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Synthesis and self-assembly study of two-armed polymers containing crown ether core

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Abstract

Two functional crown ether initiator, bis[4′-(2-bromobutyryl)]dibenzo-18-crown-6 (BBDC) was synthesized through the condensation of dibenzo-18-crown-6 with 2-bromobutyric acid in the presence of polyphosphoric acid. Atom transfer radical polymerizations of styrene (St), methyl acrylate, methyl methacrylate and butyl acrylate were carried out in bulk to produce the polymers with well-controlled molecular weights and narrow molecular weight distributions (1.12–1.32). Based on ^{1}H NMR results, both the two bromides of BBDC initiated the polymerizations. The well-defined two-armed polymers were self-assemblized in the presence of potassium cations. Their morphologies of the film obtained were studied by atomic force microscopy with tapping mode. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Two-armed polymer; Self-assembly; Atomic force microscopy

1. Introduction

Due to the special ability of crown ethers to complex with cations, they have been extensively used in chromatography, extraction, catalysis, electroanalysis and separation processes involving membranes [1–6]. In the membrane applications, it has been extensively studied that crown ethers were employed as the ligand membranes in the separation of alkali metal [4]. Thunhorst [5,6] focused on studying the fixed site carrier membranes, in which reactive sites are chemically bonded to the polymeric matrix. Thus, the notorious instability of the liquid membrane can be improved. The compounds containing crown ether can form ordered structure [7–9], for example, crown ether substituted by phthalocyanines can self-assembled into a well-defined structure [7,9], and the crown ether moieties in the assembly form ion channels [7]. The glass transition temperature of the polymers carrying crown ether as side groups increased when alkali metal ions were added, because the oxygen–metal coordination will lead the polymer to have order structure [10]. However, the self-assembly of the polymer containing crown ether has not been reported to date. We want to synthesize two-armed polymers in which crown ether is centered, and the polymer film prepared by self-assembly technology is expected to form well-defined order, such as ion channels, and will have special properties.

It is essential that the polymers have well-defined structure for the purpose of self-assembly. In recent years, a variety of polymers carrying crown ethers have been reported. The crown ethers can be part of a main chain, or pendent groups anchored to a polymer backbone or terminal groups of a macromolecular chain, their synthetic methods were reviewed by Yagci [11]. Similar to our target polymer structure, the polymers with end-standing crown ether were synthesized by two general methods. In the first method, the polymerization of a monomer is initiated by an initiation group attached to a crown ether. The only example of this method was reported by Akashi et al. [12]. Litho crown ether derivative acted as an anionic initiator for the polymerization of a vinyl substituted styrene monomer. The second, radical chain transfer polymerization has been utilized to produce polymers with crown ether end groups, in which the crown ether derivative was used as a chain transfer agent [13].

The molecular weight of the polymers prepared by the anionic living polymerization can be controlled, and their molecular weight distribution is narrow. However, such results cannot be achieved in chain transfer method. Recent progress in controlled/living radical polymerization offers the technique to synthesize well-defined polymers [14].

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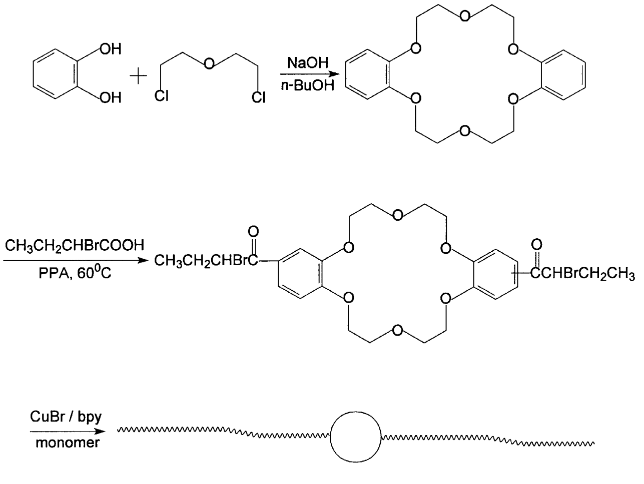


Scheme 1.

Here, we employed the first synthetic method to prepare the polymers with the crown ether centered in the polymer chain. At first, two functionalized dibenzo-18-crown-6 initiator was synthesized, and then well-defined two-armed polymers were synthesized by atom transfer radical polymerization (ATRP) (Scheme 1). In this paper, we also report their self-assembly results.

2. Experimental section

2.1. Materials

All the reagents were of analytical grade, and purchased from Shanghai Reagents Co. Styrene (St), methyl acrylate (MA), methyl methacrylate (MMA) and *n*-butyl acrylate (BA) were all washed three times with aqueous solution of sodium hydroxide (5 wt%), and then with water until neutralization. After drying with anhydrous magnesium sulfate, the monomers were distilled at reduced pressure. Dibenzo-18-crown-6 was prepared according to Peterson's paper [15]. ^{1}H NMR ($CDCl_3$, ppm) δ: 6.6–6.9 (m, ArH, 8H), 3.7–4.2 (m, 8OCH_2, 16H). Mp: 161–163 °C. Other agents were used as received without further purification.

2.2. Synthesis of bis[4′-(2-bromobutyryl)]dibenzo-18-crown-6

Into a 100 ml three-neck round-bottle flask with mechanical stir, polyphosphoric acid (PPA, 30 ml) was added. After heated up to 50–60 °C, dibenzo-18-crown-6 (1 g, 2.9 mmol) was added, and dissolved while stirring. Then, 2-bromobutyric acid (2 g, 12 mmol) was added into solution. The mixture was reacted at 70 °C under stirring for 24 h. After cooled to room temperature, distilled water (60 ml) was dropped slowly with stirring to decompose PPA. After completion of addition, the mixture was further stirred for an additional 30 min, and then extracted by chloroform (3 × 50 ml). The combined extracts were washed with saturated sodium carbonate two times, and then with distilled water until neutralization, dried over anhydrous sodium sulfate. After solvent was evaporated under reduced pressure, the crude product was obtained in 58% yield. After recrystallization from benzene, a white crystal was obtained. Mp: 165–167 °C.

IR (KBr, cm^{-1}): $\nu = 1669$ (C=O), 1596, 1516 (aromatic C=C), 1271, 1138 (aromatic and aliphatic C–O–C), 634 (C–Br).

^{1}H NMR ($CDCl_3$, ppm) δ: 7.63, 7.56, 6.87 (m, ArH, 6H), 5.05 (t, 2CHBr, 2H), 4.24, 4.04 (two t, 8OCH_2, 16H), 2.21, 2.11 (m, 2CH_2CH$_3$, 4H), 1.08 (t, 2CH_3, 6H).

2.3. ATRP

The polymerization conditions and feed ratio are listed in Table 1. A general procedure is as follows. Into a 10 ml glass tube, CuBr, bipyridine (bpy), bis[4′-(2-bromobutyryl)]dibenzo-18-crown-6 (BBDC) and monomer were successively added. The heterogeneous mixture was first degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum, and then immersed in an oil bath thermostated at presetting temperature. After the reaction was carried out for a prescribed time, the tube was rapidly

Table 1

Conditions and results for ATRP of various monomers with BBDC as initiator (all the polymerizations were carried out in bulk with feed molar ratio: [monomer]/[BBDC]/[CuBr]/[bpy] = 400:1:2:6)

Entry	Monomer	Temperature (°C)	Time (h)	Conversion[a] (%)	M_n (th)[b] ($\times 10^3$)	M_n (NMR)[c] ($\times 10^3$)	M_n (GPC) ($\times 10^3$)	MWD
1	St	110	1.5	12	5.6	5.7	5.4	1.25
2	St	110	3	29	12.7	13.6	13.7	1.25
3	MA	100	1.5	22	8.2	8.4	–	1.28
4	MA	100	3	50	17.8	17.3	–	1.11
5	BA	100	1.5	24	11.6	12.3	–	1.32
6	BA	100	3	46	21.6	21.5	–	1.12
7	MMA	60	0.5	16	7.0	7.2	–	1.18

[a] Calculated based on ^{1}H NMR data.

[b] $M_n\,(\text{th}) = (M_m \times \text{conversion} \times [M]_0/[\text{BBDC}]_0) + M_{\text{BBDC}}$, where M_m and M_{BBDC} are the molar masses of monomers and initiator BBDC, respectively.

[c] M_n (NMR) was calculated with 500 MHz ^{1}H NMR data.

cooled to room temperature by ice water, and the polymer solution in THF was passed through a short column of neutral alumina for removing the metal salt. The polymer was precipitated from an excess of methanol, filtered and dried at 50 °C under vacuum for 24 h. The conversion was obtained by ^{1}H NMR method.

2.4. Characterization

^{1}H NMR spectra were determined on a Bruker DMX-500 nuclear resonance instrument with $CDCl_3$ as solvent and tetramethylsilane (TMS) as standard. IR spectra were recorded on a Vector-22 FTIR instrument. The measurement of molecular weights and molecular weight distribution of the polymers were carried out on a water 150C gel permeation chromatography (GPC) equipped with microstyragel columns (500, 10^3 and 10^4 Å) and poly(styrene)s as standards. THF was used as eluent at a flow rate of 1.0 ml/min.

Atomic force microscopy (AFM) observation was performed on DI Nanoscope IIIa with tapping mode, and the AFM images were obtained at room temperature in air. The AFM samples were prepared as follows: a drop of 0.5 wt% of polymer solution in THF saturated with potassium iodide was placed on the surface of silicon slide, and then spin-coated at 1000 rpm for 3 min at room temperature.

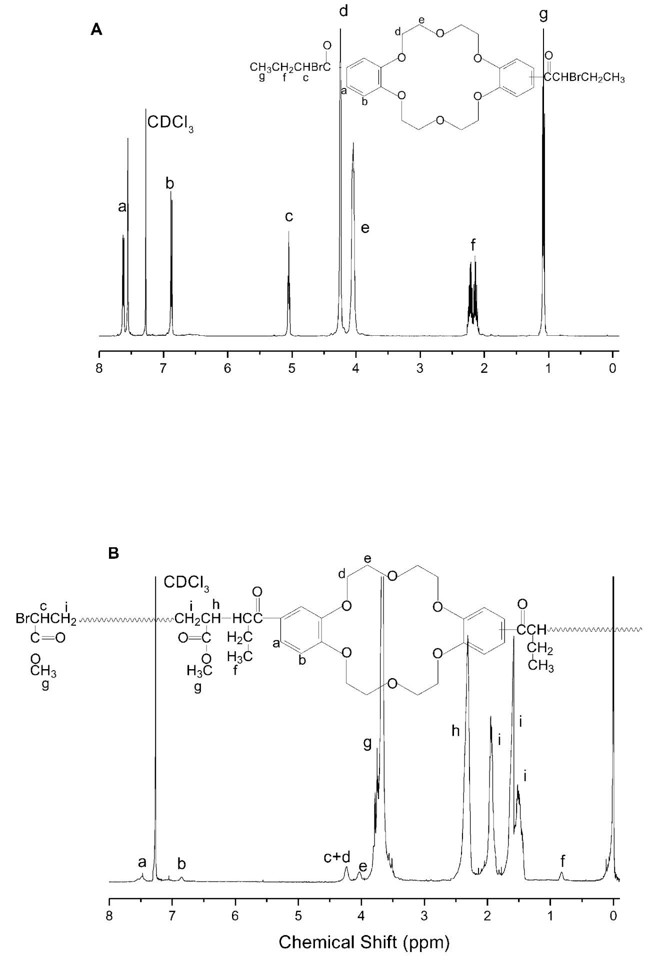


Fig. 1. The ^{1}H NMR spectra of two functional crown ether initiator BBDC (A) and polyMA initiated by BBDC (B, entry 3 in Table 1).

3. Results and discussion

3.1. Synthesis of two-armed polymer with crown ether core

The ATRP of monomers, St, MA, BA and MMA were carried out in bulk. The conditions and results are listed in Table 1. It can be observed that as polymerization proceeded, the conversion and molecular weight increased, the molecular weight distribution became narrower, which are general phenomena observed in ATRP. All the polymers obtained were characterized by ^{1}H NMR spectroscopies. Fig. 1 shows the ^{1}H NMR spectra of initiator BBDC and polyMA. In Fig. 1(B), the peaks at 3.66, 2.17 and 1.96–1.69 ppm are the methyl, methine and methylene protons of MA unit in polyMA. Peaks at 7.60–7.42 (a), 6.86 (b), 4.23 (c + d), 4.04 (e) and 0.82 ppm (f) are ascribed to the aromatic protons, end-standing methine proton and methylene protons adjacent ether oxygen, methyl protons of crown ether initiator. Comparison with the spectrum of BBDC in Fig. 1(A), the peak at 5.05 ppm (c in Fig. 1(A)) corresponding to methine proton next to bromine atom is completely disappeared, and the peak of methyl protons at 1.08 ppm in Fig. 1(A) is shifted to 0.82 ppm in Fig. 1(B). The peak at 4.23 ppm corresponding to methine proton next to bromine atom at the end of polymer is overlapped by peak of the methylene protons in crown ether unit. However, the integral ratio of the peaks at 7.60–7.42, 6.86, 4.23, 4.04 and 0.82 ppm is approximately 2:1:5:4:3, respectively, indicating that the two bromides of BBDC took part in the initiation reaction and the two-armed polymers were formed. Based on the integral values of characteristic peaks of polymer backbone and initiator core, the number average molecular weight M_n (NMR) can be calculated, and the results are listed in Table 1. The agreement of M_n (th) with M_n (NMR) demonstrates that the polymerization can be controlled. The crown ether moiety does not influence the ATRP of St, MA, BA and MMA.

3.2. The self-assembly of two-armed crown ether contained polymer

Although interaction among crown ether moieties exists, it is not strong enough to self-assembly into regular structure. For obtaining highly ordered morphology by self-assembling method, the crown ether must be modified to get strong interaction between them, such as phthalocyanine [7–9]. In addition, another way of improving the interaction between crown ether moieties is addition of alkali metal ions into a solution of the polymer with

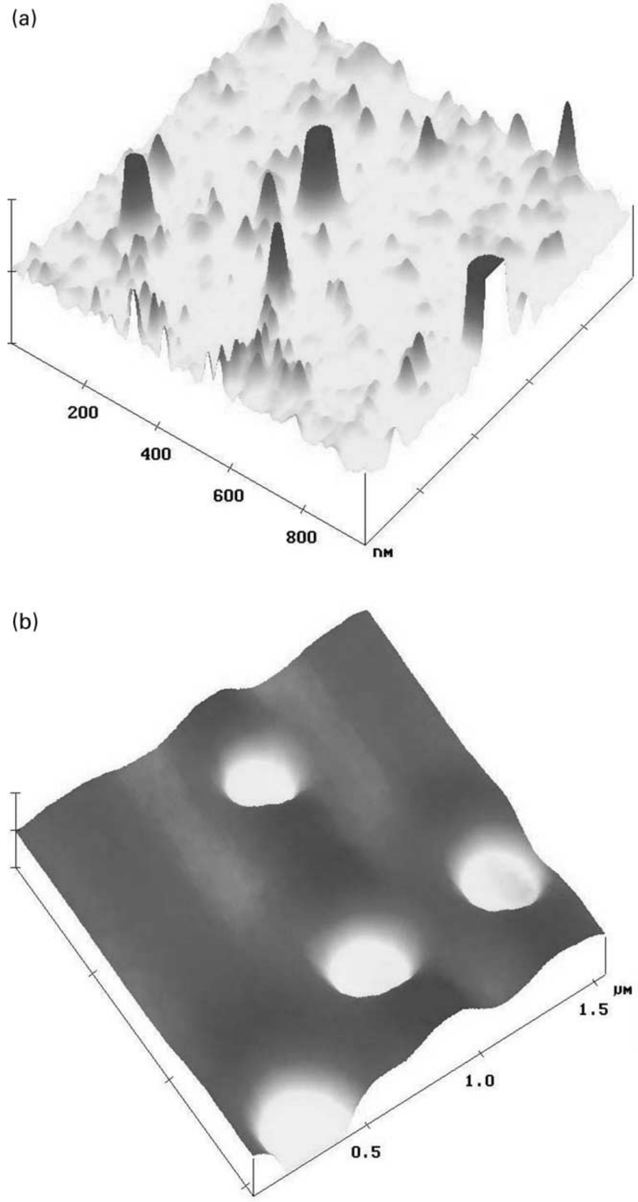


Fig. 2. The AFM images of sample polySt1 film (entry 1 in Table 1) self-assembled in pure THF solution (a) and in THF saturated with potassium iodide (b).

crown ether group. The complexation of crown ether with metal cations might impel the accumulation of the crown ether moiety, and further form ordered structure. This is the reason that the glass transition temperature of the polymers containing crown ether group increased when alkali metal ions were added [10].

Similar phenomenon was observed in our experiments. Fig. 2(a) and (b) are the AFM images of the same sample polySt1, the only difference is that in the formation of self-assembling films, the former used polymer solution in pure THF solution, the latter used solution in THF saturated with potassium iodide. Fig. 2(a) shows irregular structures due to the lack of strong interaction between crown ether moieties.

Table 2

The related data of self-assembled polymer film based an AFM images (polyMMA was detected on a Scanning Probe Microscope, Model TMX 2000 (TopoMetrix))

Sample[a]	M_n (NMR) $(\times 10^3)$	Diameter (nm)	Depth or height (nm)
PolySt1	5.7	317	45
PolySt2	13.6	1730	130
PolyMA1	8.4	–	–
PolyMA2	17.3	–	–
PolyMMA	7.2	352	51

[a] PolySt1: entry 1, PolySt2: entry 2, PolyMA1: entry 3, PolyMA2: entry 4, and PolyMMA: entry 7 in Table 1, respectively.

However, Fig. 2(b) demonstrates hole structures. This might be ascribed to the complexing interaction of crown ether with potassium cations, which will impel the accumulation of crown ether moieties and form ordered structures. The AFM images of other polymer films prepared by self-assembly are shown in Fig. 3, and related data are listed in Table 2.

During the self-assembly of the polymer with crown ether moiety, two interactions between crown ethers and between polymer chains must be considered. The energy competition between two interactions must affect the self-assembly morphologies. For the different polymers with the same interactions of crown ether moieties, the polymer chain is the key factor influencing the self-assembly results.

Considering different chain structures of polyBA, polyMA, polyMMA and polySt, we will find that the flexibility of the polymer chains increases according to the following order: polyBA $>$ polyMA $>$ polyMMA $\sim$ polySt. When these polymers have similar molecular weight, their glass transition temperatures increase in the same order. Strong flexibility will impede the formation of ordered structures. Due to low glass transition temperature of polyBA, no good morphology was acquired. However, the self-assembly of polyMA with crown ether moieties formed big hollow spots on the surface of the film, we can see clearly the polymer chain in the bottom of each spot (Fig. 3(b) and (c)). This is probably related to T_g increase of polyMA comparison with polyBA. The movement of polyMA chains during the evaporation of THF interferes the formation of regular holes, and crown ether moieties accumulate big hollow spots with diameter of $\sim 15\ \mu m$. With the flexibility decrease of polymer chains, polySt1 and polyMMA can form hole structure with diameters and depths around 300 and 50 nm, respectively (see Figs. 2(b) and 3(d)). The strong interaction between crown ether moieties will push them to form ordered structures.

As for the effect of polymer chain length on the morphologies, different results appeared for different polymers. Fig. 3(b) and (c) is the AFM images of the films prepared from self-assembly of polyMA with molecular weights of

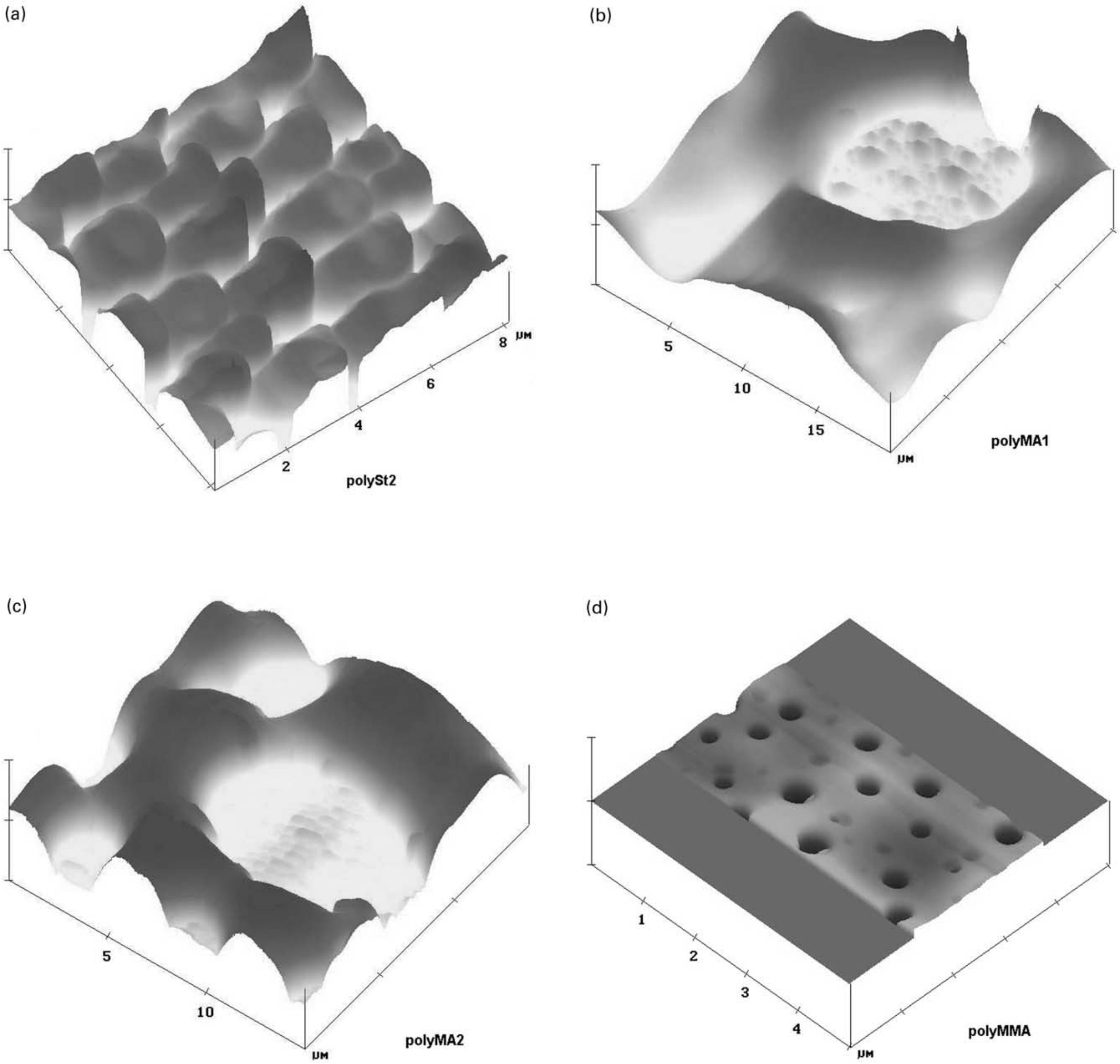


Fig. 3. The AFM images of two-armed polymers in THF solution saturated with potassium iodide after self-assembly on the surface of silicon slides, (a) polySt2 (entry 2 in Table 1), (b) polyMA1 (entry 3), (c) polyMA2 (entry 4), (d) polyMMA (entry 7). [PolyMMA was detected on a Scanning Probe Microscope, Model TMX 2000 (TopoMetrix)].

8.4×10^3 and 1.73×10^4, respectively. Comparison of Fig. 3(b) with (c), the increase of molecular weight does not influence the morphologies obviously. However, the situation of polySt is different. As we know, the chains of polySt are more stiff than that of polyMA. In another words, the interaction between polySt chains is stronger than that between polyMA chains. Fig. 2(b) demonstrates that the self-assembly of polySt1 with lower molecular weight (5.7×10^3) formed hole structures, but protuberance morphology of self-assembly film from polySt2 with higher molecular weight (1.36×10^4) was observed in Fig. 3(a). The diameter and height are around 1700 and 130 nm, respectively. The increase of molecular weight will increase the interaction between polymer chains. The two interactions between crown ethers and between polymer chains compete, leading to different morphologies. Carefully observing Fig. 4(a) enlarged from that formed by self-assembly of polySt2 with higher molecular weight (1.36×10^4), there are concavities at the center of every protuberance. Through section analysis, the concavity can be clearly seen in Fig. 4(b).

Based on the above results, the process of self-assembly was supposed as following. We know that the diameter of

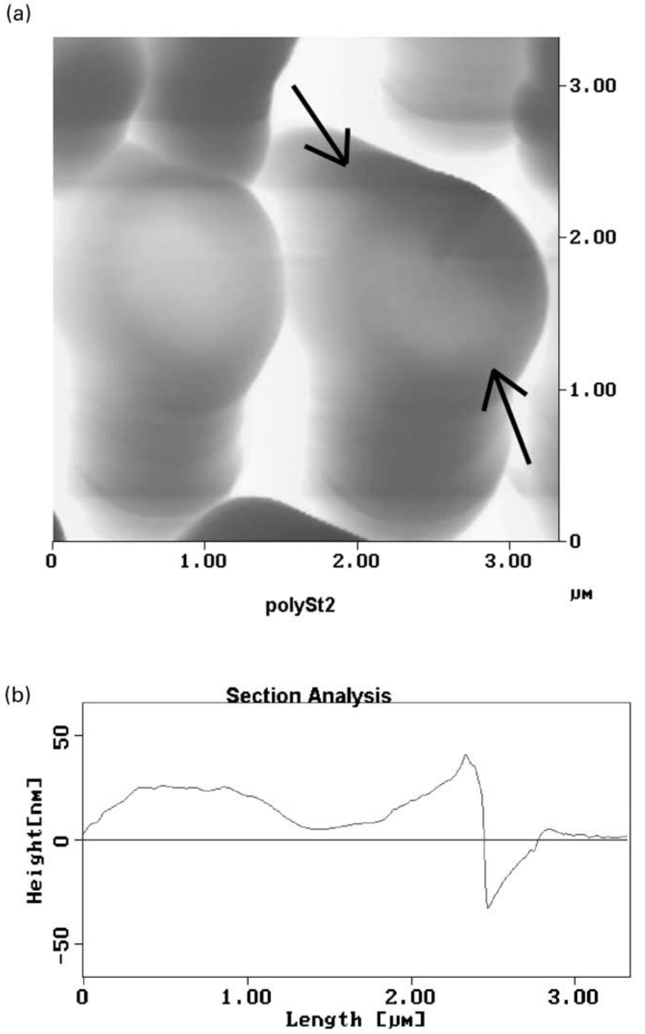
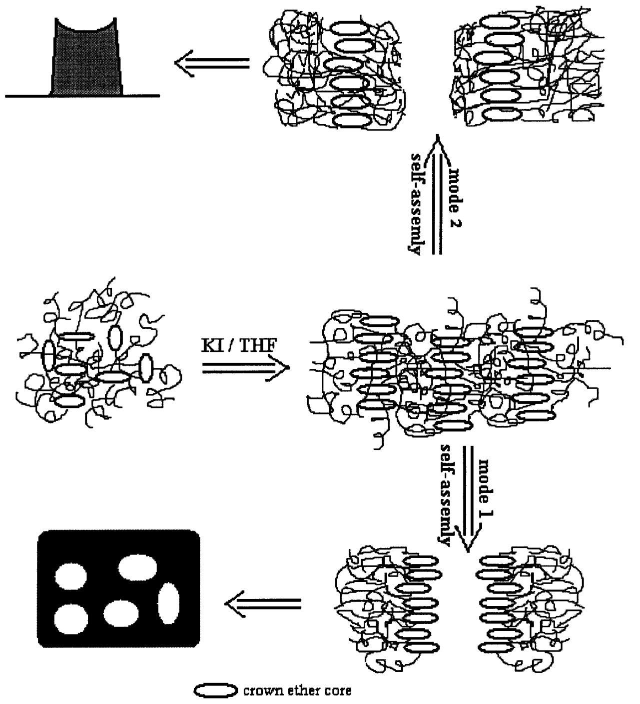


Fig. 4. The enlarged AFM image of sample polySt2 (entry 2 in Table 1) and its section analysis.

single crown ether is around 1 nm. Compared to this, the diameters of the holes are much larger. It infers that the holes are composed of many crown ether moieties. The self-assembly course of two-armed polymers is postulated in Scheme 2. Due to complexing action of crown ethers, the polymer may form an ion's channel structure in potassium iodide saturated solution. After coated on the surface of silicon slide, phase separation might take place with the evaporation of THF. Many crown ether channels are aggregated and juxtaposed, and the polymer chains for polySt1, polyMA and polyMMA are extending outward, and hole structures are formed. Eventually, the polymer films with holes are observed as shown in Figs. 2(b) and 3(b)–(d). But for longer polymer chains such as polySt2, due to stronger interaction between polymer chains, they do not extend outward completely, and much of them are aggregated among crown ethers. Thus, protuberance structures are formed. Because crown ether moieties and less polymer chains exist in the middle of each protuberance, concavity is formed as shown in Figs. 3(a) and 4.



Scheme 2.

4. Conclusions

Well-defined two-armed crown ether contained polymers were synthesized by ATRP of St, MA, BA and MMA using BBDC/CuBr/bpy initiation system. No influence of the crown ether moiety on the polymerizations was observed. Different morphologies were observed when the polymers obtained were self-assembled in the potassium iodide saturated THF solutions. The AFM images indicate that polymer film with holes was formed for polyMMA. PolySt with different molecular weight resulted in different self-assembly results. Hole morphology was obtained for low molecular weight polySt, and protuberance structure for high molecular weight polySt. Special morphology of the film prepared from self-assembly of polyBA was not formed, probably due to its low T_g. The self-assembly of polyMA formed big hollow on the surface of film. It is proposed that the morphologies are formed through accumulation of crown ether moieties. The morphologies are the result of energy competition between crown ether moieties and polymer chains.

Acknowledgements

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