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Synthesis and self-assembly of poly(benzyl ether)-*b*-poly(methyl methacrylate) dendritic-linear polymers

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Abstract

Here, the dendritic chloric poly(benzyl ether) (G_1-Cl, G_2-Cl and G_3-Cl) as the macroinitiator for the controlled atom transfer radical polymerization (ATRP) of methyl methylacrylate was investigated. Polymers obtained were characterizated by GPC, ^{1}H NMR, FT-IR, TGA and DSC. These dendritic-linear block polymers that consist of linear and dendritic segments have very good solubility in common organic solvents at room temperature. In a selective solvent (THF/H_2O), polymers can self-assembled into the micelles that have a spherical morphology in shape due to the lowest of the surface energies.

Keywords: Diblock copolymer; Atom transfer radical polymerization (ATRP); Dendritic poly(benzyl ether)

1. Introduction

The rapid growth of research on dendritic macromolecules has led to a variety of structurally intriguing materials having potential applications in the many fields such as catalysis, molecular recognition, and energy transfer [1]. Polymers and copolymers with complex, yet well-defined architectures are drawing significant attentions in the search for materials with excellent properties. They were made available either by polymerization of macromonomers, which already carried the dendron of the desired generation and peripheral substitution pattern, or by systematic attachment to an already existing polymer both by convergent and divergent routes [2]. Of these macromolecules structures, dendritic-linear block copolymers consisting of covalently bound linear and dendritic segments have shown interesting solution, solid-state, and interfacial properties [3]. The properties arise from the existence of both dendritic and linear parts of the macromolecules. Among these interesting properties, self-assembly behaviors of dendritic-linear polymers have received much attention for their potential application in nanoscopic materials and devices. In spite of the promising results achieved up to now, the synthesis of novel polymer of dendritic-linear copolymers is still of important due to the high demand for new materials with defined architecture and improved properties.

As a novel polymerization approach, atom transfer radical polymerization (ATRP) has been attracting increasing interest recently, since it furnishes control over the resulting polymers [4–9]. This method offers a new way to form well-defined and predictable multicomponent polymer structures. Up to now, ATRP has been successfully applied to the synthesis of well-defined macromolucular arichitecture such as comb, gradient, star, and dendritic macromolecules [10–14]. Here we demonstrate the application of the ATRP method to synthesize the dendritic-linear block copolymers, in which the dendritic part can be controlled by the generation from 1 to 3. The resultant polymers can be formed into spherical micelles in a selective solvent.

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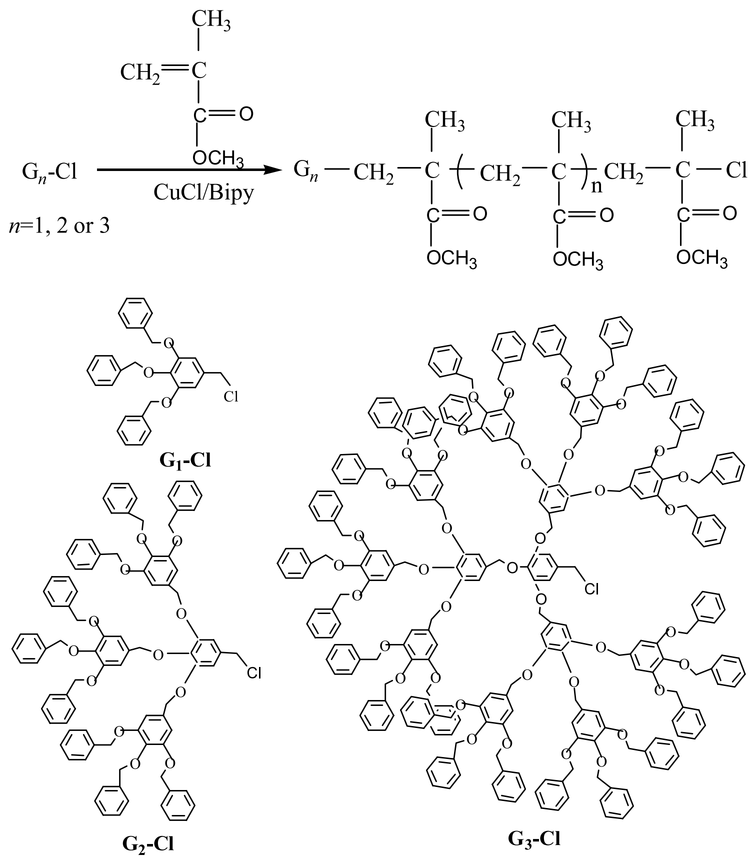

Scheme 1. Polymerization procedure of G$_n$-*b*-PMMA block copolymers.

2. Experimental

2.1. Materials

Methyl Methyacryate (MMA) from Shanghai No.1 Chemical reagent factory was distilled under reduced pressure over calcium hydride and then stored 4-A molecular sieves. 2,2′-Bipyridyl (bipy), an analytical reagent, was used as obtained from shanghai No.1 Chemical reagent factory. Copper (I) chloride (CuCl, AR grade) was purified by stirring in acetic acid, washing with methanol, and then dry under reduced pressure. The dendritic chloric poly(benzyl ether) (G$_1$-Cl, G$_2$-Cl and G$_3$-Cl) were prepared by the literature method [15,16]. All other reagents were of analytical grade and used as received.

2.2. Synthesis procedure of G$_n$-PMMA block copolymers

In a typical synthesis, bipy, CuCl, G$_n$-Cl (2:1:1 in molar ratio) and MMA with a certain molar ratio were added to a dry tube. The tube was cycled between vacuum and nitrogen >10 times to remove the oxygen. Then, the tube was sealed and placed in a preheated, thermally regulated oil bath at certain temperature. After a certain period of polymerization, the tube was removed from the oil bath and allowed to cool for a few minutes. Then, several milliliter of chloroform (CHCl$_3$) was added to the tube, and the mixture was placed for a period of time at room temperature to complete the dissolution of the polymer. The resulting solution was passed through a short column on basic aluminum oxide to remove most of the Cu complex. The excess CHCl$_3$ was evaporated under reduced pressure and the product was precipitated from a large amount of methanol, filtered, and dried under vacuum to constant weight.

^{1}H NMR (500 MHz, CDCl$_3$): G$_1$-*b*-PMMA: 0.84 and 1.02 (br, CH$_3$, PMMA), 1.71–2.01 (br, CH$_2$, PMMA), 3.80 (br, OCH$_3$, PMMA), 4.49 (s, ArCH$_2$MMA), 5.04 (s, ArCH$_2$OAr, 4 position), 5.10 (s, ArCH$_2$OAr, 3,5 positions), 6.69 (s, ArH ortho to CH$_2$MMA), 7.3–7.4 (m, ArH, 3,4,5 positions of CH$_2$OAr).

G$_2$-*b*-PMMA: 0.70–0.92 and 0.92–1.08 (br, CH$_3$, PMMA), 1.71–2.08 (br, CH$_2$, PMMA), 3.50–3.80 (br, OCH$_3$, PMMA), 4.49 (s, ArCH$_2$MMA), 5.01 (s, ArCH$_2$OAr, 4 position), 5.04 (s, ArCH$_2$OAr, 3,5 positions), 5.08 (overlapped, ArCH$_2$OAr, 3,4,5-(4′) positions), 5.11 (overlapped, ArCH$_2$OAr, 3,4,5-(3′,5′) positions), 6.10 (overlapped, Ar′H ortho to CH$_2$OArCH$_2$), 6.69 (s, ArH ortho to CH$_2$MMA), 7.30–7.49 (overlapped, Ar″H, 3,4,5 positions of CH$_2$OAr′).

G$_3$-*b*-PMMA: 0.74–0.93 and 0.93–1.09 (br, CH$_3$,

Table 1
Results and Conductions of the Polymerization of G_n-Cl and MMA

Run	Initiator	MMA/G_n-Cl	$M_n \times 10^{-4}$ (calc.)[a]	$M_n \times 10^{-4}$ (NMR)[b]	$M_n \times 10^{-4}$ (GPC)[c]	PD[d]	Conversion (%)
1	G_1-Cl	150	1.47	1.48	1.61	1.21	95.0
2		250	2.44	2.45	2.42	1.27	90.0
3		350	3.49	3.50	3.55	1.39	90.6
4	G_2-Cl	150	1.43	1.51	1.57	1.58	85.3
5		250	2.29	2.31	2.47	1.49	86.1
6		350	3.32	3.35	3.40	1.35	90.9
7	G_3-Cl	150	1.71	1.76	1.69	1.29	82.1
8		250	2.68	2.70	2.97	1.55	92.4
9		350	3.45	3.46	3.52	1.22	83.5

Polymerization at 100 °C for 12 h, in bulk.

[a] M_n (calc.) = ([MMA]$_0$ × conversion × MW_{MMA})/[macroinitiator]$_0$ + $MW_{macroinitiator}$ in g mol^{-1}.

[b] Obtained by a comparison of the signal intensity of $ArCH_2O$ and $PhCH_2O$ protons in the macroiniator (4.8–5.2 ppm) with that of methoxy ($-OCH_3$) protons of PMMA (~3.80 ppm).

[c] Determined by GPC in THF at 25 °C.

[d] PD (polydispersity) = M_w/M_n (GPC).

PMMA), 1.74–2.10 (br, CH_2, PMMA), 3.50–3.80 (br, OCH_3, PMMA), 4.49 (s, $ArCH_2MMA$), 5.01 (s, $ArCH_2OAr$, 4 position), 5.03 (s, $ArCH_2OAr$, 3,5 positions), 5.07 (overlapped, $ArCH_2OAr$, 3,4,5-(3′,4′,5′) positions), 5.13 (overlapped, $ArCH_2OAr$, 3′,4′,5′-(3″,4″,5″) positions), 6.11, 6.42, 6.71 (overlapped, ArH, Ar′H and Ar″H ortho to CH_2OAr or CH_2MMA), 7.30–7.50 (overlapped, Ar‴H, 3,4,5 positions of CH_2OAr'').

2.3. Self-assembly of dendritic-linear diblock copolymers

In order to estimate the aggregation behaviors of

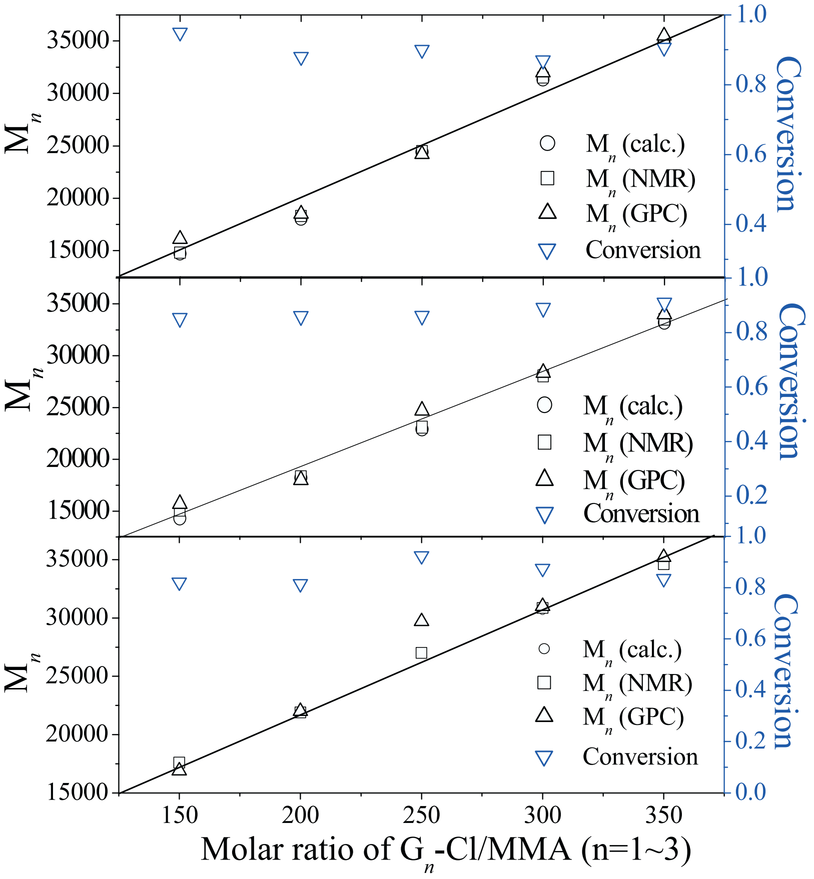

Fig. 1. Dependence of M_n and conversion of G_1-*b*-PMMA on molar ration of MMA/G_1-Cl. Polymerization conditions: [G_n-Cl]$_0$:[CuCl]$_0$:[Bipy]$_0$ = 1:1:2 (A: $n=1$; B: $n=2$; C: $n=3$), 100 °C for 12 h, in bulk.

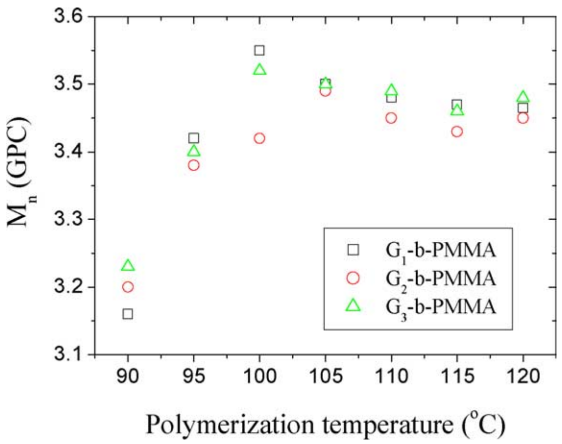

Fig. 2. Variation of M_n with polymerization temperature. Polymerization conditions: $[MMA]_0/[G_n\text{-}Cl]_0/[CuCl]/[Bipy] = 350:1:1:2$; 12 h; in bulk.

G_n-*b*-PMMA ($n = 1$–3) in solution, the polymer solutions with THF and water as solvents are prepared and the concentration of polymer fixes at 1 mg/ml in the mixed solvent. Then the mixture was shaken for 30 s and deposited for 6 h before measurement. Samples for TEM were prepared by aerosol spraying a dilute micellar solution (ca. 50 mL, ca. 1.0 mg mL^{-1}) onto 200-mesh gilder copper TEM grids.

2.4. Characterizations

^{1}H NMR spectra were recorded with an AVANCE DMX-500 NMR spectrometer by using tetramethylsilane (TMS) as internal standard at room temperature. The gel permeation chromatography (GPC) measurements were carried out on a Waters 201 with a μ-styragel column and tetrahydronfuran (THF) as an eluent, and the molecular weight was calibrated with standard polystyrene (PS). Differential scanning calorimetry (DSC) was carried out on a DS822 with a heating rate of 20 °C/min from 40 to 200 °C under nitrogen atmosphere, relative to indium standards. Infrared spectra were recorded on Jasco IR-700 infrared spectrophotometer. TGA was performed on a Netzsch STA 409 PG/PC instrument (Germany) at a heating rate of 20 °C/min from 40 to 500 °C in a flow of nitrogen. Transmission electron micrographs were obtained on a JEOL model 1200EX instrument operated at an accelerating voltage at 160 kV. The molar conversion was obtained on the basis of the weight and copolymer composition.

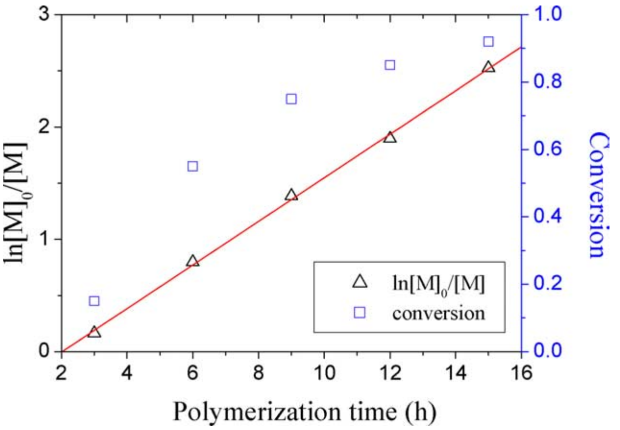

Fig. 3. Variation of M_n and conversion with polymerization time (h). Polymerization conditions: $[MMA]_0/[G_1\text{-}Cl]_0/[CuCl]/[Bipy] = 350:1:1:2$; 100 °C; in bulk.

3. Results and discussion

Macroinitiator and the synthetic strategy followed for the preparation of well-defined dendritic-linear block copolymers via the ATRP route are depicted in Scheme 1.

3.1. Polymerization analysis

As with other living radical polymerization methods [17,18], ATRP offers high degrees of conversion and tolerance for a variety of functional groups, while still allowing for control of the molecular weight and narrow molecular weight distributions. The polymerizations of MMA are carried out in a sealed tube by using CuCl as catalyst and bipy as ligand in the presence of macroinitiator (G_1-Cl, G_2-Cl and G_3-Cl) at certain temperature, the results are shown in Table 1. It is found that MMA with dendritic macroinitiator can be polymerized successfully by ATRP to give dendritic-linear block copolymers with relatively narrow polydispersity ($1.20 < M_w/M_n < 1.58$). In the polymerization of G_n-Cl with MMA at 120 °C shown in Table 1, the CuCl/bipy seems to be a suitable catalyst system and relatively high conversion and molecular weight is obtained. As shown in Table 1, the copolymers synthesized using the G_2-Cl and G_3-Cl as macroinitiators have lower molecular weights and lower conversion.

In the course of polymerization, the relation between M_n and conversion with the molar ratio of MMA to macroinitiator are shown in Fig. 1. As shown in Fig. 1, the M_n of polymers increases with the increasing of the molar ration of MMA to macroinitiator. For example, the M_n of the polymers for sample G_1-*b*-PMMA that synthesized with molar ratio of macroinitiator to MMA at 1:350 is near 2.2 times to that at 1:150. Both the M_n (NMR) and M_n (GPC) are slightly higher the expected value and the value of M_n (NMR) is much closer to M_n (calc.) than M_n (GPC). This phenomenon can be ascribed to the structure of resultant polymers because of their different hydrodynamic volumes compared with linear polymer having the same molecular weight [19]. According to Fig. 1, the polymerization reactions possess relatively high conversion. Similar relations are also observed in the polymerization of MMA with G_1-Cl and G_3-Cl.

M_n polts for the reaction temperature is shown in Fig. 2. It can be seen that M_n of three kinds of dendritic-linear copolymer increases with improving the reaction

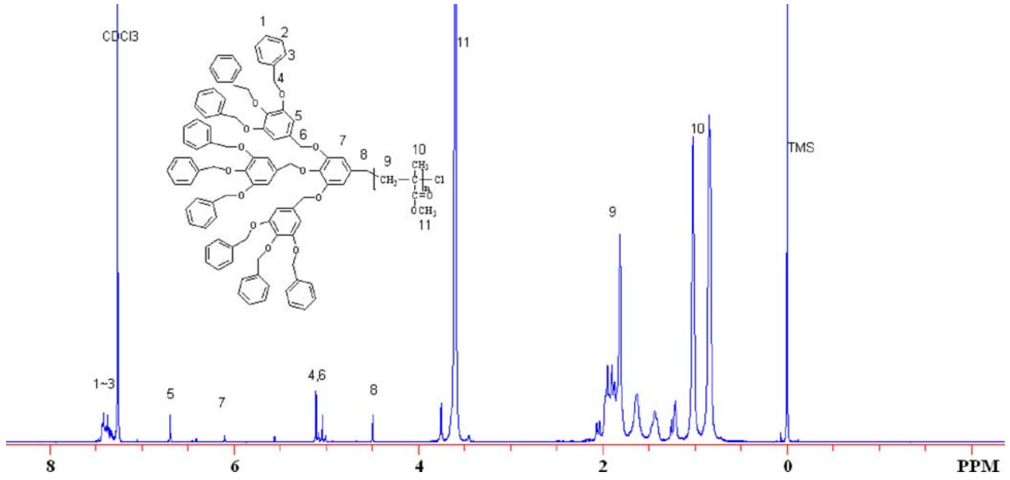

Fig. 4. ^{1}H NMR spectrum of G_2-*b*-PMMA.

temperature from 90 to 100 °C, and decreases with further improving the reaction temperature to 120 °C. This can be attributed to the fact that the speed of chain propagation increases with the increase in reaction temperature. However, the speed of chain transfer has the similar relationship. M_n decreasing at the relatively higher temperature, can be attributed to the speed of chain transfer is higher than that of chain propagation.

For when the polymerization conditions were $[MMA]_0$:$[G_1\text{-Cl}]_0$:[CuCl]:[Bipy] = 350:1:1:2, the relationship between the molar conversion and polymerization is shown in Fig. 3. The linear relationship of $\ln([M]_0/[M])$ versus time shows first order polymerization kinetics, and this suggests that the concentration of the active species is constant and the termination reactions are negligible during polymerization period [20,21].

3.2. Characterization and thermal properties

^{1}H NMR, FTIR, DSC and TGA techniques were made characterization of dendritic-linear block copolymers. The ^{1}H NMR spectrum of G_n-*b*-PMMA show the characteristic at 0.90 ppm for methyl protons, the overlapping peaks around chemical shifts from 1.71 to 2.01 ppm are derived from the protons of methylene in MMA, 3.80 ppm for methoxy (–OCH_3) protons of PMMA. These spectra are in agreement with its expected structure. Fig. 4 gives the ^{1}H NMR spectrum of block copolymer G_2-*b*-MMA.

IR spectroscopy can be used to examine the manner in which the polymer chains are intercalated, restricted, or associated with. The detail of the vibration bands of G_1-*b*-PMMA is shown in Fig. 5. The IR spectrum of the G_1-*b*-PMMA block copolymer showed characteristic absorptions at 1720 cm^{-1} and 1100 cm^{-1}due to the carbonyl group and the C–O–C stretching band of the PMMA and the absorptions at 3000–3100 cm^{-1} correspond to the C–H stretching of the phenyl groups, indicating the successful copolymerization of poly(benzyl ether) and MMA.

Thermal degradation studies with TGA. TGA is a technique used to accurately track the in situ weight changes of a sample during a heating process, thereby providing information on thermal degradation. Fig. 6 shows the TGA curves of three polymers, marked by A, B and C, respectively. From the Fig. 6, it is evident that the thermal degradation of the samples involved two different steps in the whole process. The first temperature region at around

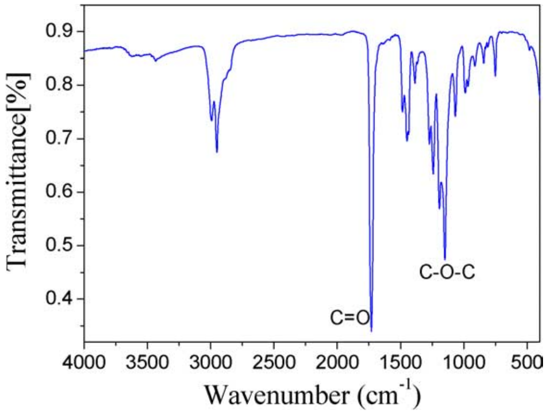

Fig. 5. FTIR spectrum of G_1-*b*-PMMA.

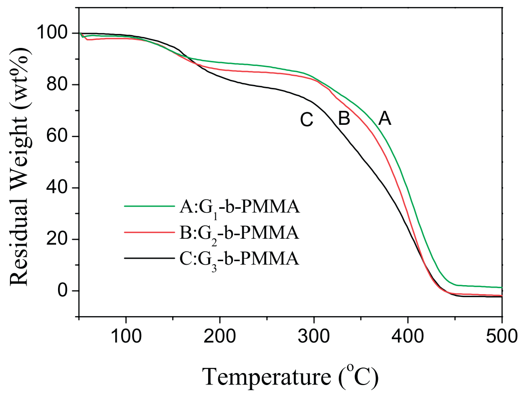

Fig. 6. TG curves of three dendritic-linear diblock copolymers.

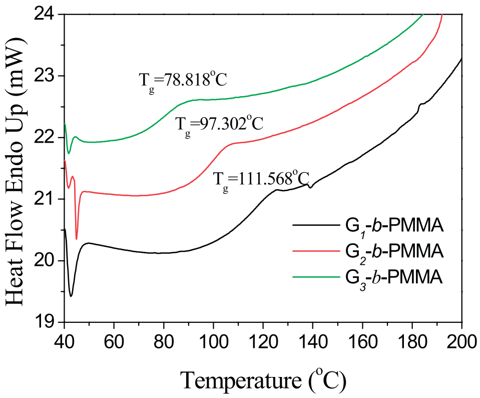

Fig. 7. DSC curves of three dendritic-linear diblock copolymers.

120 °C is mainly due to evaporation and decomposition of the unreacted free monomer in the bulk polymer. The second stage corresponds to degradation and char of the PMMA segments. Dendritic segments have little effect on the resultant polymers compared with PMMA homopolymer for the relatively low content in the polymers. Fig. 7 indicates the DSC trace of block copolymers. As expected, the generation number of the dendritic blocks affects glass transition temperature (T_g). The higher generation number of the dendritic block, the lower the T_g. Only a single T_g was observed throughout the whole composition rang, and the T_g systematically decreases with the increasing the generation number of dendritic block. All the T_g of three polymers is lower than that of PMMA homopolymer.

3.3. Self-assembly behaviors

In order to estimate the aggregation behaviors of G_n-*b*-PMMA ($n=1$–3) in solution, the polymer solutions with THF and water as selective solvents are prepared and the concentration of copolymer fixes at 1 mg/ml in the mixed solvent. The resultant mixture was shaken for 30 s and deposited for 6 h before measurement. Fig. 8 shows TEM images of spherical aggregates from the solution of G_n-*b*-PMMA in THF/H_2O mixed solvent (THF/H_2O = 9:1, v/v). Spherical aggregates have a narrow size distribution with the diameters in 0.30–0.80 μm: about more than 90% in the 0.30–0.35 μm range for G_1-*b*-PMMA, 0.45–0.66 μm for G_2-*b*-PMMA and 0.65–0.8 μm for G_3-*b*-PMMA, respectively.

Fig. 9 shows the variation of micro-sphere diameter with volume ratio of selective solvent. Clearly, the diameter of the micro-sphere increases with the increasing of the generation number of the dendritic segment of the copolymers, which possibly suggests the increasing of the steric effect and the repulsive forces of dendritic blocks to form larger micelles. Meanwhile, the aggregate size depends strongly on volume ratio of THF and H_2O in mixed solvent. When the volume ratio increases from 10 to 70%, the morphology of the resulting micelles is similar to those in Fig. 8, while the diameter decreases from 10 to 50% for G_1-*b*-PMMA and from 10 to 30% for G_2-*b*-PMMA and G_3-*b*-PMMA, and then increases from 50 to 70% for G_1-*b*-PMMA and from 30 to 70% for G_2-*b*-PMMA and G_3-*b*-PMMA.

The possible reasons for that is the dendritic poly(benzyl ether) segments have a fairly strong steric effect, they will encounter strong repulsive forces when trying to accommodate the micro-sphere's density. These repulsive forces could counterpoise the favorable association of long flexible chain blocks and prevent the infinite aggregation of diblock copolymers. A balance of attractive and repulsive forces among blocks could mediate the formation of supermolecular units. When the relatively less water in the mixed solvent, PMMA cannot dissolve completely in water and the association of weak hydrophilic polymer core is stronger than the repulsive forces of hydrophobic shell. After the evaporation of solvents, the formed micelles might have a spherical morphology in shape due to the lowest of the surface energies [22].

4. Conclusions

The preparation of hybrid dendritic-linear block copolymers by atom transfer radical polymerization was studied. The first, the dendritic poly(benzyl ether) macroinitiators were synthesized. Then, the hybrid dendritic-linear block copolymers possessing well-defined molecular weights and low polydispersities using CuCl/Bipy complex catalyst were prepared. Because the dendritic block is more liable to

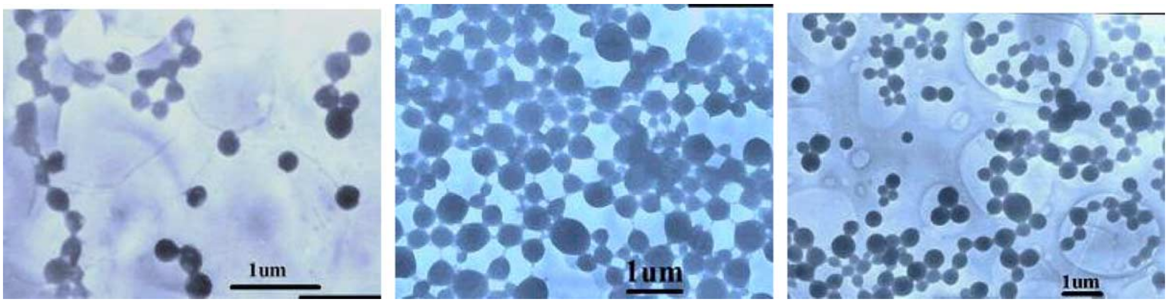

Fig. 8. TEM photograph of the micelles formed by G_1-*b*-PMMA (left), G_2-*b*-PMMA (middle) and G_3-*b*-PMMA (right) in the mixed solvent (THF/H_2O = 9:1, v/v).

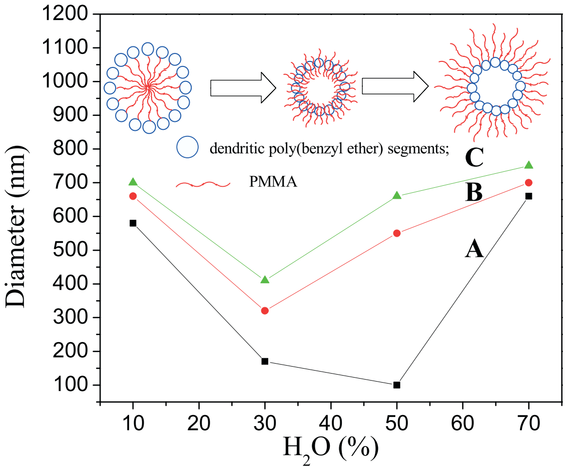

Fig. 9. Variation of diameter with volume ratio of selective solvent: (A) G_1-*b*-PMMA; (B) G_2-*b*-PMMA and (C) G_3-*b*-PMMA.

heat than the linear one, the hybrid dendritic-linear copolymers show lower thermal stability than the PMMA. Spherical micelles can be formed in selective solvents (THF/H_2O).

Acknowledgements

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