

Morphological Studies on Sn-O Coordination Driving Self-assembly of Well-defined Organotin-containing Block Copolymers^{*}

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Abstract A tin-oxygen coordination driving self-assembly was developed in the block copolymers containing organotin, which were prepared by the radical addition-fraction transfer (RAFT) method and characterized by the gel-permeation chromatography (GPC) and ¹H-NMR. And the self-assemblies of these block copolymers with various chain length ratios in the different concentrations in CHCl₃ were stable according to the results of DLS and TEM. Additionally, it was also given an insight investigation on the regulation of self-assembly of the block copolymers by adding dibutyltin dichloride and a possible mechanism was proposed.

Keywords: Organotin; RAFT; Sn-O coordination; Self-assembly.

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INTRODUCTION

The self-assembly driving force of block copolymers mainly comes from the microphase separation in selective solvent systems. This kind of microphase separation gives rise to the formation of nanoscopic micellar aggregates with various shapes (spheres, cylinders, platelets, vesicles, *etc.*) in which the soluble blocks form the corona and the insoluble blocks form a denser core^[1–11]. In recent years, various non-covalent interactions, such as H-bonding^[12–18], host-guest recognition^[19–22] and metal-ligand coordination interactions^[23–27], have been developed for driving the self-assembly of block copolymers to form the diversified morphology (Fig. 1).

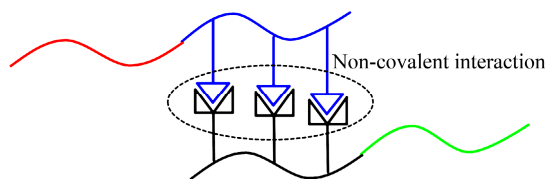


Fig. 1 Application of non-covalent interaction for driving the self-assembly of block copolymers

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Among these non-covalent interactions, the metal-ligand coordination is of particular interest because it is highly directional and a wide range of ligands are available. Moreover, the interaction can be well tuned by choosing appropriate metal ions, ligands, or solvents. In most cases, the metal-ligand coordination is realized by adding the metal ion to the solution of the synthesized ligand-carrying (carboxylic or pyridine group) block copolymers and thus acts as the cross-linker to drive the micellization of the block copolymers^[28–30]. In comparison, there are rare reports about direct coordination with both metal and ligands in the polymer chain to drive the self-assembly of block copolymer. Meanwhile, the self-assembly of organotin carboxylate has brought out considerable structural diversity and topologies^[31–38], which is attributed to the various coordination geometries and coordination numbers of tin as well as the different binding modes with the carboxylate ligand in monodentate or bidentate.

With this in our mind, the organotin carboxylates are designed and introduced into the block copolymer to develop new self-assembly morphology with Sn-O coordination of organotin carboxylate as the direct driving force. In our previous work, a monomer containing organotin (acetoxidybutyltin methacrylate) was prepared and used to synthesize a organotin-containing block copolymer poly(methyl methacrylate-*b*-polyacetoxidybutyltin methacrylate) through RAFT polymerization^[39]. As a consequence, this block copolymer was insoluble in any solvents and the assembly behavior was only roughly studied in a gel-state with THF. In spite of this, well-defined nanoparticles were observed in TEM and SEM observation due to the self-assembly induced by the strong tin-oxygen coordination action. Furthermore, this Sn-O coordination took place during the RAFT polymerization process, this metal-ligand coordination is a "real-time" procedure but not a post-modification pattern. As far as we know, it was undeveloped previously. This result intrigued us to further study the more possible morphologies of this block copolymer with various chain length ratios. Therefore, we herein synthesized three additional organotin-containing block copolymers of different chain length ratios by RAFT method.

EXPERIMENTAL

Measurement

¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker 400 spectrometer operating at 400 MHz using CDCl₃ as the solvent and TMS as the internal standard. FTIR was measured using a Bruker Tensor 27 Spectrometer. Molecular weights and molecular weight distributions were measured on an Agilent Technologies 1200 series gel permeation chromatography (GPC) equipped with a G1362A differential refractive index detector, with tetrahydrofuran (THF) as eluent at a flow rate 1 mL/min. The instrument was calibrated with mono-dispersed polystyrenes. The hydrodynamic diameters of the nanoparticles were measured by a Malvern Zeta Sizer Nano-90 dynamic light scattering (DLS) instrument. The block copolymer was dissolved in CHCl₃ with different concentration, and solution was filtered by 800 nm organic membrane for DLS analysis. The transmission electron microscope (TEM) image was obtained using a JEOL 200CX TEM (JEOL, Japan). Samples were prepared by dipping the solution of 1 mg/mL onto the carbon supported film and dried in air.

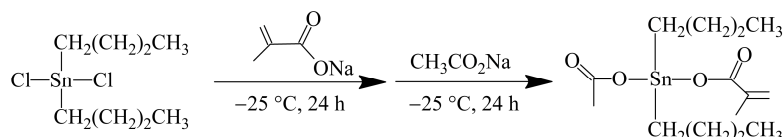
Materials

Methyl methacrylate (MMA) was purchased from Acros (99 wt%), purified by filtration through alumina (to remove inhibitors), stirred with CaH₂ for overnight, and distilled prior to use. Azobis (isobutyronitrile) (AIBN, from J&K.) was recrystallized twice from methanol. Sodium methacrylate and sodium acetate were purchased from Chemical Reagent Corporation. All the solvents were purified prior to use. 2-Cyanoprop-2-yl dithiobenzoate (CPDB) was synthesized according to the literature^[40–43]. Bu₂SnCl₂ was prepared under the literature's condition^[44] and the ¹¹⁹Sn-NMR spectrum (Fig. S1a) was consistent with that in literature^[45, 46].

The Synthesis of Acetoxidybutyltin Methacrylate (ADBTMA)

Acetoxidybutyltin methacrylate was synthesized according to Scheme 1. In a typical reaction, the mixture of 6.052 g (20 mmol) dibutyltin dichloride and 2.150 g (20 mmol, 1.0 equiv.) sodium methacrylate were added into dry dichloromethane (200 mL) and stirred for 24 h at –25 °C under nitrogen atmosphere, and then sodium

acetate (1.700 g, 20 mmol, 1.0 equiv.) was added and stirred for another 24 h at $-25\text{ }^{\circ}\text{C}$ under nitrogen atmosphere. The resulted sodium chloride was removed by filtration. Evaporation of the filtrate under vacuum yielded the product ADBTMA and was used for polymerization without further purification. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ): 6.07 (s, 1H), 5.44 (s, 1H), 1.94 (s, 3H), 1.81 (s, 3H), 1.53 (m, 8H), 1.25 (m, 4H), 0.76 (t, 6H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3 , δ): 180.90, 176.44, 135.71, 126.30, 26.13, 25.71, 24.56, 19.84, 17.93, 12.94; $^{119}\text{Sn-NMR}$: $\delta = -153.796$ (Fig. S1b).



Scheme 1 The route for the synthesis of acetoxydibutyltin methacrylate

RESULTS AND DISCUSSION

For the synthesis of the monomer, acetoxydibutyltin methacrylate (ADBTMA), some improvements were made on the basis of previous literatures^[47, 48]. Herein, we employed a step-adding material in a simple one-pot methodology to prepare the organotin monomer and characterized it by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and $^{119}\text{Sn-NMR}$ (Scheme 1). Due to its low melt point, we failed to get the single crystal of this monomer. Using this organotin containing monomer, three different organotin-containing block copolymers were then synthesized *via* RAFT polymerization by varying the length of PMMA macro-initiator (Scheme S1). To our satisfaction, these block copolymers obtained can dissolve in some organic solvents (THF, toluene and CHCl_3) but with a micelle solution state. And in $^1\text{H-NMR}$ with CDCl_3 as solvent, only the signal of the PMMA block was observed without that of organotin block. It may be caused by the self-assembly driven by the inter-chain (Fig. 2a) or intra-chain (Fig. 2b) coordination of organotin and carboxyl group. To ascertain the block ratio, a few drops of trifluoroacetic acid were added into the NMR tube, with the purpose of destroying the self-assembly behavior by dissociating organotin from the polymer chain, based on the substitution reaction between organotin carboxylate and Bronsted acid^[49–52]. As a result, the solution of block copolymer in CDCl_3 became transparent immediately and the signal of $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ on the organotin block appeared in $^1\text{H-NMR}$. Based on that, the ratios of blocks were calculated by comparing the signal of $-\text{OCH}_3$ to $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (Fig. S2). The block ratios of the three block copolymers are listed in Fig. S2.

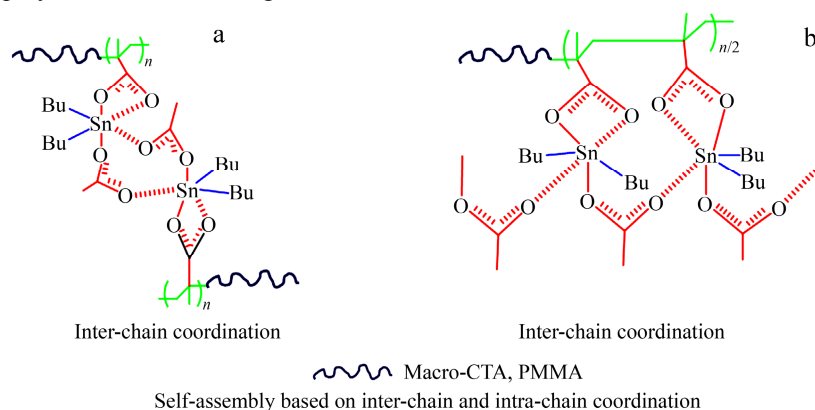


Fig. 2 Diagrammatic presentation of self-assembly

Then these three block copolymers were characterized by GPC (Fig. 3). Surprisingly, the GPC image exhibits two distributions. One is a broad peak with larger molecular weight, the other is a narrow peak with lower molecular weight. It was conjectured that the wide distribution (Fig. 3, peak 1) ascribed to the aggregation of the self-assembly of the block copolymer *via* tin-carboxyl coordination (Fig. 5a). The narrow distribution

(Fig. 3, peak 2) corresponded to the free block copolymer chains or single chains coiled due to the intra-chain coordination as depicted in Fig. 5(b). Consequently, there is a large deviation between number-average molecular weight measured by GPC and theoretical molecular weight determined by $^1\text{H-NMR}$ (Table 1). In addition, the positive proportional relationship between the self-assembly extent and the content of organotin involved in the block copolymer was reflected in the polydispersity index (PDI) changing from 1.24 to 2.10 in the region of large molecular weight (Table 1). That's to say, the more content of tin, the stronger the self-assembly extent, and thus the wider the PDI. Noteworthy, the block copolymer of $\text{PMMA}_{176}\text{-}b\text{-PADBTMA}_{28}$ has an additional shoulder aside the high molecular weight. It may be due to the second aggregation of the formed nanoparticles because of more tin content.

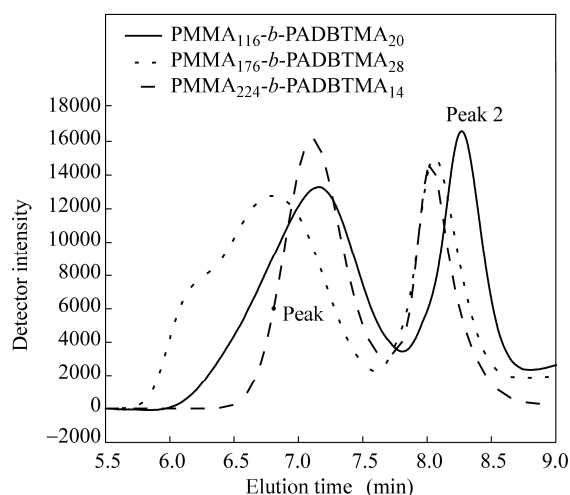


Fig. 3 GPC curves of three block copolymers

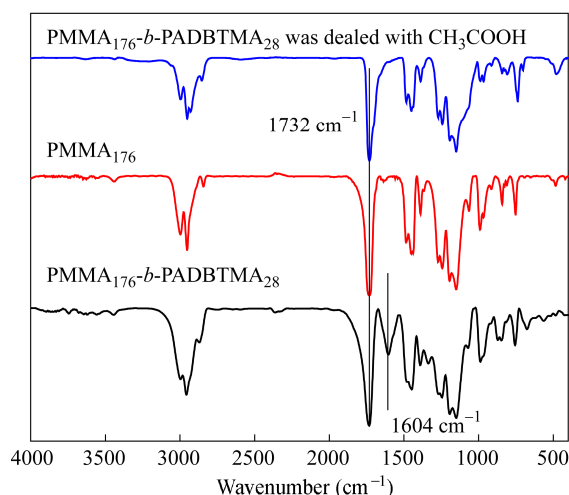


Fig. 4 The IR change of $\text{PMMA}_{176}\text{-}b\text{-PADBTMA}_{28}$ before and after dealt with acetic acid

Table 1. The molecular weight of the three different block copolymers

Block copolymer	$M_{n\text{peak 1}}$	PDI	$M_{n\text{peak 2}}$	PDI	M_n (NMR)
$\text{PMMA}_{176}\text{-}b\text{-PADBTMA}_{28}$	439000	2.10	22100	1.14	28400
$\text{PMMA}_{116}\text{-}b\text{-PADBTMA}_{20}$	208000	1.78	15000	1.11	19400
$\text{PMMA}_{224}\text{-}b\text{-PADBTMA}_{14}$	202000	1.24	22600	1.11	28000

To confirm that the self-assembly driving force comes from the coordination between tin and carboxyl group, we attempted to remove off the organotin unit from the block copolymer. Namely, the block copolymer was refluxed for 24 h in acetic acid instead of trifluoroacetic acid to avoid the possible acidolysis of PMMA block in strong acid^[49–52]. White powder was obtained after precipitating reaction mixture in petroleum ether. The IR was first used to characterize the obtained powder (Fig. 4). Compared with the spectrum of PMMA_{176} and $\text{PMMA}_{176}\text{-}b\text{-PADBTMA}_{28}$ before and after dealt with the HOAc, it was found that the characteristic absorption peak of organotin carboxylate at 1604 cm^{-1} disappeared, only the carbonyl absorption peak of PMMA block at 1732 cm^{-1} existed. Thus it was concluded that organotin was removed completely after refluxing with acetic acid as shown in Fig. 5, and new block copolymer $\text{PMMA-}b\text{-PMAA}$ was formed, which was then characterized by GPC (Fig. 6). In GPC graphics, only a single narrow peak appeared with a certain shift comparing to the PMMA. It demonstrated that there is no self-assembly action any longer and simultaneously indicated the polymerization was living controllable with the PMMA as macro-initiator. Therefore, the broad peak in GPC for the $\text{PMMA-}b\text{-PADBTMA}$ could be attributed to the self-assembly of the organotin ester part through the mutual coordination. The corresponding molecular weights are listed in Table S1. The deviation between number-average molecular weight measured by GPC and theoretical molecular weight determined by $^1\text{H-NMR}$ was in a reasonable range, and also indirectly proved the block ratios of these block copolymers determined by $^1\text{H-NMR}$ to be reliable.

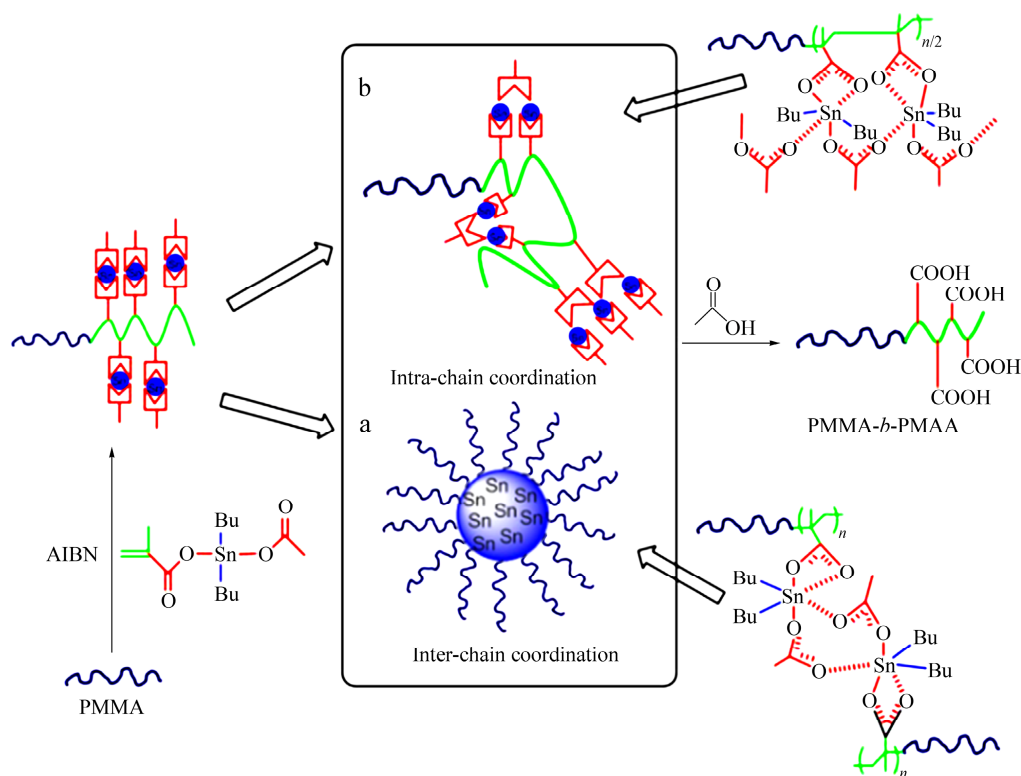


Fig. 5 The self-assembly morphology diagram

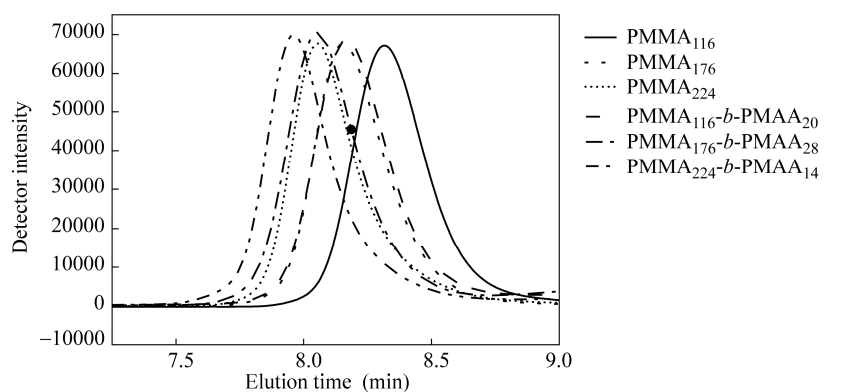


Fig. 6 GPC curves of PMMA and PMMA-*b*-PMAA

The self-assembly action of different chain length ratios block copolymers in chloroform was then seriously investigated by laser dynamic light scattering. For these three block copolymers, when the concentration was fixed at 1 mg/mL in chloroform, it was observed that the dominating sizes were 190.1 nm, 164.2 nm, 50.75 nm in intensity distribution image, 78.82 nm, 68.06 nm, 24.36 nm in number distribution one, respectively (Fig. 7). No matter in intensity distribution or in number distribution, the same trend was found that the nanoparticle sizes increased gradually with more organotin attached to the block copolymer. Just so you know, the number distribution represented the proportion of assembly with a certain size, whereas, the intensity distribution showed the light scattering intensity of some fixed-size assembly. Combining with these two distributions, it could be concluded that the small size nanoparticles are predominant but the minor larger size ones exhibit higher intensity.

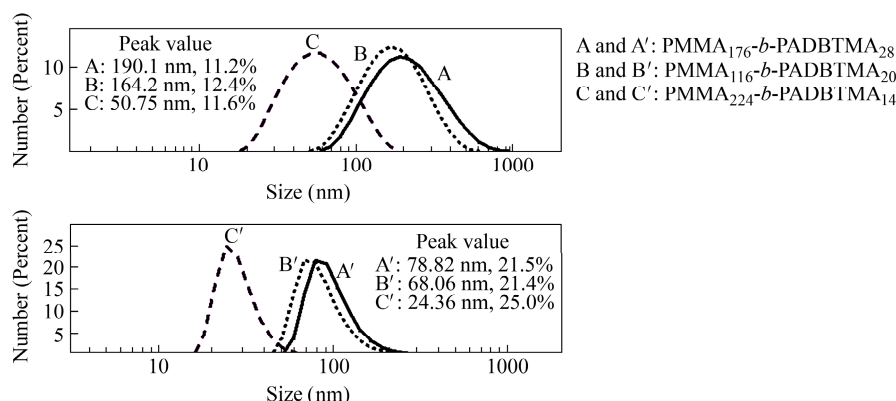


Fig. 7 The size distributions of block copolymers by intensity (upper) and number (lower)

Next, the self-assembly of the block copolymer in chloroform of different concentrations was also analyzed by DLS (Figs. 8–10). For the low content of organotin of PMMA₂₂₄-*b*-PADBTMA₁₄, the self-assembly extent is lower than that of the other two block copolymers due to weaker coordination between tin and oxygen. Thus, in order to ensure enough light scattering intensity for determination, we designed the concentration range from 4 mg/mL to 0.5 mg/mL. As a result, the average size of the self-assembly of the PMMA₂₂₄-*b*-PADBTMA₁₄ changed little with the change of the polymer concentration (Fig. 8). With regard to the other two block copolymers, because the content of organotin is high so as to be unable to dissolve in the case of the high concentration, the range from 1 mg/mL to 0.05 mg/mL was selected to examine the average size variation. Consequently, the size change was also very small (Figs. 9 and 10). It demonstrates that the self-assembly nanoparticle size has hardly been influenced by the concentration. That is to say, the preformed self-assembly was relatively stable and do not disassemble to form smaller assembly when decreasing the polymer concentration.

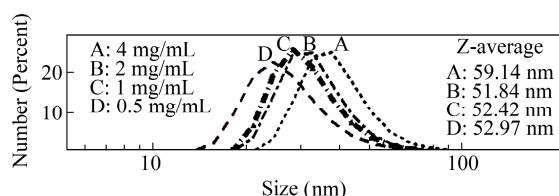


Fig. 8 The average sizes with different concentrations of PMMA₂₂₄-*b*-PADBTMA₁₄

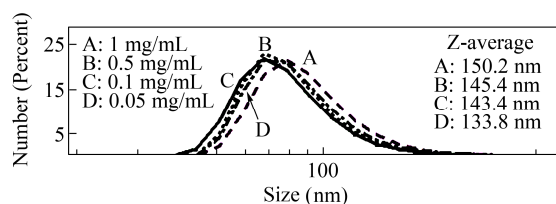


Fig. 9 The average sizes with different concentrations of PMMA₁₁₆-*b*-PADBTMA₂₀

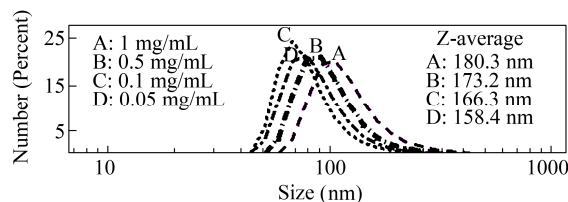


Fig. 10 The average sizes with different concentrations of PMMA₁₇₆-*b*-PADBTMA₂₈

Transmission electron microscope (TEM) was applied to investigate the self-assembly behavior (Fig. 11). The samples were prepared by dissolving in chloroform with 1 mg/mL, and then dipped onto carbon support film and dried in air for TEM analysis. After that, the sample was reused for SEM measurement. Here, the smaller diameter obtained from TEM (10–20 nm), which is different from DLS results (Fig. 7), is due to the different conditions in two measurements^[53]. DLS is manipulated just in solution; however, the samples for TEM are manipulated in vacuum. Additionally, some secondary aggregation was detected by TEM for PMMA₁₇₆-*b*-PADBTMA₂₈ with more organotin block introduced to the polymer chain.

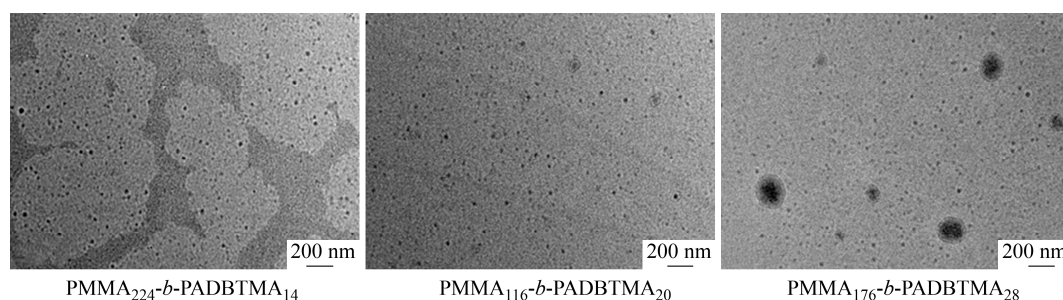


Fig. 11 The TEM images of the three block copolymers

Non-covalent coordination interaction usually can be reversibly regulated by adding competitive ligand^[54], metal ion^[55] or changing the pH^[56]. In our work, organotin unit was covalently linked to the polymer main chain, and thus the self-assembly occurs due to the inter-chain or intra-chain coordination between tin and carboxyl group. In order to examine the reversibility, we performed several additional experiments. For example, adding the great amount of bidentate ligands containing-nitrogen (such as 2,2-dipyridyl, 4,4'-dipyridyl) or containing-oxygen (2,3-pentanedione) into the polymer solution (CHCl₃) to destroy the self-assembly *via* chelating coordination mode with the tin, but the nanoparticle size has no obvious change yet, which indicated that the bidentate ligands failed to displace or disrupt the pre-existing tin-oxygen coordination mode. It further illustrated that the original coordination action is quite strong in this system, and the formed micelles are non-equilibrium structures as in literature report^[30]. Since the above experiments have demonstrated that acid can dissociate the self-assembly of the block copolymers, the strong acid HCl and strong base NaOH aqueous solutions were selected to add into the block copolymer PMMA₁₇₆-*b*-PADBTMA₂₈ in THF so as to regulate the reversible change of this self-assembly. Unfortunately, the reversibility of self-assembly was not satisfied (Figs. S3–S4).

In addition, based on exchange reaction between diorganotin dicarboxylate and diorganotin dichloride^[47, 48], the reactions of these three different ratio block copolymers with the different amounts of diorganotin dichloride for regulating the self-assembly of three block copolymers were designed. For example, when one equivalent Bu₂SnCl₂ to organotin units was added, the average size of nanoparticles sharply reduced. The average sizes of PMMA₁₁₆-*b*-PADBTMA₂₀ and PMMA₁₇₆-*b*-PADBTMA₂₈ changed from 150.2 nm and 182.1 nm to 51.52 nm and 149.1 nm, respectively (Figs. 12 and 13). However, unexpectedly, the average size reduced further when five folds Bu₂SnCl₂ was added to the solution of block copolymers.

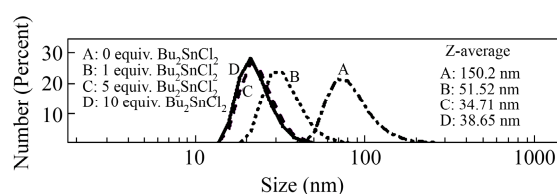


Fig. 12 The size change of PMMA₁₁₆-*b*-PADBTMA₂₀ after adding Bu₂SnCl₂

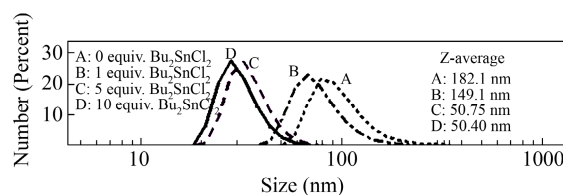


Fig. 13 The size change of PMMA₁₇₆-*b*-PADBTMA₂₈ after adding Bu₂SnCl₂

As for this phenomenon, we proposed two possible modes for the dissociation of the assembly with the addition of the Bu₂SnCl₂ (Fig. 14)^[57–59]. When the amount of Bu₂SnCl₂ is no more than 1 equivalent to organotin, the assembly was only partly disrupted by coordination with chlorine atom instead of oxygen atom (Fig. 14a), whereas for more than one equivalent amount of Bu₂SnCl₂, as more as five equivalents, all dibutyltin dicarboxylates were completely transformed to dibutylchlorotin carboxylates *via* exchange reaction (Fig. 14b).

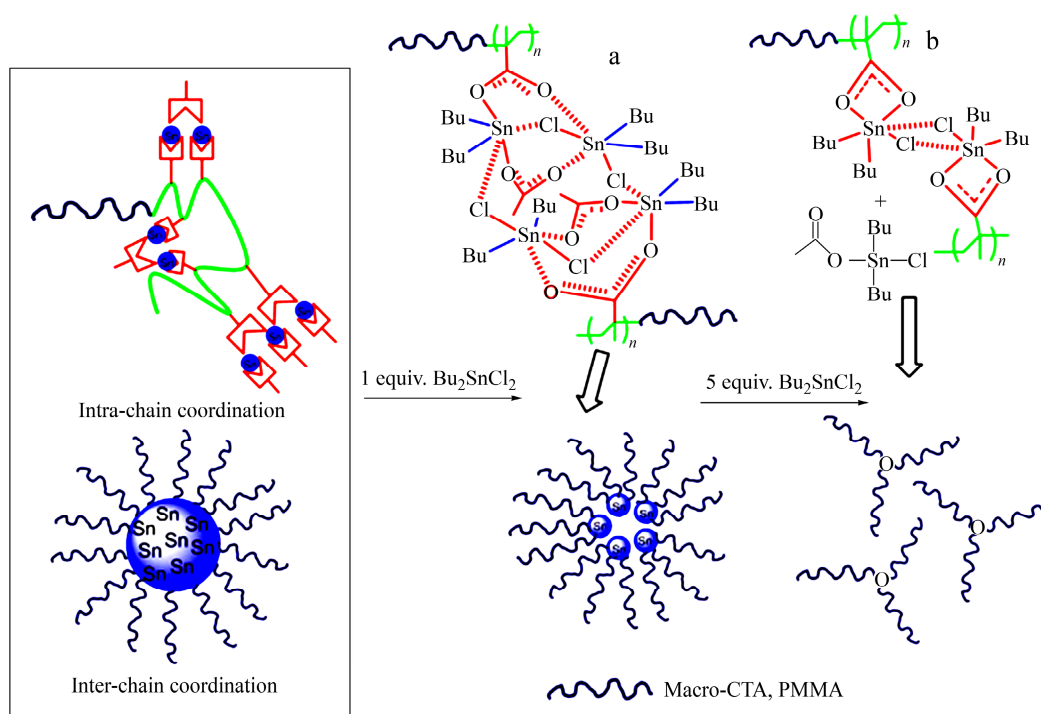


Fig. 14 Proposal mechanism of morphology change with the addition of Bu₂SnCl₂

And the side product of dibutylchlorotin acetate was traced by ¹¹⁹Sn-NMR, a new peak appeared at $\delta = -347.17$ which was consistent with five-coordination tin according to literature^[46] (Fig. 15) except for the peak at $\delta = 126.30$ assigned to Bu₂SnCl₂. In this case, new assembly formed is only dependent on the weaker chlorine bridge bond. Continuing to add the Bu₂SnCl₂ with 10 equiv. to organotin in the block copolymer, the diameter of the assembly was hardly changed (Figs. 12 and 13). It demonstrated that more sufficient Bu₂SnCl₂ did no longer affect the new assembly based on the tin-chlorine bridge bond. Similarly, to study the reversibility of this self-assembly with the addition of Bu₂SnCl₂, we used the CH₃COONa to react with the excess free Bu₂SnCl₂ and Sn-Cl bonds in the polymer chain to regenerate the organotin carboxylate. However, the size of nanoparticles had no obvious change (Figs. S5–S6), which further indicated the change of self-assembly through the chemical reaction was also irreversible.

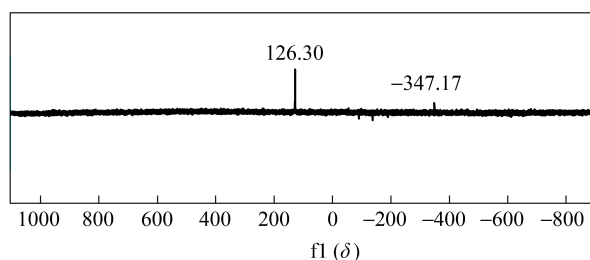


Fig. 15 The ^{119}Sn -NMR of $\text{PMMA}_{176}\text{-}b\text{-PADBTMA}_{28}$ solution by adding 5 equiv. Bu_2SnCl_2

Apart from the study of the morphology about these organotin-containing block copolymers, the catalytic activity of these block copolymers was also investigated. Generally, the small molecular organotin carboxylate can efficiently catalyze the trans-esterification of plant oil and methanol (yield > 90%)^[60, 61]. Based on this, we chose the glycerol tripalmitate and methanol as the standard trans-esterification model. But through the great amount of experimental parameters screening, the reaction product could only be obtained in 78% yield (Table S2) in the presence of the organotin-containing block copolymer $\text{PMMA}_{176}\text{-}b\text{-PADBTMA}_{28}$. It indicated that the catalytic activity of the polymer supported organotin carboxylate has some certain decrease. Further studies on structural or polymer chain change are on progress in our group.

CONCLUSIONS

The tin-oxygen coordination can well drive self-assembly of the block copolymers and form large size assemblies according to the GPC, DLS and TEM results. Block copolymers containing organotin with various chain length ratios, $\text{PMMA-}b\text{-PADBTMA}$, generate the different size assemblies in the same concentration of chloroform solvent, with the trend of the sizes increasing gradually with more organotin attached to the block copolymer. Moreover, this self-assembly is relatively stable and capable of withstanding significant dilution. Additionally, the tin-oxygen coordination assemblies can be dissociated by adding HOAc or Bu_2SnCl_2 based on the substitution and exchange reaction of dibutyltin dicarboxylate. With adding HOAc, the self-assembly was completely destroyed and changed into free polymer chains, and new small aggregates were formed *via* changing the strong Sn-O coordinated bond to the weak Sn-Cl bridge after adding Bu_2SnCl_2 . Investigation of the assembly properties of these block copolymers containing organotin serves as the subject of future reports.

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