Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 46 (2005) 5808–5819

polymer

www.elsevier.com/locate/polymer

Synthesis of well-defined star polymers and star block copolymers from dendrimer initiators by atom transfer radical polymerization

Youliang Zhao[1], Yongming Chen, Chuanfu Chen, Fu Xi*

State Key Laboratory of Polymer Physics and Chemistry, Joint Laboratory of Polymer Science and Materials, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Received 24 November 2004; received in revised form 19 April 2005; accepted 28 April 2005
Available online 23 May 2005

Abstract

Novel polyarylether dendrimers with 1,3,5-tri(4-hydroxyphenoxy)benzene core, polybenzylether interior, and benzyl 2-bromoisobutyrate surface group (CMG*n*-Br, $n=1$–3, with functionality of 6, 12, and 24, respectively) were prepared by convergent procedure. ATRP of *tert*-butyl acrylate (*t*BA) and styrene (St) with CMG*n*-Br dendrimer initiators in the presence of CuBr/pentamethyldiethylenetriamine catalytic system was investigated in detail, and a series of well-defined dendrimer-like star P*t*BA and PSt with precise arm numbers were synthesized under suitable conditions. The quantitative initiation of the dendrimer initiators was demonstrated by high initiation efficiency, ^{1}H NMR spectra, hydrolysis, and MALLS/SEC approach. Star block copolymers comprising PSt and P*t*BA segments with low polydispersity ($1.08 < M_w/M_n < 1.18$) were also successfully synthesized using functional macroinitiators by block copolymerization. In addition, the thermal properties of the resultant polymers were characterized by DSC and TGA.

Keywords: Dendrimer; Star polymer; Atom transfer radical polymerization

1. Introduction

The synthesis of polymers with controlled compositions, architectures, and functionalities continues to be a focus of current research. Living radical polymerization processes have proven to be versatile for the synthesis of polymers with well-defined structures and complex architectures. In the past few years, living radical polymerization such as nitroxide-mediated stable free radical polymerization (SFRP) [1–9], atom transfer radical polymerization (ATRP) [10–22], and reversible addition-fragmentation chain transfer (RAFT) polymerization [23–26] has witnessed a considerable growth. Among them, the transition metal mediated ATRP has been extensively investigated and successfully applied to the synthesis of well-defined macromolecular architectures such as block copolymers, alternating copolymers, graft copolymers, comb polymers, and star polymers [16,17].

Meanwhile, the synthesis of well-defined star-shaped polymers has attracted much attention due to their unique shape and possible processing advantages derived from their compact structure. In general, star polymers can be principally synthesized in two different ways: ‘arm first’ and ‘core first’ [16,17]. The arm-first approach involves the synthesis of preformed arms, usually through living polymerization, followed by reaction with a multifunctional linking reagent such as divinyl benzene, 1,4-butanediol diacrylate, and ethylene glycol dimethacrylate. The core-first approach involves the use of multifunctional initiator, and the arm numbers in star polymers can be determined by the functionality on the initiator. In the past, star polymers were primarily prepared using ionic polymerization. More recently, some reports have appeared on the synthesis of well-defined star polymers via ATRP using the ‘core first’ approach. Various families of initiators with precise functionality were designed to serve as central cores, including cyclophosphazene [27,28], calixarene derivatives [29–32], glucose [33], dendritic moieties [34–42], multifunctional aromatic sulfonyl chlorides [32,43], and

---

* Corresponding author. Tel.: +86 10 62557907; fax: +86 10 62559373. *E-mail address:* xifu@iccas.ac.cn (F. Xi).

[1] Present address: Department of Polymeric and Organic Materials, Graduate School of Science and Technology, Tokyo Institute of Technology, 2-12-1, Ohokayama, Meguro-ku, Tokyo 152-8552, Japan.

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.04.061

halogeno-2,2′-bipyridyl-based metallic complexes [44–48]. These initiators were used in conjunctions with either copper, ruthenium, or nickel halides and miscellaneous ligands to grow stars of polystyrene, poly(alkyl acrylate) or poly(alkyl methacrylate) with arm numbers ranging from 3 to 24. In some cases, however, it was found that not all sites on initiators started the growth of polymer chain [42], and the synthesis of star polymers with precise arm number was related to some factors such as the nature of initiators [36] and initiation conditions [42].

To evaluate the possibility to synthesize multiarm star polymers with predictable arm numbers initiating from multifunctional initiators, novel polyarylether dendrimers with 1,3,5-tri(4-hydroxyphenoxy)benzene (THPB) core, polybenzylether interior, and benzyl alcohol (CMG*n*-OH) [49,50] or benzyl 2-bromoisobutyrate surface group (CMG*n*-Br, $n=1$–3, with functionality of 6, 12, and 24, respectively) were designed and synthesized by our group recently (Scheme 1). These dendrimers are of relatively large molecular size and rigidity which can effectively avoid the backfolding of the dendrimer periphery, so they are expected to be used as initiators to synthesize regular star polymers [49,50]. Herein we report on the detailed synthesis of the dendrimer initiators with terminal bromide and their use in synthesis of well-defined dendrimer-like star poly (*tert*-butyl acrylate) and polystyrene with predetermined arm numbers by ATRP. Moreover, the functional star polymers with terminal bromide could be successfully used as macroinitiators to prepare well-defined star block copolymers. Meanwhile, the thermal properties of the resultant polymers were characterized by DSC and TGA.

2. Experimental

2.1. Materials

The methyl ester-terminated dendritic polyarylether benzyl bromides (MG*n*-Br, $n=1$–3) were prepared and purified according to the literature [51] by using methyl 4-bromomethylbenzoate and 3,5-dihydroxybenzyl alcohol as raw materials. 1,3,5-Tri(4-hydroxyphenoxy)benzene (THPB) was synthesized according to the previous procedure [52]. *tert*-Butyl acrylate (*t*BA), styrene (St), and pentamethyldiethylenetriamine (PMDETA) were stirred overnight over CaH_2 and distilled under reduced pressure prior to use. Toluene and tetrahydrofuran (THF) were distilled over Na and benzophenone and stored under nitrogen. Triethylamine (TEA) was distilled over *p*-toluenesulfonyl chloride. CuBr was purified by stirring in acetic acid, washing with ethanol and then dried in vacuo. The other reagents were of analytical grade and used as received.

2.2. General procedure for the synthesis of methyl ester-terminated dendritic polyarylethers

A mixture of MG*n*-Br (3.5 equiv.), THPB (1.0 equiv.), potassium carbonate (4.0 equiv.), and 18-C-6 (0.3 equiv.) in acetone was heated at reflux and stirred vigorously under nitrogen for 24 h. The mixture was cooled down and evaporated to dryness under vacuum. The residue was partitioned between water and methyl chloride, and the aqueous layer was extracted twice with methyl chloride. The combined extracts were dried over $MgSO_4$. The crude products CMG*n* ($n=1$–3) were purified by column chromatography eluting with chloroform and then with gradually increasing proportions of ethyl acetate.

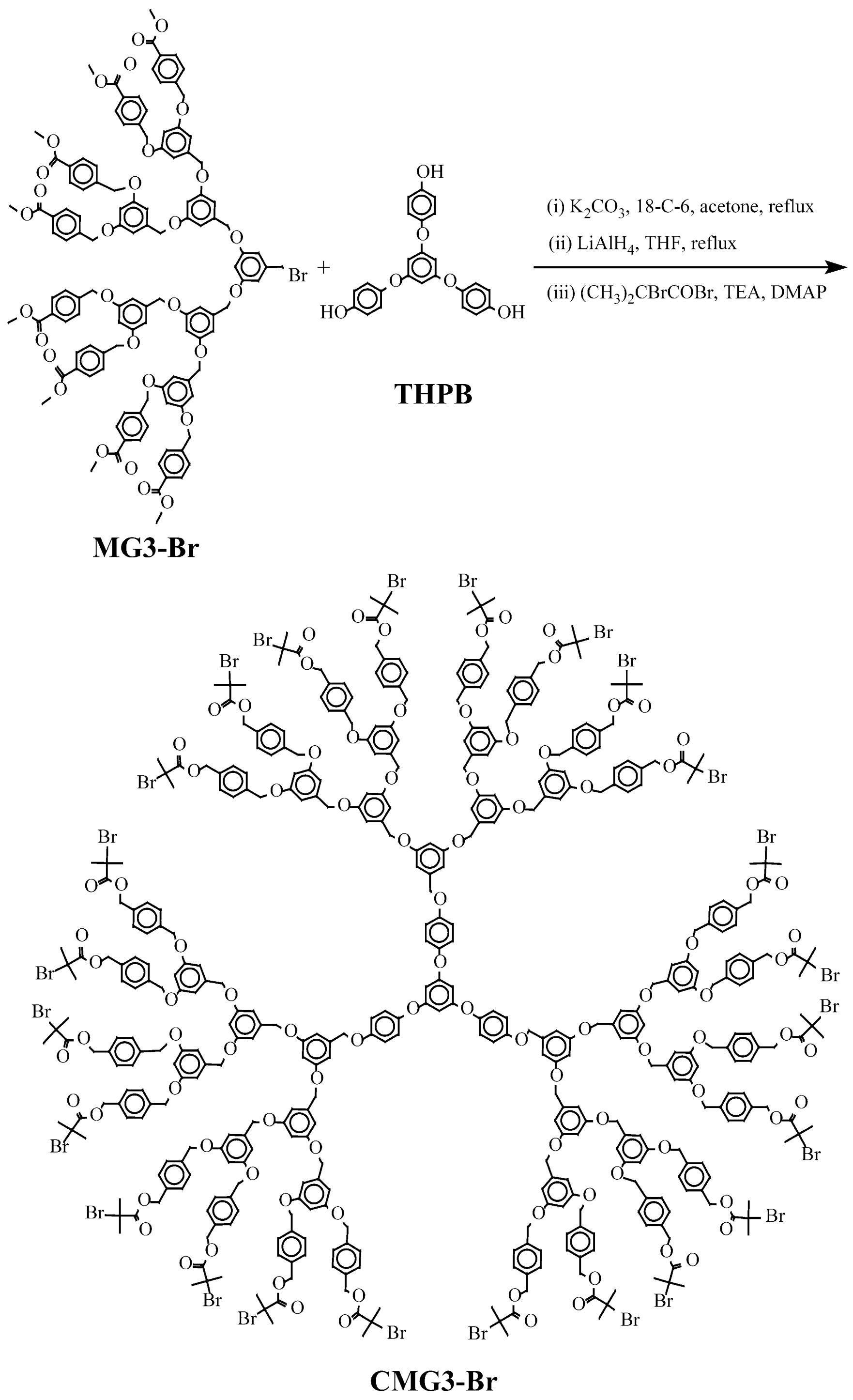
CMG1: yield 95%, colorless glass. FTIR (NaCl): 3051, 2997, 2951, 2875, 1721, 1598, 1502, 1455, 1417, 1378, 1281, 1204, 1160, 1112, 1067, 1016, 966, 837, 757, 736, 700 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.02 and 7.45 (ABq, 24H, *J* 8, Ph*H*), 6.94 and 6.90 (ABq, 12H, *J* 9, Ph*H*), 6.66 (d, 6H, *J* 2, Ar*H*), 6.53 (s, 3H, Ar*H*), 6.19 (s, 3H, Ar*H*), 5.09 (s, 12H, PhC*H*$_2$O), 4.96 (s, 6H, ArC*H*$_2$O), 3.91 (s, 18H, C*H*$_3$). Elem. Anal. Calcd for $C_{99}H_{84}O_{24}$: C, 71.73%; H, 5.11%. Found: C, 71.72%; H, 5.11%.

CMG2: yield 92%, colorless glass. FTIR (NaCl): 3055, 2997, 2951, 2875, 1721, 1597, 1502, 1453, 1417, 1375, 1281, 1203, 1159, 1112, 1060, 1017, 966, 837, 757, 736, 699 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.00 and 7.43 (ABq, 48H, *J* 8, Ph*H*), 6.93 and 6.90 (ABq, 12H, *J* 9, Ph*H*), 6.64 (s, 18H, Ar*H*), 6.51 (s, 6H, Ar*H*), 6.49 (s, 3H, Ar*H*), 6.17 (s, 3H, Ar*H*), 5.01 (s, 24H, PhC*H*$_2$O), 4.94 (s, 18H, ArC*H*$_2$O), 3.89 (s, 36H, C*H*$_3$). Elem. Anal. Calcd for $C_{195}H_{168}O_{48}$: C, 71.42%; H, 5.16%. Found: C, 71.40%; H, 5.14%.

CMG3: yield 88%, colorless glass. FTIR (NaCl): 3055, 2997, 2951, 2875, 1721, 1597, 1502, 1451, 1417, 1374, 1281, 1202, 1159, 1111, 1056, 1019, 966, 838, 757, 736, 701 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.97 and 7.53 (ABq, 96H, *J* 8, Ph*H*), 6.89 and 6.87 (ABq, 12H, *J* 9, Ph*H*), 6.62 (s, 36H, Ar*H*), 6.50 (s, 18H, Ar*H*), 6.48 (s, 9H, Ar*H*), 6.16 (s, 3H, Ar*H*), 5.00 (s, 48H, PhC*H*$_2$O), 4.89 (s, 42H, ArC*H*$_2$O), 3.87 (s, 72H, C*H*$_3$). Elem. Anal. Calcd for $C_{387}H_{336}O_{96}$: C, 71.26%; H, 5.19%. Found: C, 71.22%; H, 5.20%.

2.3. General procedure for the synthesis of dendritic benzyl alcohol

Under vigorous stirring, the solution of CMG*n* (1.0 equiv. of methyl ester group) in absolute THF was added dropwise to the suspended solution of $LiAlH_4$ (1.2 equiv.) in THF. The solution was refluxed for 2 h before it was treated with water. The solvent was evaporated under reduced pressure, and diethyl ether and water were added. The two phases were separated, and the water phase was extracted twice with diethyl ether. The extracts were dried over $MgSO_4$ overnight and condensed to give the products CMG*n*-OH ($n=1$–3) as a colorless glass with quantitative yield.



Scheme 1. Synthesis of the third generation dendrimer initiator by convergent procedure.

CMG1-OH: FTIR (NaCl): 3337, 2959, 2933, 2872, 1595, 1500, 1455, 1423, 1374, 1340, 1296, 1203, 1156, 1117, 1042, 1011, 954, 828, 771, 749, 681 cm^{-1}. ^{1}H NMR (THF-d_8): δ 7.34 and 7.32 (ABq, 24H, J 8, Ph*H*), 6.94 and 6.91 (each s, 12H, Ph*H*), 6.68 (s, 6H, Ar*H*), 6.57 (s, 3H, Ar*H*), 6.16 (s, 3H, Ar*H*), 5.02 (s, 12H, PhCH_2O), 4.96 (s, 6H, ArCH_2O), 4.55 (s, 12H, PhCH_2OH). Elem. Anal. Calcd for $C_{93}H_{84}O_{18}$: C, 74.98%; H, 5.68%. Found: C, 75.00%; H, 5.62%.

CMG2-OH: FTIR (NaCl): 3345, 2960, 2934, 2873, 1595, 1500, 1455, 1423, 1374, 1341, 1296, 1204, 1155, 1117, 1045, 1012, 954, 830, 767, 749, 683 cm^{-1}. ^{1}H NMR (THF-d_8): δ 7.33 and 7.31 (ABq, 48H, J 8, Ph*H*), 6.94 and 6.91 (each s, 12H, Ph*H*), 6.68 (s, 18H, Ar*H*), 6.58 (s, 6H, Ar*H*), 6.56 (s, 3H, Ar*H*), 6.14 (s, 3H, Ar*H*), 5.01 (s, 24H, PhC*H*$_2$O), 4.97 (s, 18H, ArC*H*$_2$O), 4.54 (s, 24H, PhC*H*$_2$OH). Elem. Anal. Calcd for $C_{183}H_{168}O_{36}$: C, 74.68%; H, 5.75%. Found: C, 74.60%; H, 5.74%.

CMG3-OH: FTIR (NaCl): 3313, 2928, 2871, 1595, 1500, 1451, 1423, 1372, 1340, 1298, 1203, 1154, 1044, 1012, 954, 828, 770, 751, 724, 683 cm^{-1}. ^{1}H NMR (THF-d_8): δ 7.32 and 7.30 (ABq, 96H, *J* 8, Ph*H*), 6.90 and 6.87 (ABq, 12H, *J* 9, Ph*H*), 6.65 (s, 36H, Ar*H*), 6.53 (s, 18H, Ar*H*), 6.50 (s, 9H, Ar*H*), 6.10 (s, 3H, Ar*H*), 4.94 (s, 48H, PhC*H*$_2$O), 4.88 (s, 42H, ArC*H*$_2$O), 4.54 (s, 48H, PhC*H*$_2$OH). Elem. Anal. Calcd for $C_{363}H_{336}O_{72}$: C, 74.52%; H, 5.79%. Found: C, 74.50%; H, 5.78%.

2.4. General procedure for the synthesis of dendrimer initiator

CMG*n*-OH (1.0 equiv. of hydroxyl group), TEA (1.0 equiv.), and 4-(dimethylamino)pyridine (DMAP, 1.2 equiv.) were dissolved in absolute THF. To the stirred solution under nitrogen was added dropwise the solution of 2-bromoisobutyryl bromide (1.1 equiv.) in THF at 0 °C over 30 min period. The reaction mixture was stirred 48 h at room temperature, concentrated, and washed with water. The crude product was extracted with methyl chloride, and the combined organic phases were dried over $MgSO_4$. The product CMG*n*-Br ($n=1$–3) was purified by column chromatography eluting with 1:1 (v/v) petroleum ether/chloroform and then with gradually increasing proportions of chloroform (to pure chloroform).

CMG1-Br: yield 92%, colorless glass. FTIR (NaCl): 3042, 2974, 2930, 2872, 1735, 1597, 1501, 1457, 1373, 1274, 1204, 1157, 1110, 1062, 1011, 970, 828, 778, 739, 684 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.41 and 7.40 (ABq, 24H, *J* 8, Ph*H*), 6.95 and 6.92 (ABq, 12H, *J* 9, Ph*H*), 6.68 (s, 6H, Ar*H*), 6.55 (s, 3H, Ar*H*), 6.19 (s, 3H, Ar*H*), 5.21 (s, 12H, PhC*H*$_2$OCO), 5.03 (s, 12H, PhC*H*$_2$O), 4.96 (s, 6H, ArC*H*$_2$O), 1.95 (s, 36H, C*H*$_3$). MALDI-TOF MS: *m/z* 2423 ([M+K]$^+$). Elem. Anal. Calcd for $C_{117}H_{114}Br_6O_{24}$: C, 58.96%; H, 4.82%; Br, 20.11%. Found: C, 59.06%; H, 4.83%; Br, 20.20%.

CMG2-Br: yield 91%, colorless glass. FTIR (NaCl): 3030, 2976, 2928, 2871, 1735, 1596, 1501, 1458, 1372, 1275, 1204, 1157, 1110, 1056, 1012, 970, 829, 752, 683 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.40 and 7.39 (ABq, 48H, *J* 8, Ph*H*), 6.94 and 6.93 (ABq, 12H, *J* 9, Ph*H*), 6.67 (s, 18H, Ar*H*), 6.54 (s, 9H, Ar*H*), 6.18 (s, 3H, Ar*H*), 5.20 (s, 24H, PhC*H*$_2$OCO), 5.01 (s, 24H, PhC*H*$_2$O), 4.96 (s, 18H, ArC*H*$_2$O), 1.94 (s, 72H, C*H*$_3$). MALDI-TOF MS: *m/z* 4770 ([M+K]$^+$). Elem. Anal. Calcd for $C_{231}H_{228}Br_{12}O_{48}$: C, 58.64%; H, 4.86%; Br, 20.27%. Found: C, 58.60%; H, 4.80%; Br, 20.35%.

CMG3-Br: yield 84%, colorless glass. FTIR (NaCl): 3055, 2975, 2934, 2874, 1734, 1596, 1502, 1457, 1372, 1274, 1204, 1156, 1108, 1053, 1012, 970, 828, 772, 682 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.37 and 7.36 (ABq, 96H, *J* 8, Ph*H*), 6.92 and 6.91 (ABq, 12H, *J* 9, Ph*H*), 6.65 (s, 36H, Ar*H*), 6.52 (s, 18H, Ar*H*), 6.50 (s, 9H, Ar*H*), 6.15 (s, 3H, Ar*H*), 5.17 (s, 48H, PhC*H*$_2$OCO), 4.98 (s, 48H, PhC*H*$_2$O), 4.93 (s, 42H, ArC*H*$_2$O), 1.92 (s, 144H, C*H*$_3$). MALDI-TOF MS: *m/z* 9465 ([M+K]$^+$). Elem. Anal. Calcd for $C_{459}H_{456}Br_{24}O_{96}$: C, 58.49%; H, 4.88%; Br, 20.34%. Found: C, 58.52%; H, 4.87%; Br, 20.50%.

2.5. ATRP of tBA initiated with CMGn-Br

The polymerization of *t*BA was conducted at 60 °C in acetone. A representative feed was $[t\mathrm{BA}]_0$:$\{F[\mathrm{CMG}n\text{-}\mathrm{Br}]_0\}$:$[\mathrm{CuBr}]_0$:$[\mathrm{PMDETA}]_0=80:1:1:1$ (where *F* stands for the functionality of the dendrimer initiator), and the total monomer concentration ($[t\mathrm{BA}]_0$) was 5.2 mol/L. The materials were accurately weighed and placed into a dry glass tube, then acetone was added. The reaction mixture was degassed with three freeze-evacuate-thaw cycles and polymerized in a sealed tube. At timed intervals, the glass tube was removed and cooled to room temperature. The contents were dissolved in THF and then passed through a short column of neutral alumina to remove the copper salts. The polymer was precipitated from a mixture of water/methanol (1:1). After decanting off the solvent, the polymer was redissolved in THF, and the precipitation procedure was repeated twice. The star poly(*tert*-butyl acrylate) (CMG*n*-P*t*BA) was dried under vacuum to constant weight.

CMG3-P*t*BA: FTIR (KBr): 2979, 2935, 1729, 1599, 1480, 1454, 1392, 1369, 1257, 1150, 846, 752 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.37 and 7.34 (ABq, Ph*H*), 6.98 (m, Ph*H*), 6.5–6.7 (m, Ar*H*), 6.15 (s, Ar*H*), 5.06 (s, PhC*H*$_2$OCO), 5.02 (s, PhC*H*$_2$O), 4.99 (s, ArC*H*$_2$O), 4.0–4.2 (m, terminal C*H*Br), 2.23 (s, C*H* P*t*BA), 1.82 (m, C*H*$_2$ P*t*BA), 1.44 (m, C*H*$_3$ P*t*BA).

2.6. Dendrimer initiators for bulk polymerization of styrene

For bulk polymerization of styrene initiated with dendrimer initiators, the typical feed was $[\mathrm{St}]_0$:$\{F[\mathrm{CMG}n\text{-}\mathrm{Br}]_0\}$:$[\mathrm{CuBr}]_0$:$[\mathrm{PMDETA}]_0=400:2:1:1$. The materials were added to the glass tube. After three freeze-evacuate-thaw cycles, the tube was sealed under vacuum and placed in an oil bath thermostated at 100 °C. At a given time, the glass tube was removed and cooled to room temperature. The contents were dissolved in chloroform and then passed through an alumina column. The polymer was precipitated from a large amount of methanol. The resultant star polystyrene (CMG*n*-PSt) was a white fine powder.

CMG3-PSt: FTIR (KBr): 3060, 3026, 2924, 2851, 1729, 1600, 1494, 1451, 1370, 1299, 1201, 1154, 1058, 1028, 908, 838, 759, 669 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 6.2–7.3 (m, Ph*H* in PSt and Ar*H* in dendrimer), 4.91 (broad s, ArC*H*$_2$O and PhC*H*$_2$O in dendrimer), 4.49 (m, terminal C*H*(Ph)Br), 0.9–2.6 (m, C*H* and C*H*$_2$ in PSt).

2.7. Core destruction of star CMG3-PSt

To the solution of CMG3-PSt (0.20 g, $M_n = 41{,}800$, $M_w/M_n = 1.08$) in THF (10 mL) were added ethanol (3.6 mL), water (0.4 mL), and KOH (0.80 g) under nitrogen, then the mixture was refluxed for 48 h. The solution was concentrated under reduced pressure, neutralized with dilute HCl, and precipitated from cold methanol. The resulting polymer was filtered and dried under vacuum.

2.8. Characterization

Fourier transform infrared spectroscopic (FTIR) analyses were performed on a Perkin–Elmer 2000 spectrometer. ^{1}H NMR spectra were recorded on a Varian 300-MHz spectrometer in $CDCl_3$ or THF-d_8 at room temperature. MALDI-TOF MS (matrix assisted laser desorption ionization time-of-flight mass spectrometry) was detected on an Instrum Biflex III spectrometer with α-cyano-4-hydroxycinnamic acid (CCA) as a matrix. The molecular weight and molecular weight distribution were measured on a Waters 150-C gel permeation chromatography (GPC) equipped with Ultrastyragel columns (HT2, HT3, and HT4) at 35 °C. THF was used as eluent and polystyrene standards were used as calibrations. The actual molecular weights of star polymers were calculated from the response of a multiangle laser light scattering (MALLS) detector (Wyatt Technology) that was connected to the size exclusion chromatography (SEC) line. Specific refractive index increments (dn/dc) for star polystyrenes were determined in THF at 25 °C with a laser source operating at 633 nm. Differential scanning calorimetric analysis (DSC) was carried out on a Perkin–Elmer DSC7 series thermal analysis system with a heating rate of 10 °C/min under N_2 atmosphere. Thermogravimetric analysis (TGA) was conducted on a Perkin–Elmer thermogravimetric analyzer under N_2 atmosphere.

3. Results and discussion

3.1. Synthesis of functional dendrimer initiators

In this study, novel polyarylether dendrimers with 1,3,5-tri(4-hydroxyphenoxy)benzene (THPB) core, polybenzylether interior, and benzyl 2-bromoisobutyrate surface group (CMGn-Br, $n = 1$–3, with functionality of 6, 12, and 24, respectively) were synthesized by convergent procedure. First, the methyl ester-terminated dendritic polyarylether benzyl bromides (MGn-Br, $n = 1$–3) were prepared according to the procedure described by Hawker et al. [51] by using methyl 4-bromomethylbenzoate and 3,5-dihydroxybenzyl alcohol as raw materials. Coupling of MGn-Br with the trifunctional core, THPB, occurred readily in the presence of potassium carbonate and 18-C-6 in acetone heated at reflux, which afforded methyl ester-terminated dendritic polyarylethers CMGn with high yield after purification. Reaction of CMGn with the reducing agent $LiAlH_4$ in absolute THF gave the dendritic benzyl alcohol CMGn-OH with quantitative yield. CMGn-OH is of amphiphilic nature and belongs to a class of unimolecular micelle, which can dissolve in THF, DMF, DMSO, and some mixed solvents such as mixture of chloroform and methanol. Last, the dendrimer initiator with terminal bromide CMGn-Br ($n = 1$–3) was successfully synthesized by reaction of CMGn-OH with 2-bromoisobutyryl bromide in THF with TEA and DMAP catalysts.

To demonstrate their high purity, the dendrimers obtained were characterized by FTIR, ^{1}H NMR, MALDI-TOF MS and elemental analysis, respectively. To further investigate whether some byproducts with low molecular weight exist in the dendrimer initiators, GPC measure was also used. Although the GPC method cannot afford the real molecular weight of dendrimers, it is convenient to evaluate the purity of dendrimers by determining the molecular weight distribution. The GPC traces as shown in Fig. 1 are symmetric and unimodal, and the molecular weight distribution is less than 1.02, verifying the high purity of the dendrimer initiators with different generations.

3.2. ATRP of tBA initiated with CMGn-Br

In this study, the polymerization of tBA was conducted at 60 °C in 25 vol% acetone, and a representative feed was $[t\mathrm{BA}]_0{:}\{F[\mathrm{CMG}n\text{-Br}]_0\}{:}[\mathrm{CuBr}]_0{:}[\mathrm{PMDETA}]_0 = 80{:}1{:}1{:}1$. When dendrimer initiators with different generations (CMGn-Br, $n = 1$–3) were used to initiate the atom transfer radical polymerization of tBA, the polymerization results are listed in Table 1. In Table 1, the molecular weight determined by ^{1}H NMR spectra (M_n(NMR)) was determined by the ratios of integrated peak areas of the aromatic signals of the initiator core (PhH, 7.3–7.5 ppm) and the methine protons in PtBA (2.23 ppm). It is noted that the molecular weight determined by ^{1}H NMR, which is very close to the theoretical calculated molecular weight (M_n (Calcd)), is much higher than that obtained by GPC (M_n(GPC)), this phenomenon can be ascribed to the unique molecular structure of star-shaped polymers. For star-shaped polymer, it is well known that the GPC analysis is

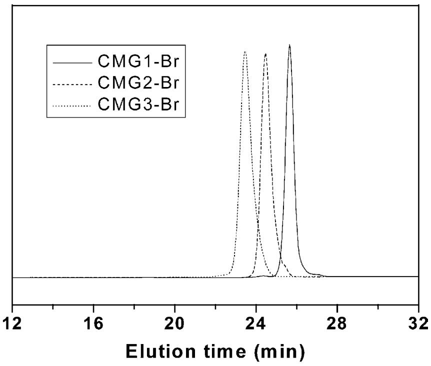


Fig. 1. GPC traces of dendrimer initiators with different generations.

Table 1
ATRP of *tert*-butyl acrylate initiated with dendrimer initiators

Run	Initiator	F^{a}	Time (h)	C (%)	M_n(Calcd)[b]	M_n(GPC)[c]	M_w/M_n[c]	M_n(NMR)[d]
1	CMG1-Br	6	3	39.5	26,700	18,800	1.10	24,000
2	CMG1-Br	6	5	57.6	37,800	28,400	1.10	35,600
3	CMG1-Br	6	8	75.6	48,900	37,200	1.09	48,400
4	CMG2-Br	12	4	41.8	56,200	33,500	1.12	52,000
5	CMG2-Br	12	6	55.4	72,900	47,600	1.08	70,200
6	CMG2-Br	12	9	70.5	91,500	57,200	1.08	90,000
7	CMG3-Br	24	3	30.7	85,000	39,600	1.11	76,500
8	CMG3-Br	24	6	51.7	136,700	64,000	1.10	130,000
9	CMG3-Br	24	10	70.0	181,700	86,300	1.07	176,000

[a] Polymerization conditions: $[t\mathrm{BA}]_0$:$\{F[\mathrm{CMG}n\text{-Br}]_0\}$:$[\mathrm{CuBr}]_0$:$[\mathrm{PMDETA}]_0 = 80{:}1{:}1{:}1$, $[t\mathrm{BA}]_0 = 5.2$ mol/L, at 60 °C in 25% acetone, where F stands for the functionality of dendrimer initiators.

[b] $M_n(\mathrm{Calcd}) = 128.17([t\mathrm{BA}]_0/[\mathrm{CMG}n\text{-Br}]_0 \times \mathrm{conversion}) + \mathrm{MW}_{\mathrm{dendrimer}}$.

[c] Determined by GPC in THF at 35 °C.

[d] Obtained by ^{1}H NMR from the ratios of integrated peak areas of the aromatic signals of the initiator core (Ph*H*, 7.3–7.5 ppm) and the methine protons in P*t*BA (2.23 ppm).

not the method of choice to determine the molecular weight. Since, it has smaller hydrodynamic volume than that of linear polystyrene having the same molecular weight, the GPC analysis always underestimates the molecular weight of star-shaped polymers [28,29].

Although the GPC method can only afford the apparent molecular weight of star polymers, it is convenient to determine the molecular weight distribution. From the results in Table 1, it can be seen that the molecular weight distribution of star CMG*n*-P*t*BA tends to decrease with increasing monomer conversion. In all cases, the molecular weight distribution is rather low ($1.07 < M_w/M_n < 1.12$) until a high conversion of 80% or so. Meanwhile, the value of M_n(NMR) is very close to that of M_n(Calcd), indicating the high initiation activity of the dendrimer initiators. In ^{1}H NMR spectra of star polymers obtained at various conversions, the signal corresponding to $\mathrm{PhC}H_2\mathrm{OCO}$ protons of the dendrimer initiator was completely disappeared and a new signal at a slightly high magnetic field was found, indicating that all the terminal groups have initiated the polymerization even at low conversions. For instance, the ^{1}H NMR spectra of the resultant star CMG3-P*t*BA exhibit a signal at 5.06 ppm which can be assigned to the resonance of $\mathrm{PhC}H_2\mathrm{OCO}$ protons in dendrimer core. As for the signal corresponding to $\mathrm{PhC}H_2\mathrm{OCO}$ protons of CMG3-Br (5.17 ppm), it has completely disappeared, indicating that all C–Br sites on the dendrimer initiator have efficiently initiated the ATRP of *t*BA.

For polymerization of *t*BA initiated with the CMG3-Br/CuBr/PMDETA initiating system, the semilogarithmic kinetic plot is shown in Fig. 2. The plot of $\ln([M]_0/[M])$ versus reaction time maintains a good linear relationship up to a conversion of 80%, indicating the first-order polymerization kinetics. This means that the concentration of propagating radicals is constant during the procedure.

Fig. 3 indicates the effect of monomer conversion on the number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n). It can be seen that the plots of M_n(NMR) versus polymerization conversion are reasonably linear and approximately consistent with the theoretical calculated values. This indicates that the anticipated average molecular weight of the resultant star polymer can be manipulated by the control of polymerization conversion. Meanwhile, it is also noted that the molecular weights determined by GPC are deviated from theory, which can be ascribed to the lower hydrodynamic volumes of star polymers relative to linear analogues of the same molecular weight. In such cases, the ^{1}H NMR method is thought of as a more reliable approach to determining the molecular weight.

From Fig. 3, it is also found that the resulting star polymers possess rather low polydispersities ($1.08 < M_w/M_n < 1.12$), and the GPC traces as shown in Fig. 4 are symmetrical and monomodal, which suggests that the contribution of chain breaking and transfer as well as termination reactions during polymerization can be neglected until higher conversion. The above results indicate that the polymerization process of *t*BA initiated with

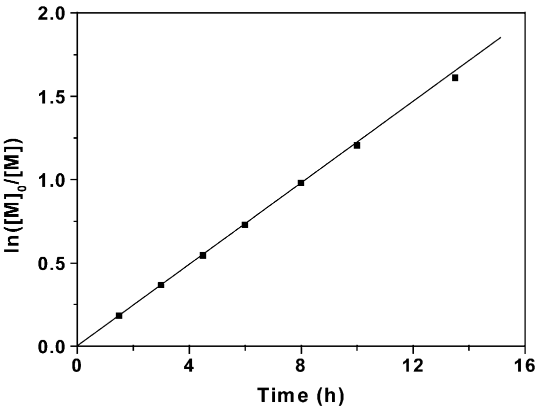


Fig. 2. First-order kinetic plot for ATRP of *t*BA at 60 °C in 25% acetone. $[t\mathrm{BA}]_0$:$\{24[\mathrm{CMG3\text{-}Br}]_0\}$:$[\mathrm{CuBr}]_0$:$[\mathrm{PMDETA}]_0 = 80{:}1{:}1{:}1$, $[t\mathrm{BA}]_0 = 5.2$ mol/L.

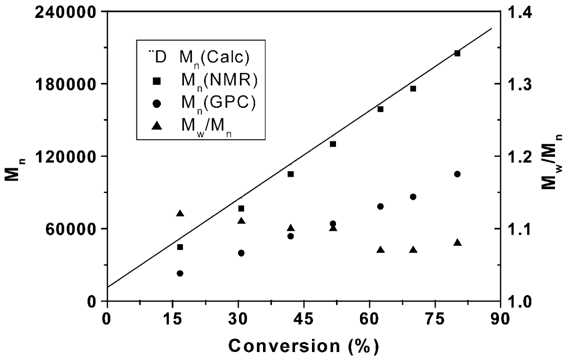


Fig. 3. Evolution of molecular weights and polydispersities with monomer conversion for ATRP of *t*BA initiated with CMG3-Br. See Fig. 2 for polymerization conditions.

CMG3-Br in acetone is controllable and of living characteristics.

3.3. Block copolymerization using a star CMG3-PtBA macroinitiator

In some polymerization systems such as ATRP of acrylates, it was reported that the structure of end group was rather complex [53–57]. With increasing conversion, the polymers obtained may progressively lose functionality. To evaluate whether all arms of star P*t*BAs synthesized via ATRP are of terminal bromine, star CMG3-P*t*BA (M_n=23,200, M_w/M_n=1.12) was used a macroinitiator to initiate ATRP of styrene at 100 °C in bulk, and the polymerization condition was $[St]_0$:{24[CMG3-P*t*BA]$_0$}:$[CuBr]_0$:$[PMDETA]_0$=100:1:1:1. After polymerization, the star block copolymer was isolated by precipitation into a mixture of water/methanol (1:2). When the monomer conversion was controlled below 30%, the block copolymerization can afford well-defined star block copolymers CMG3-P*t*BA-*b*-PSt with low polydispersity. For instance, the polymerization conducted for 2 and 3 h afforded copolymers with molecular weights of 42,500 and 57,200, while the polydispersity is rather low (M_w/M_n=1.09). No shoulder and tail are observed in the GPC traces (Fig. 5), indicating the relatively high blocking efficiency. This result also suggests that no functionality was lost in the course of polymerization.

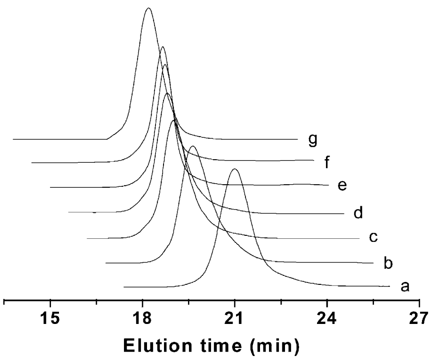


Fig. 4. GPC traces of star CMG3-P*t*BA synthesized via ATRP initiated with CMG3-Br. See Fig. 2 for polymerization conditions. (a) M_n=23,200, M_w/M_n=1.12; (b) M_n=39,600, M_w/M_n=1.11; (c) M_n=53,500, M_w/M_n=1.10; (d) M_n=64,000, M_w/M_n=1.10; (e) M_n=78,200, M_w/M_n=1.07; (f) M_n=86,300, M_w/M_n=1.07; (g) M_n=105,000, M_w/M_n=1.08.

3.4. CMGn-Br as initiators for bulk ATRP of styrene

In the course of ATRP of styrene to prepare star polymers, it was reported that more radical–radical coupling took place in solution polymerizations relative to those performed in bulk even at lower conversion presumably due to the increased mobility of the reactive chain ends in solution [28,29]. Accordingly, the polymerization of styrene was carried out at 100 °C in bulk in this study, and a representative feed was $[St]_0$:{F[CMG*n*-Br]$_0$}:$[CuBr]_0$:$[PMDETA]_0$=400:2:1:1. When CMG*n*-Br (n=1–3) was used as initiators for polymerization, the results at various conversions are shown in Table 2. In Table 2, the value of M_n(NMR) was obtained by ^{1}H NMR spectra from the ratios of integrated peak areas of $PhCH_2O$ and $ArCH_2O$ protons in dendrimer (4.91 ppm) and CH and CH_2 protons in PSt (0.9–2.6 ppm). As expected, the molecular weight of star CMG*n*-PSt determined by ^{1}H NMR is very close to the theoretical calculated molecular weight, both are much higher than that obtained by GPC. As previously described, the GPC approach can only offer apparent molecular weights of star polymers since the hydrodynamic volume of star CMG*n*-PSt is obviously different from that of linear polystyrene.

From Table 2, it is found that the polymerization at conversion below 30% can afford polymers with controlled molecular weight and low polydispersity ($1.08 < M_w/M_n < 1.18$). When the monomer conversion is beyond 30%, however, a shoulder derived from radical–radical coupling reaction appears in the high molecular weight side of the GPC traces, which leads to an increase in molecular weight

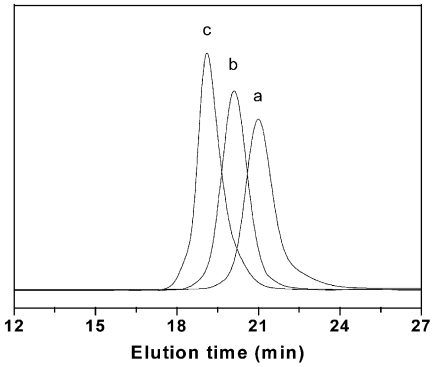


Fig. 5. GPC traces of star block copolymers CMG3-P*t*BA-*b*-PSt (b), (c) and their precursors CMG3-P*t*BA (a): (a) M_n=23,200, M_w/M_n=1.12; (b) t=2 h, 12.8% conversion, M_n=42,500, M_w/M_n=1.09; (c) t=3 h, 25.0% conversion, M_n=57,200, M_w/M_n=1.09. Polymerization conditions: $[St]_0$:{24[CMG3-P*t*BA]$_0$}:$[CuBr]_0$:$[PMDETA]_0$=100:1:1:1, at 100 °C in bulk.

Table 2
Bulk ATRP of styrene initiated with dendrimer initiators

Run	Initiator	F^a	Time (h)	C (%)	M_n (Calcd)^b	M_n (GPC)^c	M_w/M_n^{c}	M_n(NMR)^d
1	CMG1-Br	6	1	9.5	14,300	10,800	1.12	12,800
2	CMG1-Br	6	2	18.0	24,900	18,400	1.10	23,600
3	CMG1-Br	6	4	33.6	44,400	35,600	1.24^e	43,500
4	CMG2-Br	12	1	8.4	25,700	14,800	1.18	23,200
5	CMG2-Br	12	2	16.2	45,200	26,500	1.12	42,400
6	CMG2-Br	12	4	30.2	80,200	56,000	1.27^e	77,800
7	CMG3-Br	24	1	8.0	49,400	23,500	1.08	43,500
8	CMG3-Br	24	3	21.5	117,000	47,500	1.09	108,000
9	CMG3-Br	24	5	36.2	190,400	152,000	1.20^e	184,000

[a] Polymerization conditions: $[\mathrm{St}]_0$:{F[CMGn-Br]$_0$}:$[\mathrm{CuBr}]_0$:$[\mathrm{PMDETA}]_0 = 400{:}2{:}1{:}1$, in bulk at 100 °C, where F stands for the functionality of dendrimer initiators.

[b] $M_n(\mathrm{Calcd}) = 104.15([\mathrm{St}]_0/[\mathrm{CMG}n\text{-Br}]_0 \times \mathrm{conversion}) + \mathrm{MW}_{\mathrm{dendrimer}}$.

[c] Determined by GPC in THF at 35 °C.

[d] Obtained by ^{1}H NMR from the ratios of integrated peak areas of PhCH_2O and ArCH_2O protons in dendrimer (4.91 ppm) and CH and CH_2 protons in polystyrene (0.9–2.6 ppm).

[e] A shoulder was observed in the GPC traces.

distribution. In this case, it is obvious that the ^{1}H NMR approach cannot afford the precise number-average molecular weight since this method does not take account of the increasing average arm numbers in star polymers due to the star–star coupling. Presuming that the arm numbers in star polymers are constant, however, it is meaningful in determining the initiation efficiency of initiators when the coupling phenomenon is not serious. In Table 2, the value of M_n(NMR) of star polystyrene obtained at low monomer conversion (less than 30%) is very close to that of M_n(Calcd), suggesting the high initiation efficiency.

When CMG3-Br was used as macroinitiator for ATRP of styrene, the polymerization kinetics was investigated in detail. The semilogarithmic kinetic plot is shown in Fig. 6, and the dependence of molecular weight and polydispersity of star CMG3-PSt on monomer conversion is described in Fig. 7. It is found that there are three stages in bulk polymerization of styrene. At the first stage below 25–30% conversion, the polymerization took place smoothly and the first-order polymerization is maintained. In this period, the polymerization is of living nature, the GPC traces as shown in Fig. 8(a)–(e) are symmetrical and unimodal, and the predetermined molecular weight of the star polymer can be reached by the manipulation of monomer conversion. Meanwhile, the plots of M_n(GPC) and M_n(NMR) versus conversion keep a good linear relationship. Beyond 25–30% conversion the polymerization came into the second stage, where the molecular weight control is lost and the plot of M_n(GPC) versus conversion strongly depart from the linear relationship at the first stage. For star polymers synthesized at this stage, a shoulder is observed in the high molecular weight side of the GPC traces (Fig. 8(f)–(h)), this phenomenon can be attributed to the irreversible coupling of the growing radicals between different stars [29]. Moreover, the shoulder due to intermolecular termination becomes more pronounced with increasing monomer conversion. At the last stage with conversion beyond 45–48%, a large amount of insoluble gels were produced, this can be attributed to the formation of network due to cross-linking of the arms.

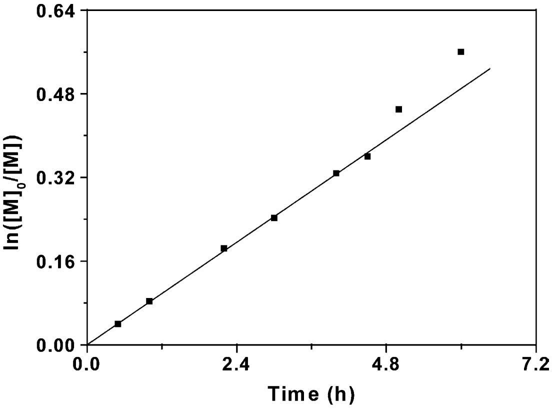


Fig. 6. Semilogarithmic kinetic plot for ATRP of St at 100 °C in bulk. $[\mathrm{St}]_0$:{24$[\mathrm{CMG3\text{-}Br}]_0$}: $[\mathrm{CuBr}]_0$:$[\mathrm{PMDETA}]_0 = 400{:}2{:}1{:}1$.

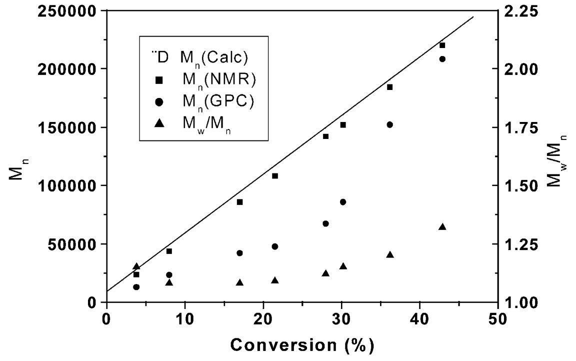


Fig. 7. Dependence of molecular weight and polydispersity of star CMG3-PSt on monomer conversion. See Fig. 6 for reaction conditions.

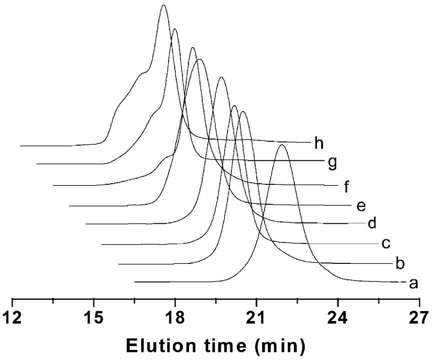


Fig. 8. GPC traces of star CMG3-PSt prepared by ATRP initiated with CMG3-Br. See Fig. 6 for reaction conditions. (a) $M_n = 12{,}800$, $M_w/M_n = 1.15$; (b) $M_n = 23{,}500$, $M_w/M_n = 1.08$; (c) $M_n = 41{,}800$, $M_w/M_n = 1.08$; (d) $M_n = 47{,}500$, $M_w/M_n = 1.09$; (e) $M_n = 67{,}200$, $M_w/M_n = 1.12$; (f) $M_n = 85{,}700$, $M_w/M_n = 1.15$; (g) $M_n = 152{,}000$, $M_w/M_n = 1.20$; (h) $M_n = 208{,}000$, $M_w/M_n = 1.32$.

3.5. Determination of the actual functionality of star CMG*n*-PSt

For star polymers, it is necessary to verify whether each of the alkyl halide fragments of the initiators had participated in the ATRP process and the synthesized star polymers indeed had low polydispersity. Some methods have been developed to determine the precise arm numbers in star polymers, including hydrolysis approach [29,31,50], kinetic approach [28], mixed initiator approach [29], ^{1}H NMR spectra approach using partially deuterated monomer [42], and multiangle laser light scattering/size exclusion chromatography (MALLS/SEC) approach [29,30,43]. In this study, the combination of hydrolysis approach and MALLS/SEC approach was used to determine the actual functionality (*f*) of star CMG*n*-PSt, and the results are shown in Table 3. In Table 3, the hydrolyzed PSt arms possess low polydispersity ($1.15 < M_w/M_n < 1.18$) and predetermined arm length, and the calculated functionality (*f*(Calcd)) determined by $M_{n,star}$(LLS) and $M_{n,arm}$(GPC) is in good agreement with the theoretical value (*f*(Theo)), indicating that star CMG*n*-PSt synthesized in this study indeed have low polydispersity and desired number of arms. For instance, when the 24-arm CMG3-PSt ($M_n = 41{,}800$, $M_w/M_n = 1.08$, with 17.0% monomer conversion) was submitted to hydrolysis by treatment under basic conditions to cleave the ester functions linking the PSt arms, the GPC traces of star CMG3-PSt and hydrolyzed linear polystyrene are shown in Fig. 9. It can be seen that the molecular weight of the PSt arm after hydrolysis is 3480, which is very close to the expected value of 3600 according to the monomer conversion. The hydrolyzed PSt arm exhibits monomodal distribution and low polydispersity, indicating no obvious side reactions such as star–star coupling, chain breaking and transfer as well as termination reactions during polymerization [29,30]. Meanwhile, a signal at 4.91 ppm assigned to the resonance of PhCH_2OCO protons in dendrimer core was observed in ^{1}H NMR spectra of the star CMG3-PSt, while the signal corresponding to PhCH_2OCO protons of the dendrimer initiator (5.17 ppm) completely disappeared. All the above results indicate the dendrimer initiators can quantitatively initiate the bulk polymerization of styrene.

3.6. Block copolymerization of CMG3-PSt with tBA

The star CMG*n*-PSt with terminal bromine can be used as macroinitiator to prepare well-defined star block copolymers. In this study, CMG3-PSt ($M_n = 12{,}800$, $M_w/M_n = 1.15$) was chosen as a typical sample for block copolymerization of *t*BA, and the reaction conditions were $[t\text{BA}]_0$:{24[CMG3-PSt]$_0$}:$[\text{CuBr}]_0$:$[\text{PMDETA}]_0$ = 100:1:1:1, at 80 °C in bulk. The resultant copolymer was purified by precipitation into a mixture of water/methanol (1:4). When the polymerization was performed for 2 and 4 h, the GPC traces of the resulting star block CMG3-PSt-*b*-P*t*BA are shown in Fig. 10. No tail or shoulder is observed in the GPC traces of the star block copolymers, indicating the high blocking efficiency. The low molecular weight distribution ($M_w/M_n < 1.10$) indicates a controlled growth of the P*t*BA blocks. This result means that the star CMG3-PSt can successfully initiate the ATRP of *t*BA.

3.7. Thermal properties

In some cases, it was reported that the thermal properties of star polymers were obviously different from their linear analogue due to the branching effect [58–60]. For instance, the glass transition temperature (T_g), melting point, and

Table 3
Determination of the actual functionality of polystyrene stars

Sample	*f*(Theo)	$M_{n,star}$[a]	M_w/M_n[a]	$M_{n,star}$(LLS)[b]	$M_{n,arm}$[c]	M_w/M_n[c]	$M_{n,arm}$(Calcd)[d]	*f*(Calcd)[e]
CMG1-PSt	6	18,400	1.10	24,800	3720	1.15	3800	6.0
CMG2-PSt	12	26,500	1.12	45,400	3450	1.18	3420	11.8
CMG3-PSt	24	41,800	1.08	93,300	3480	1.17	3600	24.1

[a] Apparent molecular weight and polydispersity of star PSt determined by GPC in THF at 35 °C.
[b] Actual molecular weight of star PSt determined by MALLS/SEC approach.
[c] Molecular weight and polydispersity of hydrolyzed PSt arms measured by GPC in THF at 35 °C.
[d] Theoretically calculated molecular weight of PSt arm on the basis of molar ratio of monomer to initiator and conversion.
[e] Actual functionality calculated from $f(\text{Calcd}) = (M_{n,star}(\text{LLS}) - \text{MW}_{dendrimer})/M_{n,arm}(\text{GPC})$.

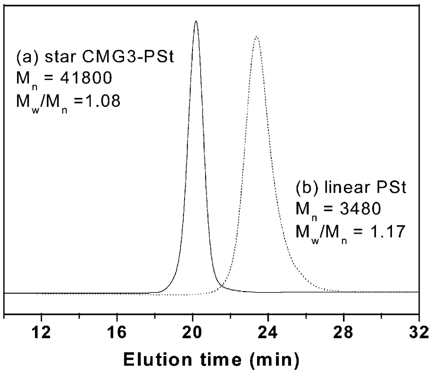


Fig. 9. GPC traces of PSt polymers before (a) and after (b) hydrolysis of the ester function.

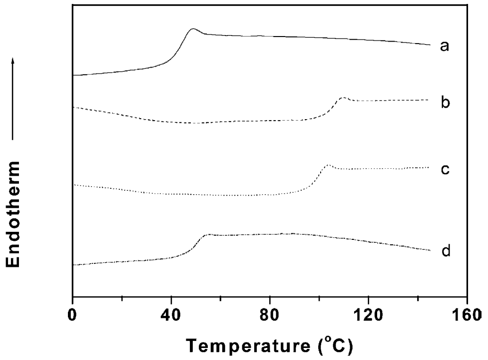


Fig. 11. DSC traces of CMG3-P*t*BA (a), CMG3-P*t*BA-*b*-PSt (b), CMG3-PSt (c) and CMG3-PSt-*b*-P*t*BA (d).

maximum decomposition temperature of star-shaped polylactides were liable to decrease as the number of arms increased [60]. In this study, the thermal properties of the dendrimer-like star polymers and star block copolymers were characterized by DSC and TGA, respectively.

For various 24-arm stars, the second heating DSC curves are shown in Fig. 11. The T_g values of CMG3-P*t*BA and CMG3-PSt are 36.5 and 93.4 °C, which are similar to those of their linear counterparts, indicating no obvious branching effect. For 24-arm star block copolymers, although only a single T_g corresponding to the outer block is observed, it is very difficult to determine the morphology by DSC analysis since the central block is relatively short. To investigate the influence of number of arms on T_g values and the morphology, 6-arm and 12-arm star block copolymers with similar arm length of the outer block were also synthesized, and the results are shown in Table 4. These copolymers obviously show the expected two-phase structure, as evidenced by two T_gs. Similarly, no obvious branching effect is observed for various star block copolymers since the T_g values corresponding to the outer block are similar, and the dual effects of branching on T_g can account for this phenomenon. On one hand, polymers with more branching have more free volume due to more chain ends, which will reduce T_g. On the other hand, the branches also hinder the chain mobility, like large side groups, which will increase T_g. In this study, no obvious difference in T_g of the outer block in star block copolymers is observed, indicating that both counteract with each other.

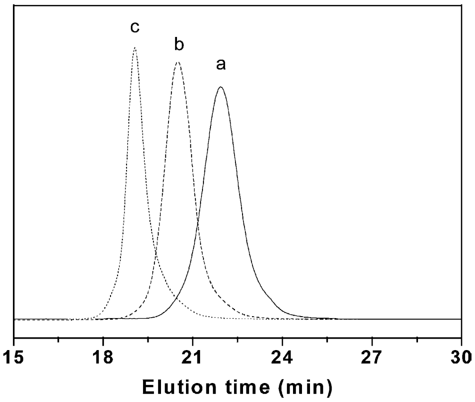


Fig. 10. GPC traces of star block copolymers CMG3-PSt-*b*-P*t*BA (b), (c) and their precursors CMG3-PSt (a): (a) $M_n = 12{,}800$, $M_w/M_n = 1.15$; (b) $t = 2$ h, 18.4% conversion, $M_n = 36{,}400$, $M_w/M_n = 1.10$; (c) $t = 4$ h, 35.6% conversion, $M_n = 59{,}600$, $M_w/M_n = 1.08$. Reaction conditions: $[t\text{BA}]_0$:{24 $[\text{CMG3-PSt}]_0$}:$[\text{CuBr}]_0$: $[\text{PMDETA}]_0 = 100{:}1{:}1{:}1$, at 80 °C in bulk.

In addition, the thermally stable properties of various polymers were also investigated. From TGA thermograms as shown in Fig. 12, it is found the thermal stability of various polymers decreased in the order CMG3-PSt > CMG3-P*t*BA-*b*-PSt > CMG3-PSt-*b*-P*t*BA > CMG3-P*t*BA. This result can be ascribed to lower thermal stability of P*t*BA than PSt.

4. Conclusions

Novel bromide-terminated polyarylether dendrimers (CMG*n*-Br, *n* = 1–3) were successfully prepared by convergent procedure. ATRP of *t*BA and St with CMG*n*-Br initiators in the presence of CuBr/PMDETA catalytic system was successfully conducted under suitable conditions, and a series of well-defined dendrimer-like star P*t*BA and PSt with precise arm numbers were synthesized.

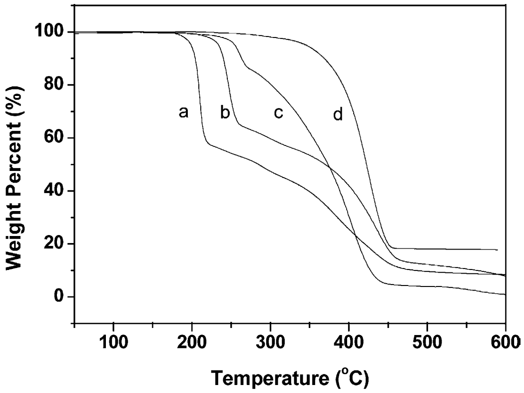


Fig. 12. TGA thermograms of various star polymers and star block copolymers: CMG3-P*t*BA (a), CMG3-PSt-*b*-P*t*BA (b), CMG3-P*t*BA-*b*-PSt (c), and CMG3-PSt (d).

Table 4
Effects of arm number on T_g of star block copolymers

Sample	$M_{n,macroinitiator}$(GPC)	DP(Calcd)[a]	M_n(GPC)[b]	M_w/M_n[b]	T_g (°C)[c]
CMG1-P*t*BA-*b*-PSt	28,400	92.4	73,600	1.15	41.5, 98.2
CMG1-PSt-*b*-P*t*BA	18,400	97.0	78,200	1.12	45.0, 92.4
CMG2-P*t*BA-*b*-PSt	33,500	95.0	106,500	1.11	40.4, 96.5
CMG2-PSt-*b*-P*t*BA	26,500	98.4	112,000	1.08	43.8, 90.6
CMG3-P*t*BA-*b*-PSt	23,200	96.5	152,400	1.18	99.6
CMG3-PSt-*b*-P*t*BA	12,800	100	172,000	1.09	44.1

[a] Calculated degree of polymerization for the outer block on the basis of molar ratio of monomer to macroinitiator and monomer conversion.
[b] Apparent molecular weight and polydispersity of star block copolymers determined by GPC in THF at 35 °C.
[c] Determined by the second heating DSC curves.

The quantitative initiation of the dendrimer initiators was demonstrated by high initiation efficiency, ^{1}H NMR spectra, hydrolysis, and MALLS/SEC approach. On this basis, star block copolymers CMG*n*-P*t*BA-*b*-PSt and CMG*n*-PSt-*b*-P*t*BA with low polydispersity ($1.08 < M_w/M_n < 1.18$) were successfully prepared with functional macroinitiators by block copolymerization. In addition, the thermal properties of the resultant polymers were characterized by DSC and TGA, respectively.

Acknowledgements

The financial support to this work by the National Natural Science Foundation of China (Grants 50073026 and 50273042) and the fund of Polymer Chemistry laboratory, Chinese Academy of Sciences and China Petro-Chemical Corporation, is gratefully acknowledged.

References

[1] Hawker CJ, Hedrick JL. Macromolecules 1995;28:2993.
[2] Hawker CJ, Fréchet JMJ, Grubbs RB, Dao J. J Am Chem Soc 1995; 117:10763.
[3] Hawker CJ, Hedrick JL, Malmström EE, Trollsås M, Mecerreyes D, Moineau G, et al. Macromolecules 1998;31:213.
[4] Bosman AW, Heumann A, Klaerner GG, Benoit DG, Fréchet JMJ, Hawker CJ. J Am Chem Soc 2001;123:6461.
[5] Hawker CJ, Bosman AW, Harth E. Chem Rev 2001;101:3661.
[6] Detrembleur C, Sciannamea V, Koulic C, Claes M, Hoebeke M, Jérôme R. Macromolecules 2002;35:7214.
[7] Robin S, Guerret O, Couturier JL, Gnanou Y. Macromolecules 2002; 35:2481.
[8] Bowden NB, Dankova M, Wiyatno W, Hawker CJ, Waymouth RM. Macromolecules 2002;35:9246.
[9] Yamago S, Iida K, Yoshida J. J Am Chem Soc 2002;124:2874.
[10] Kato M, Kamigaito M, Sawamoto M, Higashimura T. Macromolecules 1995;28:1721.
[11] Wang JS, Matyjaszewski K. Macromolecules 1995;28:7901.
[12] Wang JS, Matyjaszewski K. J Am Chem Soc 1995;117:5614.
[13] Percec V, Barboiu B. Macromolecules 1995;28:7970.
[14] Wang JS, Matyjaszewski K. Macromolecules 1995;28:7572.
[15] Moineau G, Dubois Ph, Jérôme R, Senninger T, Teyssié Ph. Macromolecules 1998;31:545.
[16] Matyjaszewski K, Xia J. Chem Rev 2001;101:2921.
[17] Kamigaito M, Ando T, Sawamoto M. Chem Rev 2001;101:3689.
[18] Zhao YL, Jiang J, Liu HW, Chen CF, Xi F. J Polym Sci, Part A: Polym Chem 2001;39:3960.
[19] Zhao YL, Zhang JM, Jiang J, Chen CF, Xi F. J Polym Sci, Part A: Polym Chem 2002;40:3360.
[20] Zhao YL, Chen CF, Xi F. J Polym Sci, Part A: Polym Chem 2003;41: 2156.
[21] Wang XZ, Zhang HL, Zhong GQ, Wang XY. Polymer 2004;45:3637.
[22] Huang CF, Lee HF, Kuo SW, Xu HY, Chang FC. Polymer 2004;45: 2261.
[23] Chong YK, Le TPT, Moad G, Rizzardo E, Thang SH. Macromolecules 1999;32:2071.
[24] Kırcı B, Lutz JF, Matyjaszewski K. Macromolecules 2002;35:2448.
[25] Schilli C, Lanzendörfer MG, Müller AHE. Macromolecules 2002;35: 6819.
[26] Lansalot M, Davis TP, Heuts JPA. Macromolecules 2002;35:7582.
[27] Matyjaszewski K, Miller PJ, Fossum E, Nagakawa Y. Appl Organomet Chem 1998;12:667.
[28] Matyjaszewski K, Miller PJ, Pyun J, Kickelbick G, Diamanti S. Macromolecules 1999;32:6526.
[29] Angot S, Murthy KS, Taton D, Gnanou Y. Macromolecules 1998;31: 7218.
[30] Angot S, Murthy KS, Taton D, Gnanou Y. Macromolecules 2000;33: 7261.
[31] Ueda J, Kamigaito M, Sawamoto M. Macromolecules 1998;31:6762.
[32] Percec V, Barboiu B, Bera TK, van der Sluis M, Grubbs RB, Fréchet JMJ. J Polym Sci, Part A: Polym Chem 2000;38:4776.
[33] Haddleton DM, Edmonds R, Heming AM, Kelly EJ, Kukulj D. New J Chem 1999;23:477.
[34] Ueda J, Matsuyama M, Kamigaito M, Sawamoto M. Macromolecules 1998;31:557.
[35] Kasko AM, Heintz AM, Pugh C. Macromolecules 1998;31:256.
[36] Hedrick JL, Trollsås M, Hawker CJ, Atthoff B, Claesson H, Heise A, et al. Macromolecules 1998;31:8691.
[37] Heise A, Hedrick JL, Frank CW, Miller RD. J Am Chem Soc 1999; 121:8647.
[38] Heise A, Hedrick JL, Trollsås M, Miller RD, Frank CW. Macromolecules 1999;32:231.
[39] Haddleton DM, Waterson C. Macromolecules 1999;32:8732.
[40] Wu X, Fraser CL. Macromolecules 2000;33:4053.
[41] Heise A, Nguyen C, Malek R, Hedrick JL, Franck CW, Miller RD. Macromolecules 2000;33:2346.
[42] Heise A, Diamanti S, Hedrick JL, Franck CW, Miller RD. Macromolecules 2001;34:3798.
[43] Robello DR, André A, McCovick TA, Kraus A, Mourey TH. Macromolecules 2002;35:9334.
[44] Collins JE, Fraser CL. Macromolecules 1998;31:6715.
[45] Fraser CL, Davis AP. J Polym Sci, Part A: Polym Chem 2000;38: 4704.
[46] Johnson RM, Corbin PS, Ng C, Fraser CL. Macromolecules 2000;33: 7404.
[47] Wu X, Fraser CL. Macromolecules 2000;33:7776.

[48] Wu X, Collins JE, McAlvin JE, Cutts RW, Fraser CL. Macromolecules 2001;34:2812.
[49] Zhao YL, Shuai XT, Chen CF, Xi F. Chem Commun 2004;1608.
[50] Zhao YL, Shuai XT, Chen CF, Xi F. Macromolecules 2004;37:8854.
[51] Hawker CJ, Wooley KL, Fréchet JMJ. J Chem Soc Perkin Trans 1 1993;1287.
[52] Chen YM, Chen CF, Liu WH, Xi F. Polym Bull 1996;37:557.
[53] Bednarek M, Biedron T, Kubisa P. Macromol Rapid Commun 1999;20:59.
[54] Bednarek M, Biedron T, Kubisa P. Macromol Chem Phys 2000;201:58.
[55] Biedroń T, Kubisa P. Macromol Rapid Commun 2001;22:1237.
[56] Biedroń T, Kubisa P. J Polym Sci, Part A: Polym Chem 2002;40:2799.
[57] Schön F, Hartenstein M, Müller AHE. Macromolecules 2001;34:5394.
[58] Choi YK, Bae YH, Kim SW. Macromolecules 1998;31:8766.
[59] Zhao YL, Cai Q, Jiang J, Shuai XT, Bei JZ, Chen CF, et al. Polymer 2002;43:5819.
[60] Zhao YL, Shuai XT, Chen CF, Xi F. Chem Mater 2003;15:2836.