [Poly(L-lactide)]$_2$ (PLLA$_2$)-PS-[Poly(L-lactide)]$_2$(PLLA$_2$),[21] Zhang and coworkers[22] synthesized an asymmetric H-shaped copolymer (PS)$_2$-PEO-[Poly(methyl methacrylate)]$_2$(PMMA$_2$).

More recently, using the click chemistry, which was testified as an efficient method and used extensively in polymer chemistry owing to its high efficiency and technical simplicity,[7] Tunca and coworkers synthesized H-shaped copolymers including PS/[Poly(*tert*-butyl acrylate)](P*t*BA)-PEO-PS/[Poly(*tert*-butyl acrylate)](P*t*BA) and (PS/P*t*BA)-Poly(propylene oxide) (PPO)-(P*t*BA/PS),[23] (PS/PMMA)-P*t*BA-(PS/PMMA) and (PS/PMMA)-PEO-(PS/PMMA),[24] (PCL/PS)-P*t*BA-(PEO/PMMA).[25] Whittaker et al.[26] also reported the synthesis of (PS/P*t*BA)-PS-(PS/P*t*BA) and (P*t*BA)$_2$-PS-(P*t*BA)$_2$ using the sequential click chemistry.

Similarly, the dendrimer-like [A-A$_2$]$_n$ or [A-B$_2$]$_n$ ($n \geq 3$) copolymers were also realized by several strategies, for example, the combination of ROP with ATRP by Hedrick et al.,[27] Gnanou and coworkers,[19,28] and Pan and coworkers,[29] the combination of anionic polymerization mechanism with coupling method by Hirao et al.,[30] the combination of living radical polymerization with irreversible terminator multifunctional initiator (TERMINI) by Percec et al.[31,32] and Matmour and Gnanou,[33] the combination of ATRP with click chemistry by Chen and coworkers[34] and Monteiro and coworkers.[35] However, the dendrimer-like [A-(B/C)]$_n$ ($n \geq 3$) copolymers with the ABC star-shaped copolymers as arms were rarely reported.[36] Because of the special compositions and space confinement of the dendrimer-like [A-(B/C)]$_n$, these copolymers may show some interesting morphologies in selective solvents or bulk, which is differed from their linear counterparts.

The synthesis of model dendrimer-like [A-(B/C)]$_n$ would be the prerequisite for their property investigation. However, the strategies used to synthesize the dendrimer-like [A-A$_2$]$_n$ or [A-B$_2$]$_n$ could not be applied into the synthesis of dendrimer-like [A-(B/C)]$_n$. Thus, we try to seek an improved and versatile route for preparation of dendrimer-like [A-(B/C)]$_n$ by the click chemistry.

Herein, as an extended study for a previous work,[37] we reported the synthesis of a novel kind of dendrimer-like [A-(B/C)]$_n$ ($n \geq 2$) copolymers consisting of poly(ethoxyethyl glycidyl ether) (PEEGE) as interior chain (A) (which could be converted into the poly(glycidyl) (PG) in acid conditions), PS(B) and PEO(C) as exterior chains. The click chemistry between the miktoarm star-shaped precursors star[PS-PEO-(PEEGE-Alkyne)] with alkyne group at PEEGE segment end (here, the star[PS-PEO-(PEEGE-Alkyne)] was termed as [PEEGE-(PS/PEO)]$_1$ for the following consistent description) and small molecule 1,4-diazidobutane (DAB) with two azide groups or pentaerythritol tetrakis (2-azidoisobutyrate) (PTAB) with four azide groups were performed, respectively.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF, 99%) was refluxed and distilled from sodium naphthalenide solution. Propargyl bromide (>99%), N,N-dimethylformamide (DMF) and toluene were distilled from CaH$_2$ just before use. Copper(I) bromide (CuBr, 95%) was stirred overnight in acetic acid, filtered, washed with ethanol and diethyl ether successively, and dried *in vacuo*. Bromoisobutyryl bromide (98%, Aldrich), N,N,N',N,''N''-pentamethyldiethylenetriamine (PMDETA, Aldrich), sodium azide (NaN$_3$, >98%), pentaerythritol, and 1,4-dibromobutane were all used as received. All other regents and solvents were purified by the standard procedure, and all the chemicals were purchased from Sinopharm Chemical Reagent Co. (SCR) except declaration.

Diphenylmethylpotassium (DPMK) solution was freshly prepared by the reaction of potassium naphthalenide with diphenylmethane in THF according to the literature,[28a] the concentration was 0.61 mol/L.

Measurements

Size-exclusion chromatography (SEC) was performed in THF at 35 °C with an elution rate of 1.0 mL/min on an Agilent1100 with a G1310A pump, a G1362A refractive index detector and a G1314A variable wavelength detector. One 5 μm LP gel column (500 E, molecular range, 500–2 $\times$ 10^4 g/mol) and two 5 μm LP gel mixed bed column (molecular range, 200–3 $\times$ 10^6 g/mol) were calibrated by polystyrene standard samples. ^{1}H-NMR spectra were obtained at a DMX500 MHz spectrometer with tetramethylsilane (TMS) as the internal standard and CDCl$_3$ or DMSO-d$_6$ as the solvent. Fourier transform infrared (FT-IR) spectra were recorded on a Magna-550 FT-IR spectrometer by casting film on a NaCl tablet. The Ultra Filtration Separator was purchased from Shanghai Institute of Nuclear Research, Chinese Academy of Science, the cut-off molecular weight of used poly(ether sulfone) membrane was calibrated by global protein.

Preparation of [PEEGE-(PS/PEO)]$_1$ Copolymer with Alkyne Group at PEEGE Segment End

According to the previous work,[37,38] the star-shaped copolymer star[PS-PEO-(PEEGE-OH)] was prepared by sequential anionic polymerization of St and following the capping reaction with EEGE, then ROP of EO using PS-EEGE as macro-initiator and the blocking of the hydroxyl end group of PEO with benzyl bromide. After that, the protected hydroxyl group at the middle part of PS-PEO diblock copolymer was deprotected and the second ROP of EEGE was conducted. Finally, the [PEEGE-(PS/PEO)]$_1$ copolymer with alkyne group at PEEGE segment end was obtained by the reaction of star[PS-PEO-(PEEGE-OH)] with propargyl bromide.

Typically, to a 250 mL dried ampoule, 4.0 g dried copolymer star[PS-PEO-(PEEGE-OH)] ($M_{n,NMR}$ = 12,500 g/mol) and 50 mL THF were added. Then, the system was bubbled with N$_2$ and DPMK solution was introduced until the solution color was turned into reddish-brown. After the ampoule was placed into ice bath, propargyl bromide (1.5 mL, 2.7 g, 26.2 mmol) was added

dropwise during 2 h and the reaction was continued for 24 h at room temperature. The copolymer [PEEGE-(PS/PEO)]$_1$ was obtained by separation of the formed salts and precipitation in cold petroleum ether (30–60 °C) twice, and dried under vacuum at 40 °C for 12 h till to a constant weight. ^{1}H-NMR (CDCl$_3$) of [PEEGE-(PS/PEO)]$_1$, δ ppm: 0.80 (CH_3CH$_2$—), 1.13 (CH_3CH$_2$O—), 1.22 (—CH (CH_3)—), 1.26–2.01 (m, 3H, aliphatic main chain —CH_2CH— of PS), 2.43(—C≡CH), 3.30–3.50 (m, CH$_3$CH_2O—, —CHCH_2O—), 3.50–3.80 (m, 7H, —CH_2 CH_2O— of PEO block and —CH_2CHO— of PEEGE block), 4.35(—OCH_2C≡CH), 4.65–4.76 (—OCH (CH$_3$)O— of PEEGE block), 4.56 (—CH_2—C$_6$H$_5$), 6.30–7.30 (m, 5H, aromatic —C$_6$$H_5$ of PS chain), 7.34 (—CH_2—C$_6$$H_5$). FT-IR (cm^{-1}): 1600, 1582, 1492, 1452 (aromatic —C—C—), 1121(—C—O—C—), 3252(—C≡CH).

Preparation of 1,4-Diazidobutane (DAB) and Pentaerythritol Tetrakis (2-Azidoisobutyrate) (PTAB)

The 1,4-diazidobutane (DAB) was prepared by azidation of the commercial 1,4-dibromobutane.[39] For example, DMF (20 mL), NaN$_3$ (0.65 g, 10.0 mmol), and 1,4-dibromobutane (0.20 mL, 1.67 mmol) were added into a round-bottom flask. The mixture was stirred at room temperature for 24 h and the excessive NaN$_3$ and the formed salt were removed by centrifugation, the above solution was stored at −20 °C for direct use.

Pentaerythritol tetrakis (2-azidoisobutyrate) (PTAB) was synthesized by azidation of pentaerythritol tetrakis (2-bromoisobutyrate), the latter was synthesized according to the literature by the reaction between pentaerythritol and bromoisobutyryl bromide.[40] Typically, 2.0 g (15 mmol) of pentaerythritol was placed into a 150 mL round-bottom flask with 60 mL of THF and 15 mL of triethylamine (TEA). Then, 11.9 mL of 2-bromo-isobutyryl bromide was added dropwise under nitrogen at 0 °C and then the reaction was conducted under ice/water bath for another 24 h. The mixture was transferred to a 500 mL separatory funnel with 150 mL of diethyl ether and extracted consecutively with H$_2$O, NaHCO$_3$ (0.5 M) and H$_2$O. The organic phase was dried over MgSO$_4$ and filtered, and the solvent was removed by rotary evaporation. The obtained crude product was separated by passing through a silica gel column using CH$_2$Cl$_2$ as elution, and the obtained fraction was concentrated and recrystallized from petroleum ether (60–90 °C). ^{1}H-NMR (CDCl$_3$) of

pentaerythritol tetrakis (2-bromoisobutyrate), δ ppm: 4.33 (C—CH_2—O—), 1.94 (C(Br)—CH_3).

Similarly, the PTAB was also prepared using the same procedure as DAB. For example, DMF (40 mL), NaN$_3$ (0.70 g, 10.8 mmol), and pentaerythritol tetrakis (2-bromoisobutyrate) (0.20 mL, 0.29 mmol) were added into the round-bottom flask and the mixture was reacted at room temperature for 24 h. After the excessive NaN$_3$ and the formed salt were removed by centrifugation, the above solution was stored at -20 °C for direct use.

Preparation of Dendrimer-Like [PEEGE-(PS/PEO)]$_n$ by Click Chemistry

Taking the procedure for dendrimer-like [PEEGE-(PS/PEO)]$_2$ as example. Typically, in a 50 mL ampoule, [PEEGE-(PS/PEO)]$_1$ (0.25 g, 0.02 mmol), DAB solution (0.12 mL, 0.084 mmol/mL, 0.01mmol), DMF(1.0 mL), CuBr (28.6 mg, 0.20 mmol, 10 eq.) and PMDETA (1.24 μL, 0.20 mmol, 10 eq.) were charged. The reaction mixture was then vacuumed by three freeze-thaw cycles, purged with nitrogen and immersed into the 80 °C oil bath for 48 h. After the evaporation of DMF, the reaction mixture was diluted with THF and passed through a neutral alumina column to remove the copper salts. Then the crude product was diluted with CH$_2$Cl$_2$ and precipitated in petroleum ether. The uncoupling [PEEGE-(PS/PEO)]$_1$ was removed by ultra filtration membrane in methanol, and the final product was concentrated and dried under vacuum at 45 °C for 12 h till to a constant weight.

Similarly, the dendrimer-like [PEEGE-(PS/PEO)]$_4$ was synthesized by the coupling reaction of [PEEGE-(PS/PEO)]$_1$ with PTAB in the feed ratio of alkyne group to azide group 2:1 and 1:1, respectively. ^{1}H-NMR (CDCl$_3$) for dendrimer-like [PEEGE-(PS/PEO)]$_2$, δ ppm: 0.80 (CH_3CH$_2$—), 1.13 (CH_3CH$_2$O—), 1.22 (—CH(CH_3)—), 1.26–2.01 (m, 3H, aliphatic main chain —CH_2CH— of PS), 3.30–3.50 (m, CH$_3$CH_2O—, —CHCH_2O—), 3.50–3.80 (m, 7H, —CH_2CH$_2$O— of PEO block and —CH_2CHO— of PEEGE block), 4.65–4.76 (—OCH(CH$_3$)O— of PEEGE block), 4.56 (—CH_2—C$_6$H$_5$), 4.81 (—OCH_2—(4-triazole)—), 6.30–7.30 (m, 5H, aromatic —C$_6$$H_5$ of PS chain), 7.34 (—CH$_2$—C$_6$$H_5$), 7.76 (—C$H$— of the triazole ring).

Transformation of PEEGE Segment into PG by Hydrolysis

Typically, 0.10 g dendrimer-like copolymers was dissolved in 30 mL mixed solvent of THF/metha-

nol (v/v = 1/1), then 3.0 mL HCL(37%) was added and stirred for 2 h at room temperature. After the THF and methanol was evaporated, the system was neutralized by 2.0 mol/L NaOH aqueous solution, and the formed salt was separated by extraction. The crude product was concentrated and precipitated in petroleum ether, and dried under vacuum at 45 °C for 12 h till to a constant weight. ^{1}H-NMR (DMSO-d$_6$) for dendrimer-like [PG-(PS/PEO)]$_2$, δ ppm: 0.80 (CH_3CH$_2$—), 1.26–2.01 (m, 3H, aliphatic main chain —CH_2CH— of PS), 3.30–3.50 (—CHCH_2O—), 3.50–3.80 (m, 7H, —CH_2CH$_2$O— of PEO block and —CH_2CHO— of PEEGE block), 4.56 (—CH_2—C$_6$H$_5$), 4.81 (—OCH_2—(4-triazole)—), 6.30–7.30 (m, 5H, aromatic —C$_6$$H_5$ of PS chain), 7.34 (—CH$_2$—C$_6$$H_5$), 7.76 (—C$H$— of the triazole ring).

RESULTS AND DISCUSSION

Synthesis and Characterization of Dendrimer-Like [PEEGE-(PS/PEO)]$_2$

According to the previous work, the star[PS-PEO-(PEEGE-OH)] was prepared by sequential anionic polymerization and two steps of ROP mechanisms,[38] but the benzyl bromide was used to block the PEO oxo-anionic end to substitute the bromoethane, because the clear signals of benzyl group was convenient for the following characterization by ^{1}H-NMR. After the second ROP of EEGE, the formed star[PS-PEO-(PEEGE-OH)] were then reacted with propargyl bromide in THF using DPMK as the deprotonation agent (Scheme 1).
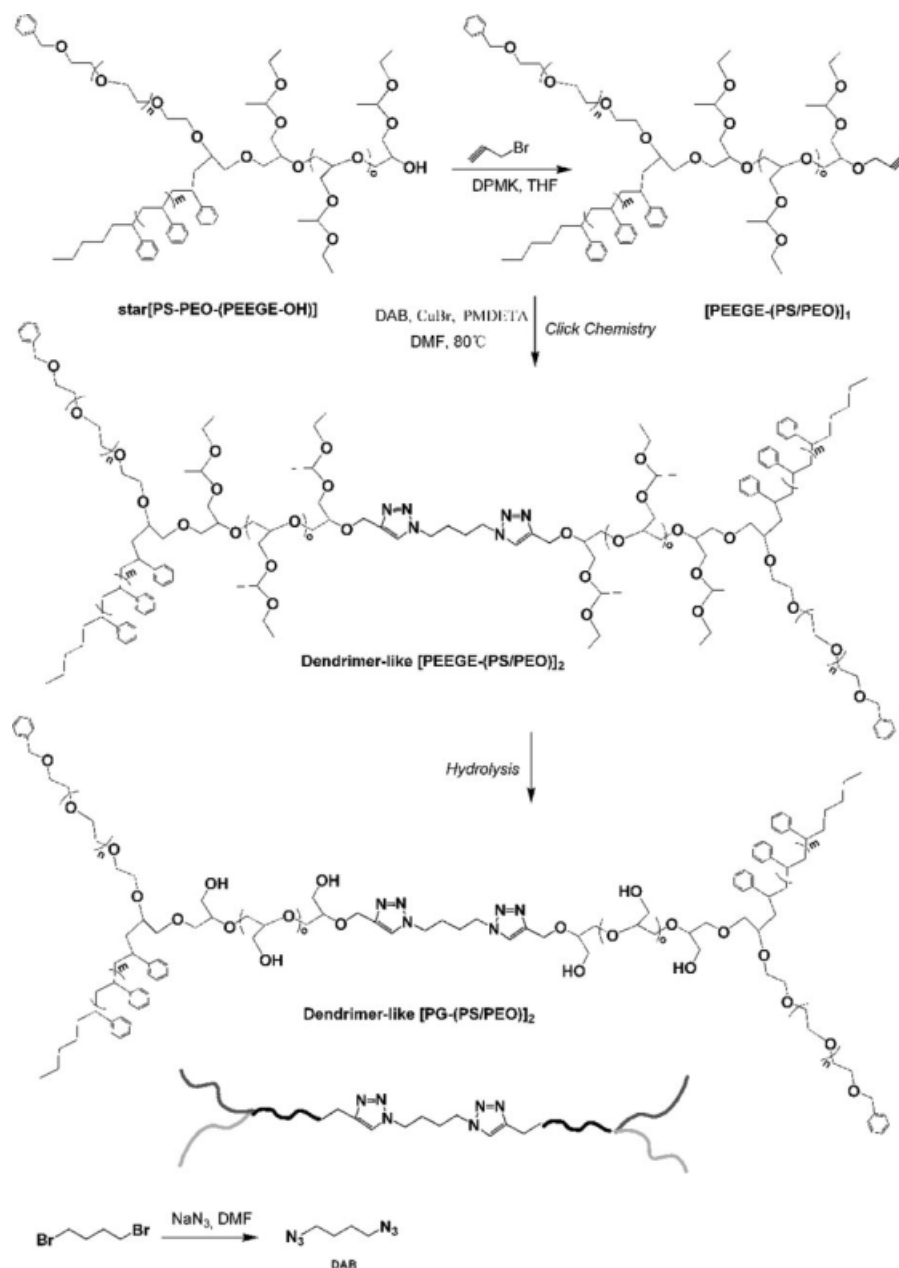
From its spectrum (Fig. 1), the methylene protons (—CH_2—C$_6$H$_5$) were observed at 4.56 ppm, and the aromatic protons (—CH$_2$—C$_6$$H_5$) were found at 7.34 ppm. By comparing the integral area (A_a) of methyl protons (—CH_3) at 0.80 ppm for PS end residue and that (A_d) of methylene protons (—CH_2—C$_6$H$_5$), the high blocking efficiency of PEO end by benzyl group ($E.F._{(Benzyl)}$, almost 100%) could be calculated using the eq 1:

$$E.F._{\cdot(Benzyl)} = \frac{3 \times A_d}{2 \times A_a} \times 100\% \tag{1}$$

The reaction efficiency ($E.F.$) between the hydroxyl group of star[PS-PEO-(PEEGE-OH)]and propargyl bromide could be calculated by analyzing the ^{1}H-NMR (Fig. 1) using eq 2:

$$E.F._{\cdot(Alkyne)} = \frac{3 \times A_k}{A_a} \times 100\% \tag{2}$$

Here A_a and A_k were the integral area of methylene protons (—CH_2—C≡CH) at 4.35 ppm and

Scheme 1. The synthesis of dendrimer-like [PEEGE-(PS/PEO)]$_2$ and [PG-(PS/PEO)]$_2$ copolymers.

the methyl protons (—CH_3) at 0.80 ppm, respectively. The *E.F.* value was close to 100%, which confirmed the successful synthesis and modification of the precursor [PEEGE-(PS/PEO)]$_1$.

In the presence of CuBr and PMDETA, the click chemistry between [PEEGE-(PS/PEO)]$_1$ and DAB was then performed at 80 °C (Scheme 1). Figure 2 showed the SEC curves of dendrimer-like [PEEGE-(PS/PEO)]$_2$ and its precursor [PEEGE-(PS/PEO)]$_1$ (curve A), and there was a shoulder peak at the longer elution time (curve B)

after the click chemistry, which was attributed to the uncoupled materials. Obviously, there were only some uncoupled [PEEGE-(PS/PEO)]$_1$ and the product dendrimer-like [PEEGE-(PS/PEO)]$_2$ coexisted. After the purification by ultra filtration separator, the monomodal peak for dendrimer-like [PEEGE-(PS/PEO)]$_2$ (curve C) could be observed. Using the software origin 7.0, the SEC curve B was split into two peaks (curve B1 and B2) corresponding to the final product [PEEGE-(PS/PEO)]$_2$ and uncoupled precursors, and then the efficiency

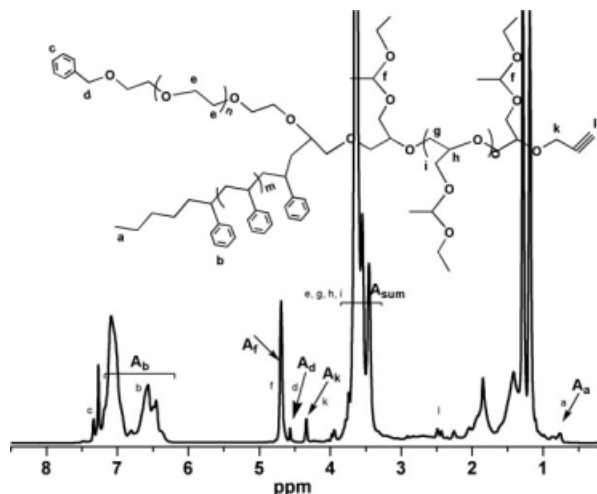**Figure 1.** ¹H-NMR spectrum of the precursor [PEEGE-(PS/PEO)]₁ (in CDCl₃).

(*E.F.*) of click chemistry could be estimated by comparing their integral area, the value exceeded 60% and listed in Table 1.

Figure 3 showed the ¹H-NMR spectrum of dendrimer-like [PEEGE-(PS/PEO)]₂. Comparing with its precursor in Figure 1, besides the resonance signal at 6.30–7.30 ppm for aromatic protons (—C₆H_5) on PS segment, the signal at 4.65–4.76 ppm for ethoxyethyl group proton (—CH(CH₃)—) on PEEGE segment and the signal at 3.53–3.70 ppm for the characteristic methylene group protons (—CH_2CH₂O—, —CH_2CH(—CH_2O)O—) on PEO and PEEGE segment, the resonance of methylene protons of alkyne end group was shifted from 4.35 ppm to 4.81 ppm, and a signal at 7.76 ppm attributed to the resonance of

methine proton of the triazole ring provided direct evidence for the successful coupling. However, the signals for methylene protons (—traizaole—CH_2CH₂—) were overlapped by other signals and could not be discriminated clearly.

Synthesis and Characterization of Dendrimer-Like [PEEGE-(PS/PEO)]₄ Copolymers

In literature, there was much work concerned the dendrimer-like copolymers with AB₂ or AA₂ type arms. However, the copolymers with ABC star-shaped as the arms were rarely reported. Thus, a molecule with four azide groups (PTAB) was designed for the synthesis of target dendrimer-like [PEEGE-(PS/PEO)]₄ copolymers. According to the references,[40,41] pentaerythritol tetrakis (2-bromoisobutyrate) was firstly synthesized from pentaerythritol and bromoisobutyryl bromide by the esterification, the purified product was traced with ¹H-NMR and its structure was confirmed. Then, the bromide groups were converted into the azide group quantitatively in DMF using the same method for DAB. Finally, the click chemistry was completed in the presence of CuBr and PMDETA (Scheme 2).

When the feed ratio of alkyne group to azide group was 1:1, the mixture of some twifold, triple, fourfold products and the uncoupled precursors might be coexisted [dendrimer-like [PEEGE-(PS/PEO)]ₙ (n = 1–4)] because of the steric effect and the intrinsic character of click chemistry.

Figure 4 showed the SEC results of crude product dendrimer-like [PEEGE-(PS/PEO)]ₙ copolymers (curve B). Differing from the SEC tendency for former dendrimer-like [PEEGE-(PS/PEO)]₂
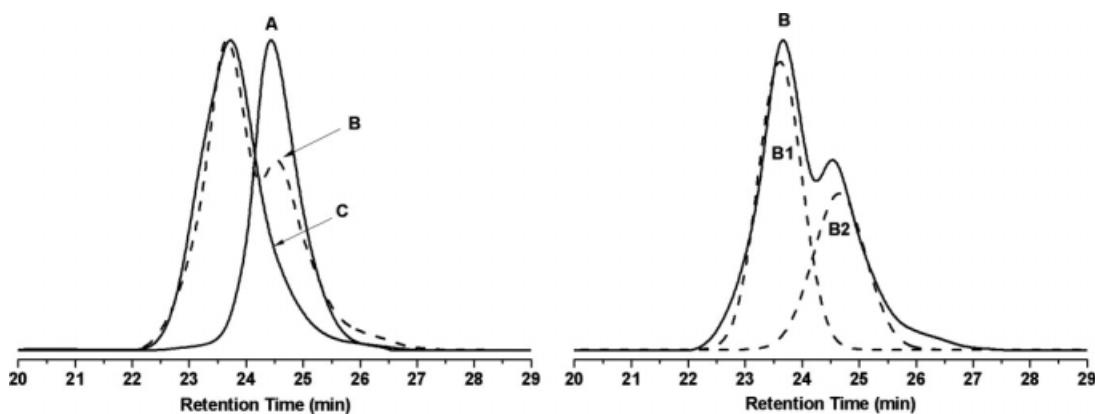

Figure 2. SEC curve of dendrimer-like [PEEGE-(PS/PEO)]₂ (C for purified product: $M_{n(SEC)}$ = 20,600 g/mol, PDI = 1.09 and B for crude product) and its precursor [PEEGE-(PS/PEO)]₁ (A: $M_{n(SEC)}$ = 11,400 g/mol, PDI = 1.07), the curve B1 and B2 were the split peaks for curve B.

Table 1. The Data for Dendrimer-like [PEEGE-(PS/PEO)]$_n$ Copolymers

| | [PEEGE-(PS/PEO)]$_1$ | | | | | Dendrimer-Like [PEEGE-(PS/PEO)]$_n$ ($n \geq 2$) | | | | |
Sample[a]	$M_{n(SEC)}$[b]	PDI[b]	$M_{n(NMR)}$[c]	E.F.[d]	R[e]	$M_{n(SEC)}$[b]	PDI[b]	$M_{n(theo.)}$[f]	E.F.[g]	R[e]
D2A	5100	1.07	5900	>99	0.864	9600	1.10	12,800	62.1	0.750
D2B	11,400	1.07	12,500	>99	0.912	20,600	1.09	25,100	60.0	0.821
D3A	5100	1.07	5900	>99	0.864	4600	1.08	18,500	77.1	0.249
D3B	11,400	1.07	12,500	>99	0.912	9600	1.07	38,300	81.9	0.251
DnA						3300	1.04	57,000	62.5	0.058
DnB						3900	1.10	93,000	63.9	0.042
DnC						5900	1.14	114,000		0.052
DnD						6700	1.09	193,000		0.035

[a] The D2, D3, and Dn represent the dendrimer-like [PEEGE-(PS/PEO)]$_2$, [PEEGE-(PS/PEO)]$_3$, and [PEEGE-(PS/PEO)]$_n$ ($n > 4$, the data were picked from ref. 26) copolymers, respectively, A, B, C, and D also represent the different series.
[b] Determined by SEC using PS as standard and THF as solvent.
[c] Calculated by ^{1}H-NMR using the already known $M_{n(SEC)}$ of PS as reference.
[d] E.F. was the efficiency of alkyne group functionality and determined by ^{1}H-NMR.
[e] R were the ratios of $M_{n(SEC)}$ to $M_{n(theo.)}$ for dendrimer-like [PEEGE-(PS/PEO)]$_n$.
[f] $M_{n(theo.)}$ was the theoretical M_n for [PEEGE-(PS/PEO)]$_n$ using the formula: $M_{n(theo.)} = n \times M_{n(NMR)\ ([PEEGE-(PS/PEO)]1)} + M_{core}$, M_{core} represent the molecular weight of core molecules such as DAB, PTAB, or the PEO main chain for [PEEGE-(PS/PEO)]$_n$($n > 4$), respectively.
[g] E.F. were the click efficiency and determined by SEC using the split peak method.

copolymers, the SEC curves of crude product dendrimer-like [PEEGE-(PS/PEO)]$_n$ shift to the longer elution time comparing with [PEEGE-(PS/PEO)]$_1$ precursors, which meant that the [PEEGE-(PS/PEO)]$_2$ was absent in the crude product. From curve B, a shoulder peak at the shorter elution time corresponding to the uncoupled precursors was observed. By analyzing the split peak for curve B, the integral area ratio of peak B1 to B2 was 27.8:93.7, which was just slightly larger than the theoretical ratio of 1:4 for the [PEEGE-(PS/PEO)]$_4$ and smaller than that of 1:3 for [PEEGE-(PS/PEO)]$_3$. Using the following equations set, it could be calculated that the crude product was composed by large quantity (68.7%) of [PEEGE-(PS/PEO)]$_3$ and small amount (8.44%) of [PEEGE-(PS/PEO)]$_4$, as well as some uncoupled precursors (22.9%).

$$\begin{cases} \dfrac{x}{3} + \dfrac{y}{4} = \dfrac{1}{4} & (1) \\[2mm] x + y + z = 1 & (2) \\[2mm] \dfrac{z}{x+y} = \dfrac{27.8}{93.7} & (3) \end{cases} \Rightarrow \begin{cases} x = 68.7\% \\[2mm] y = 8.44\% \\[2mm] z = 22.9\% \end{cases}$$

where x, y, and z were the weight fraction of [PEEGE-(PS/PEO)]$_3$, [PEEGE-(PS/PEO)]$_4$, and [PEEGE-(PS/PEO)]$_1$, respectively. The high content of [PEEGE-(PS/PEO)]$_3$ in crude product might be contributed to the steric effect in this

system during the click chemistry. After the purification, the monomodal peak for the main product dendrimer-like [PEEGE-(PS/PEO)]$_3$ (89.1%) was obtained (curve C), and the [PEEGE-(PS/PEO)]$_4$ (10.9%) could be ignored (Scheme 2).

To investigate the effect of feed molar ratio on the click chemistry between PTAB and [PEEGE-(PS/PEO)]$_1$, the feed ratio of alkyne groups to azide groups was changed to 2:1, then we found that the weight fraction of x:y:z was turned to 32.1:7.2:60.7, which meant that the efficiency of click chemistry decreased with the increase of feed ratio of alkyne groups to azide groups.
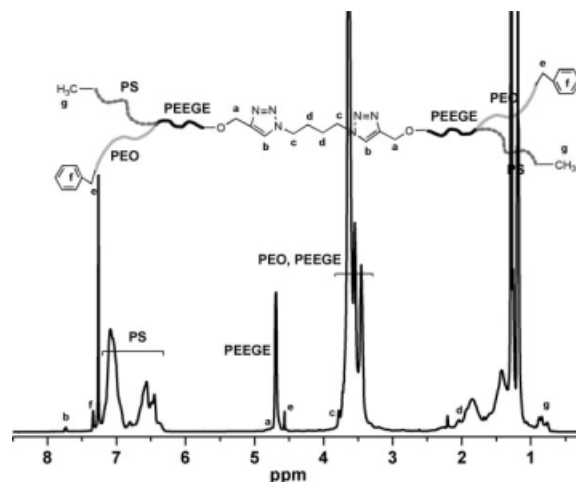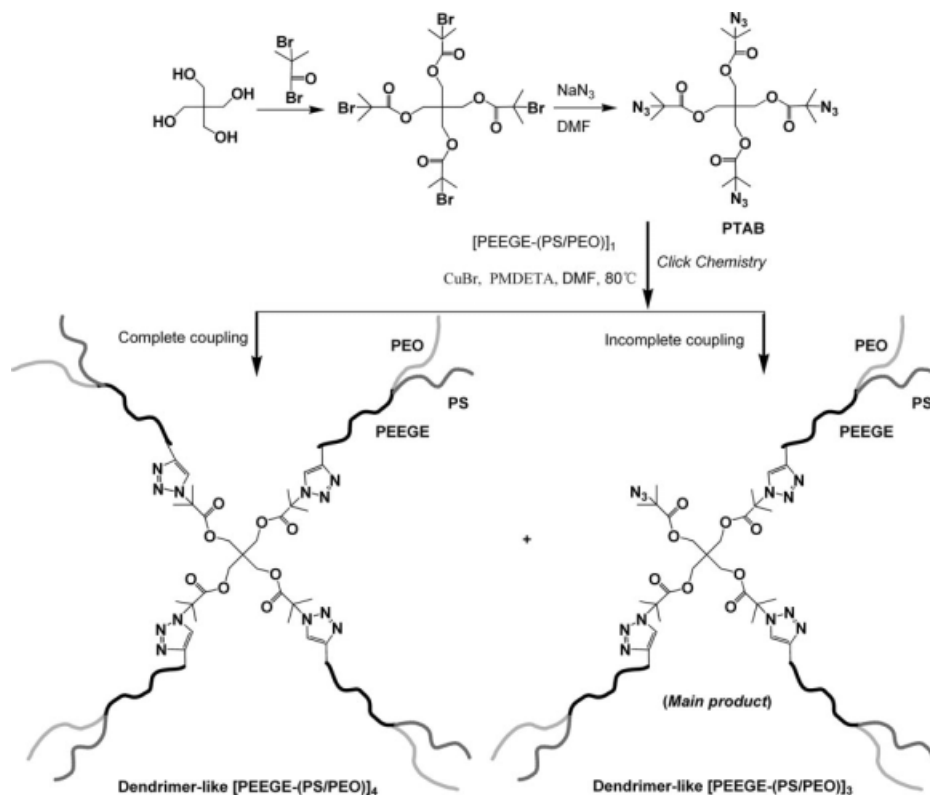

Figure 3. ^{1}H-NMR spectrum of dendrimer-like [PEEGE-(PS/PEO)]$_2$ copolymers (in CDCl$_3$).

Scheme 2. The synthesis of dendrimer-like [PEEGE-(PS/PEO)]$_n$ ($n = 3$ or 4) copolymers.

On the other hand, from the ^{1}H-NMR spectrum (Fig. 5) of the purified product, the signal for methylene protons (C(CH_2OOC—)$_4$) connected to ester bond in center of the dendrimer-like [PEEGE-(PS/PEO)]$_n$ (in dashed cycle) as well as the signal for the formed triazole ring could not be observed, it might be encapsulated by the periph-

eral PS and PEO arms. Finally, the PEEGE segment could be converted into its counterpart poly(glycidyl) (PG) by hydrolysis and the functional hydroxyl groups were introduced into the center part of copolymers.

Particularly, in our work, it was noted that the SEC curves of dendrimer-like copolymer showed a
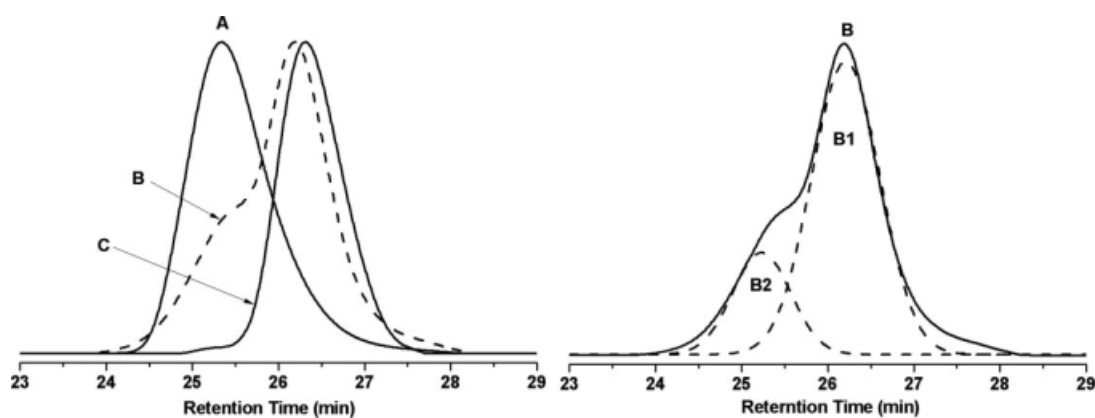

Figure 4. SEC curve of dendrimer-like [PEEGE-(PS/PEO)]$_n$ (C for purified product: $M_{n(SEC)}$ = 4600 g/mol, PDI = 1.08 and B for the crude product) and its precursor [PEEGE-(PS/PEO)]$_1$ (A: $M_{n(SEC)}$ = 5100 g/mol, PDI = 1.07), the curve B1 and B2 were the splited peaks for curve B.

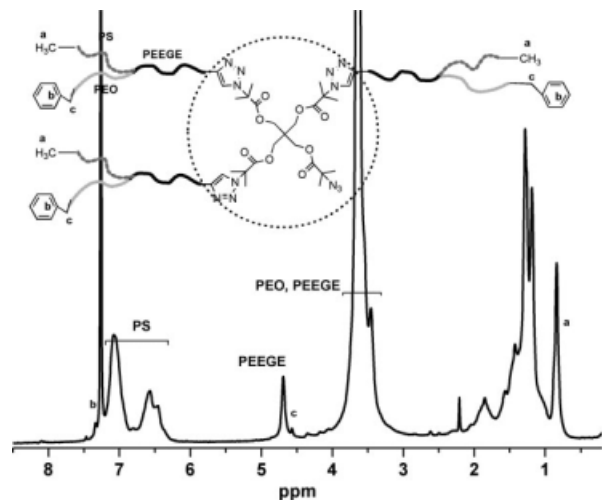**Figure 5.** ^{1}H-NMR spectrum of dendrimer-like [PEEGE-(PS/PEO)]$_n$ copolymers (in CDCl$_3$).

tendency to the longer elution time in THF elution with the branched degree increased. In literature, the similar phenomenon was also observed by Perny et al.[18] As we mentioned before, the SEC curve of dendrimer-like [PEEGE-(PS/PEO)]$_2$ was shifted to the shorter elution time comparing with the SEC of star-shaped precursor [PEEGE-(PS/PEO)]$_1$, whereas the dendrimer-like [PEEGE-(PS/PEO)]$_3$ (main product in our work) was shifted to the longer elution time. In the SEC traces for graft copolymer Poly(EO-co-Gly)-g-star(PS-PEO-PEEGE)[26] (also simplified as dendrimer-like [PEEGE-(PS/PEO)]$_n$, $n > 4$) the curve was also shifted to the longer elution time.

Herein, we introduced the parameter R (the ratio of $M_{n(SEC)}$ to $M_{n(theo.)}$) to definite the derivation of the apparent molecular weight to the theoretical one (Table 1). In SEC, because the PS was used as the standard samples, and the R value for the linear PS sample should be 1.00. Thus, the R values of 0.750 (D2A) and 0.821 (D2B) for dendrimer-like [PEEGE-(PS/PEO)]$_2$ were slightly

lower than R values of the corresponding 0.864 and 0.912 for [PEEGE-(PS/PEO)]$_1$, respectively, whereas the R values of 0.249 (D3A) and 0.251 (D3B) for [PEEGE-(PS/PEO)]$_3$ had a large decrease. Furthermore, for [PEEGE-(PS/PEO)]$_n$ ($n > 4$), the R values dramatically decreased to 0.058 (DnA), 0.042 (DnB), 0.052 (DnC), and 0.035 (DnD), respectively. Obviously, the lower R value corresponded to the larger derivation of the $M_{n(SEC)}$ to $M_{n(theo.)}$. These results could be explained on the volume change of copolymers when n was varied. For example, when $n = 2$, the branched arms could outspread sufficiently and be dissolved by THF, which lead to a low-degree of entanglement between intramolecular segments and a larger molecule volume compared with its precursors ($n = 1$). When n value was increased to 3 or 4, the additional star-shaped arms were introduced and the entanglement degree was also increased, each segment was almost confined in their own space and looked like a solid sphere with a smaller volume. Simultaneously, the steric effect resulted from these entanglement limited the introduction of the fourth star-shaped arm, and the [PEEGE-(PS/PEO)]$_3$ constituted the main product. Again, when n value exceeded 4, the graft copolymer with multiple star-shaped branches (M_n was not more that 10,000 g/mol[37]) can also be looked like a sphere, which demonstrated a smaller volume (illustrated as Fig. 6). Thus, it could be summarized that the higher the branched degree of the copolymers with complicate structure, the higher the degree of entanglement between the intramolecular segments, resulted the ultimately denser molecules.

CONCLUSIONS

The dendrimer-like [PEEGE-(PS/PEO)]$_n$ ($n \geq 2$) copolymers based on star(PS-PEO-(PEEGE-Alkyne) terpolymers were synthesized by click
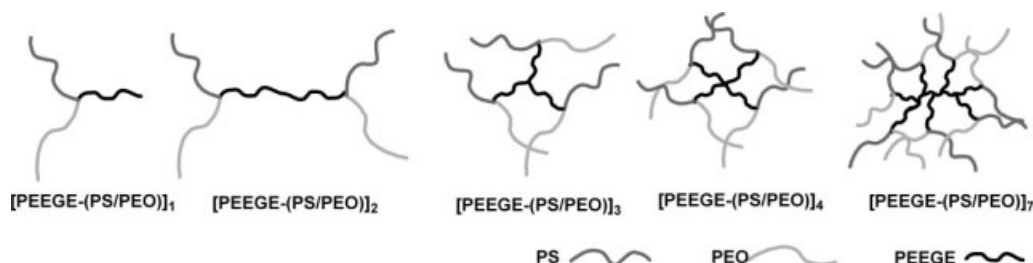

Figure 6. The illustration of complicated structure with different numbers of star-shaped arms.

chemistry. The small molecule DAB with two azide groups and PTAB with four azide groups were designed and used as the coupling agent. In the latter case, it was confirmed that the [PEEGE-(PS/PEO)]$_3$ was the main product due to the steric effect.

REFERENCES AND NOTES

1. Matyjaszewski, K.; Xia, J. Chem Rev 2001, 101, 2921–2990.

2. Hawker, C. J.; Bosman, A. W.; Harth, E. Chem Rev 2001, 101, 3661–3688.

3. Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. Macromolecules 1998, 31, 5559–5562.

4. (a) Percec, V.; Barboiu, B.; Bera, T. K.; van der Sluis, M.; Grubbs, R. B.; Jean, M. J.; Frechet, J. M. J. Polym Sci Part A: Polym Chem 2000, 38, 4776–4791; (b) Percec, V.; Barboiu, B. Macromolecules 1995, 28, 7970–7972; (c) Percec, V.; Guliashvili, T.; Ladislaw, J. S.; Wistrand, A.; Stjerndahl, A.; Sienkowska, M. J.; Monteiro, M. J.; Sahoo, S. J Am Chem Soc 2006, 128, 14156–14165; (d) Percec, V.; Barboiu, B.; Grigoras, C.; Bera, T. K. J Am Chem Soc 2003, 125, 6503–6516.

5. (a) Fu, Q.; Lin, W.; Huang, J. Macromolecules 2008, 41, 2381–2387. (b) Lin, W.; Fu, Q.; Zhang, Y.; Huang, J. Macromolecules 2008, 41, 4127–4135.

6. (a) Sarbu, T.; Lin, K. Y.; Ell, J.; Siegwart, D. J.; Spanswick, J.; Matyjaszewski, K. Macromolecules 2004, 37, 3120–3127; (b) Sarbu, T.; Lin, K. Y.; Spanswick, J.; Gil, R. R.; Siegwart, D. J.; Matyjaszewski, K. Macromolecules 2004, 37, 9694–9700; (c) Kopping, J. T.; Tolstyka, Z. P.; Maynard, H. D. Macromolecules 2007, 40, 8593–8599; (d) Tolstyka, Z. P.; Kopping, J. T.; Maynard, H. D. Macromolecules 2008, 41, 599–606.

7. (a) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. Angew Chem Int Ed 2001, 40, 2004–2021; (b) Binder, W. H.; Sachsenhofer, R. Macromol Rapid Commun 2007, 28, 15–54; (c) Sumerlin, B. S.; Tsarevsky, N. V.; Louche, G.; Lee, R. Y.; Matyjaszewski, K. Macromolecules 2005, 38, 7540–7545; (d) Tsarevsky, N. V.; Sumerlin, B. S.; Matyjaszewski, K. Macromolecules 2005, 38, 3558–3561; (e) Malkoch, M.; Schleicher, K.; Drockenmuller, E.; Hawker, C. J.; Russell, T. P.; Wu, P.; Fokin, V. V.

    Macromolecules 2005, 38, 3663–3678; (f) Helms, B.; Mynar, J. L.; Hawker, C. J.; Frechet, J. M. J. J Am Chem Soc 2004, 126, 15020–15021; (g) Durmaz, H.; Dag, A.; Altintas, O.; Erdogan, T.; Hizal, G.; Tunca, U. Macromolecules 2007, 40, 191–198; (h) Gao, H.; Matyjaszewski, K. Macromolecules 2006, 39, 4960–4965; (i) Gao, H. F.; Matyjaszewski, K. J Am Chem Soc 2007, 129, 6633–6639.

8. Yagci, Y.; Tasdelen, M. A. Prog Polym Sci 2006, 31, 1133–1170.

9. (a) Zhang, H.; Ruckenstein, E. Macromolecules 2000, 33, 814–819; (b) Se, K.; Yamazaki, H.; Shibamoto, T.; Takano, A.; Fujimoto, T. Macromolecules 1997, 30, 1570–1576.

10. Gauthier, M.; Tichagwa, L.; Downey, J. S.; Gao, S. Macromolecules 1996, 29, 519–527.

11. Lee, C.; Lee, H.; Lee, W.; Chang, T.; Roovers, J. Macromolecules 2000, 33, 8119–8121.

12. Teng, J.; Zubarev, E. R. J Am Chem Soc 2003, 125, 11840–11841.

13. Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. Chem Rev 2001, 101, 3747–3792.

14. (a) Hadjichristidis, N. J Polym Sci Part A: Polym Chem 1999, 37, 857–871; (b) Hadjichristidis, N.; Pispas, S.; Pitsikalis, M.; Iatrou, H.; Vlahos, C. Adv Polym Sci 1999, 142, 71–127.

15. (a) Gido, S. P.; Lee, C.; Pochan, D. J.; Pispas, S.; Mays, J. W.; Hadjichristidis, N. Macromolecules 1996, 29, 7022–7028; (b) Mcleish, T. C. B.; Allgaier, J.; Bick, D. K.; Bishko, G.; Biswas, P.; Blackwell, R.; Blottiere, B.; Clarke, N.; Gibbs, B.; Groves, D. J.; Hakiki, A.; Heenan, R. K.; Johnson, J. M.; Kant, R.; Read, D. J.; Young, R. N. Macromolecules 1999, 32, 6734–6758; (c) Heinrich, M.; Pyckhout-Hintzen, W.; Allgaier, J.; Richter, D.; Straube, E.; Read, D. J.; Mcleish, T. C. B.; Groves, D. J.; Blackwell, R. J.; Wiedenmann, A. Macromolecules 2002, 35, 6650–6664; (d) Jabbarzadenh, A.; Atkinson, J. D.; Tanner, R. I. Macromolecules 2003, 36, 5020–5031; (e) Roovers, J. Macromolecules 1984, 17, 1196–1200.

16. Dreyfuss, P.; Quirk, R. P.; In Encyclopedia of Polymer Science and Engineering, Wiley-Interscience: New York, 1987; Vol. 7, pp 551–579.

17. (a) Roovers, J.; Toporowski, P. M. Macromolecules 1981, 14, 1174–1178; (b) Hakiki, A.; Young, R. N.; McLeish, T. C. B. Macromolecules 1996, 29, 3639–3641; (c) Iatrou, H.; Avgeropoulos, A.; Hadjichristidis, N. Macromolecules 1994, 27, 6232–6233; (d) Christodoulou, S.; Driva, P.; Iatrou, H.; Hadjichristidis, N. Macromolecules 2008, 41, 2607–2615.

18. Perny, S.; Allgaier, J.; Cho, D.; Lee, W.; Chang, T. Macromolecules 2001, 34, 5408–5415.

19. Angot, S.; Taton, D.; Gnanou, Y. Macromolecules 2000, 33, 5418–5426.

20. Han, D. H.; Pan, C. Y. J Polym Sci Part A: Polym Chem 2007, 45, 789–799.

21. (a) Li, Y. G.; Shi, P. J.; Pan, C. Y. Macromolecules 2004, 37, 5190–5195; (b) Han, D. H.; Pan, C.Y. J Polym Sci Part A: Polym Chem 2006, 44, 2794–2801.

22. Yu, X.; Shi, T.; Zhang, G.; An, L. Polymer 2006, 47, 1538–1546.

23. Durmaz, H.; Karatas, F.; Tunca, U.; Hizal, G. J Polym Sci Part A: Polym Chem 2006, 44, 3947–3957.

24. Gungor, E.; Cote, G.; Erdogan, T.; Durmaz, H.; Demirel, A. L.; Hizal, G.; Tunca, U. J Polym Sci Part A: Polym Chem 2007, 45, 1055–1065.

25. Gungor, E.; Durmaz, H.; Hizal, G.; Tunca, U. J Polym Sci Part A: Polym Chem 2008, 46, 4459–4468.

26. Whittaker, M. R.; Urbani, C. N.; Monteiro, M. J. J Am Chem Soc 2006, 128, 11360–11361.

27. Hedrick, J. L.; Trollss, M.; Hawker, C. J.; Atthoff, B.; Claesson, H.; Heise, A.; Miller, R. D.; Mecerreyes, D.; Jerome, R.; Dubois, P. H. Macromolecules 1998, 31, 8691–8705.

28. (a) Francis, R.; Taton, D.; Logan, J. L.; Masse, P.; Gnanou, Y.; Duran, R. S. Macromolecules 2003, 36, 8253–8259; (b) Joncheray, T. J.; Bernard, S. A.; Matmour, R.; Lepoittevin, B.; El-Khouri, R. J.; Taton, D.; Gnanou, Y.; Duran, R. S. Langmuir 2007, 23, 2531–2538.

29. Yuan, W. Z.; Yuan, J. Y.; Zhou, M.; Pan, C. Y. J Polym Sci Part A: Polym Chem 2008, 46, 2788–2798.

30. (a) Hirao, A.; Watanabe, T.; Ishizu, K.; Ree, M.; Jin, S.; Jin, K. S.; Deffieux, A.; Schappacher, M.; Carlotti, S. Macromolecules 2009, 42, 682–693; (b) Deffieux, A.; Schappacher, M.; Hirao, A.; Watanabe, T. J Am Chem Soc 2008, 130, 5670–5672; (c) Hirao, A.; Sugiyama, K.; Tsunoda, Y.; Matsuo, A.; Watanabe, T. J Polym Sci Part A: Polym Chem 2006, 44, 6659–6687.

31. Percec, V.; Grigoras, C.; Bera, T. K.; Barboiu, G.; Bissel, P. J Polym Sci Part A: Polym Chem 2005, 43, 4894–4906.

32. Percec, V.; Bera, T. K.; De, B. B.; Sanai, Y.; Smith, J.; Holerca, M. N.; Barboiu, B.; Grubbs, R. B.; Frechet, J. M. J. J Org Chem 2001, 66, 2104–2117.

33. Matmour, R.; Gnanou, Y. J. Am Chem Soc, 2008, 130, 1350–1361.

34. Liu, Q. C., Zhao, P.; Chen, Y. M. J Polym Sci Part A: Polym Chem 2007, 45, 3330–3341.

35. (a) Urbani, C. N.; Lonsdale, D. E.; Bell, C. A.; Whittaker, M. R.; Monteiro, M. J. J Polym Sci Part A: Polym Chem 2008, 46, 1533–1547; (b) Urbani, C. N.; Bell, C. A.; Lonsdale, D.; Whittaker, M. R.; Monteiro, M. J. Macromolecules 2008, 41, 76–86.

36. Altintas, O.; Demirel, A. L.; Hizal, G.; Tunca, U. J Polym Sci Part A: Polym Chem 2008, 46, 5916–5928.

37. Luo, X.; Wang, G.; Pang, X.; Huang, J. Macromolecules 2008, 41, 2315–2317.

38. Wang, G.; Huang, J. Macromol Rapid Commun 2007, 28, 298–304.

39. Joralemon, M. J.; O'Reilly, R. K.; Matson, J. B.; Nugent, A. K.; Hawker, C. J.; Wooley, K. L. Macromolecules 2005, 38, 5436–5443.

40. Tang, X.; Gao, L.; Han, N.; Fan, X.; Zhou, Q. J Polym Sci Part A: Polym Chem 2007, 45, 3342–3348.

41. Li, J.; Shi, L.; An, Y.; Li, Y.; Chen, X.; Dong, H. Polymer 2006, 47, 8480–8487.