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A facile strategy for the synthesis of block copolymers bearing an acid-cleavable junction

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Post-cleavable block copolymers are crucially important for the fabrication of nanoporous structures from the self-assembly of block copolymers by the selective etching of one block. Here, we present a facile and inexpensive approach to synthesize block copolymers bearing an acid-cleavable junction. A difunctional inifer containing an acetal group is synthesized for the sequential reversible addition–fragmentation transfer (RAFT) polymerization of *tert*-butyl methacrylate and atom transfer radical polymerization (ATRP) of styrene. Moreover, the polymerization sequence of the monomers can be altered. The acetal junctions in the resulting block copolymers can be readily cleaved by acid under ambient conditions. Aldehyde or monoglyceride end groups are left at the ends of the PS residues, which can be used as binding sites for future applications.

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1. Introduction

Block copolymers can self-assemble into various ordered nanostructures (spherical, cylindrical, gyroidal, lamellar) depending on the volume fraction and the Flory–Huggins interaction of the blocks.^{1,2} This offers promising applications in the fields of nanoscience and nanotechnology, such as capacitors,^{3,4} surface patterning,^{5–7} separation membranes,^{8–11} and so on. If one phase in the microphase separated structure is selectively removed, nanoporous structures with periodic styles are formed, which is particularly useful for templating nanodots,^{12–15} nanowires,^{16–18} etc.

In the past few years, much effort has focused on the synthesis of cleavable block copolymers and the creation of nanoporous structures. UV-etching techniques have been widely used. UV degradation of polymethyl methacrylate (PMMA) in PMMA based block copolymers leads to ordered nanoporous thin films.^{19,20} Also, photochemically sensitive groups, such as *ortho*-nitrobenzyl,^{21–24} photodimer of anthracene,²⁵ triphenylmethyl ether,^{26,27} etc., have been used as linkers. Although the UV-etching technique has the advantages of easy operation

and being contamination free, the target samples are always limited to submicrometer thickness. Further, deep UV exposure may cause unexpected side reactions with the other blocks.

There are also treatments confined to specific polymers, such as ozonolysis of polydienes,²⁸ hydrolysis of polyesters,²⁹ HF etching of PDMS,³⁰ hydroiodic acid degrading of PEO,³¹ and removing fillers in the supramolecular assembling process.^{32–35} These methods have limited application scope. Some treatments are carried out under harsh reaction conditions. We are interested in developing a versatile and facile synthetic methodology that provides access to a broad class of block copolymers, with the block copolymers cleaved under mild conditions.

In this contribution, we put a type of acid-cleavable junction, an acetal linkage, into block copolymers. Acetal groups have been widely used in protection/deprotection strategies for aldehydes and ketones. Acetal groups are stable under neutral and basic conditions, while unstable under acidic conditions.^{36–43} We synthesized a heterofunctional inifer containing an acetal group (see Scheme 1). The agents we used here are all cheap and easy to prepare. Meanwhile, two different initiation sites are introduced, which are able to work *via* different polymerization mechanisms selectively and independently. The choice of monomers and the polymerization sequences are arbitrary. Moreover, the potential end groups of the residues are controllable. The atom transfer radical polymerization (ATRP) method is one of the most efficient controlled radical polymerization (CRP) techniques, with very good architectural and molecular weight control. A large number of monomers have been successfully polymerized

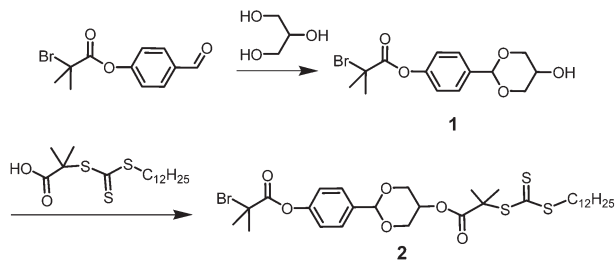
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Scheme 1 Synthesis of the acid-cleavable initiator with an ATRP initiator group and a RAFT agent.

using ATRP, including styrenics, (meth)acrylates, (meth)acrylamides, and acrylonitrile.^{44,45} The reversible addition-fragmentation chain transfer (RAFT) method is another powerful and versatile CRP technique for the preparation of well-defined architectures, and is also tolerant of a wide scope of monomers.^{46,47}

2. Experimental

Materials

Chlorobenzene (Analytical purity, Beijing Chemical Reagents Co.) was treated with powdered CaH_2 and distilled before use. Toluene, THF (Analytical purity, Beijing Chemical Reagents Co.), was distilled from Na/benzophenone under N_2 . CuBr was synthesized from CuBr_2 . 7-Hydroxyl-4-methylcoumarin (CA, Analytical purity, Beijing Chemical Reagents Co.), N,N',N'',N''' -pentamethyldiethylenetriamine (PMDETA, 99.5%, TCI), and 1-(chloromethyl)-4-vinylbenzene (97%, Aldrich) were used as received. Styrene (Analytical purity, Beijing Chemical Reagents Co.) was distilled prior to use. 4-Formylphenyl 2-bromo-2-methylpropanoate was prepared according to the literature.⁴⁸ The RAFT CTA agent was synthesized following the previously reported method.⁴⁹

Measurements

All of the characterization methods, such as ^1H NMR spectroscopy and gel permeation chromatography (GPC), used in this study were similar to those reported previously.⁹

Synthesis of glycerol protected ATRP initiator 1. 3.54 g of 4-formylphenyl 2-bromo-2-methylpropanoate (13.0 mmol) and 6.80 g of glycerol (73.9 mmol) were added into 50 mL of benzene in a flask equipped with an oil–water separator. A catalytic amount of 4-methylbenzene-1-sulfonyl chloride was added. The mixture was refluxed for 12 h. Then, the mixture was washed with a solution of sodium carbonate to remove the acid catalyst and the remaining glycerol. The organic solution was dried with MgSO_4 . The crude product was purified by column separation to obtain a white solid (4.213 g, yielding 93.8%). ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) 2.07 (s, 6H), 3.57–4.39 (m, 5H), 5.21–6.00 (m, 1H), 7.13 (m, 2H), 7.51 (m, 2H).

Synthesis of acid-cleavable difunctional initiator 2. 1.10 g of compound 1 (3.19 mmol), 1.45 g of CTA (3.98 mmol), 1.53 g of EDC (7.97 mmol), and 0.0973 g of DMAP (0.797 mmol) were

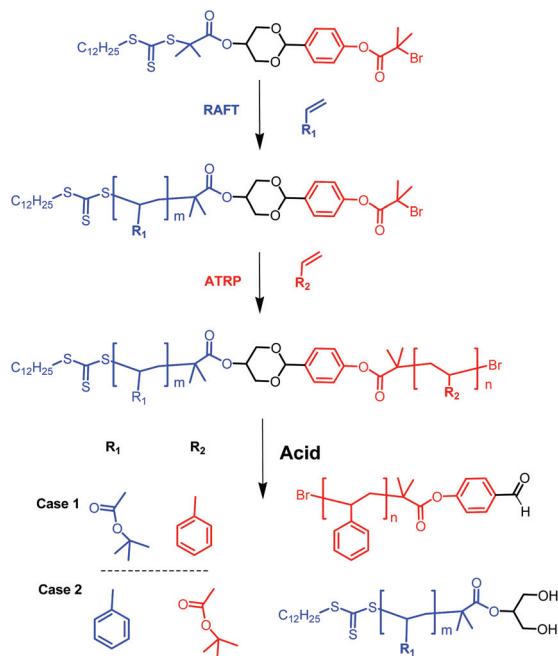
added into 50 mL of CH_2Cl_2 . The mixture was stirred at room temperature for 72 h. The product was purified by column separation (1.59 g, yielding 72%). ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) 0.87 (t, 3H), 1.24–1.73 (m, 26H), 2.07 (s, 6H), 3.25 (m, 2H), 4.26 (m, 4H), 4.45 (m, 1H), 5.94 (m, 1H), 7.13 (m, 2H), 7.53 (m, 2H). Mass spectrum (ESI, m/z): 691 ($[\text{M} + 1]^+$).

RAFT polymerization of PtBA. In a typical procedure, 10.0 g of *tert*-butyl acrylate (0.078 mol) was dissolved in 12.0 g of chlorobenzene. Then, 0.270 g of CTA (0.39 mmol) and 12.7 mg of AIBN (0.078 mmol) were added. The mixture was degassed by three freeze–pump–thaw cycles, and sealed under vacuum. The reaction tube was placed in an oil bath at 60 °C. After 20 h, the reaction was quenched by dipping the tube in ice/water and the tube was broken. After concentrating the mixture, 2 mL of THF was added, and the product was precipitated in a methanol–water (6 : 4) solution. The polymer was filtered and dried under vacuum. The product (7.8 g, yielding 78.0%) was a yellow solid. The molecular weight by GPC was 39 900, PDI = 1.17.

RAFT polymerization of PS. In a typical procedure, 8.0 g of styrene (76.9 mmol) and 1.3 g of coumarin derived styrene (4.4 mmol) were dissolved in 1.0 g of chlorobenzene.⁸ Then, 66.5 mg of CTA (0.0962 mmol) and 1.05 mg of AIBN (0.0064 mmol) were added. The mixture was degassed by three freeze–pump–thaw cycles, and sealed under vacuum. The reaction tube was placed in an oil bath at 65 °C. After 48 h, the reaction was quenched by dipping the tube in ice/water and the tube was broken. After concentrating the mixture, 2 mL of CH_2Cl_2 was added, and the product was precipitated in methanol. The polymer was filtered and dried under vacuum. The product was a canary yellow solid (3.5 g, yielding 43.8%). $M_{n,\text{PS}}$ = 26 400, PDI = 1.21.

General procedure for the synthesis of PtBA-*b*-PS with PtBA-Br macroinitiator. In a typical procedure, 0.70 g of PtBA macroinitiator (M_n = 39.9 kg mol^{−1}, PDI = 1.17, 0.0175 mmol) was dissolved in 3 mL of chlorobenzene. 8.0 mg of CuBr (0.0556 mmol), 20.0 mg of PMDETA (0.116 mmol) and 1.0 g of styrene (9.62 mmol) were added. The mixture was degassed by three freeze–pump–thaw cycles, and sealed under vacuum. The reaction tube was placed in an oil bath at 90 °C. After 20 h, the reaction was quenched by dipping the tube in ice/water and the tube was broken. The mixture was diluted with CH_2Cl_2 , passed through a basic alumina column, and precipitated in methanol. The block copolymer was filtered and dried under vacuum. The product was a canary yellow solid.

General procedure for the synthesis of PS-*b*-PtBA with PS-Br macroinitiator. In a typical procedure, 0.7 g of PS macroinitiator (M_n = 26.4 kg mol^{−1}, PDI = 1.21, 0.0269 mmol) was dissolved in 3 mL of chlorobenzene. 5.0 mg of CuBr (0.0347 mmol), 15 mg of PMDETA (0.0867 mmol), and 1 g of *tert*-butyl acrylate (7.81 mmol) were added. The mixture was degassed by three freeze–pump–thaw cycles, and sealed under vacuum. The reaction tube was placed in an oil bath at 90 °C. After 20 h, the reaction was quenched by dipping the tube in ice/water and the tube was broken. The mixture was diluted with CH_2Cl_2 , passed through a basic alumina column, and



Scheme 2 Synthetic procedure for the block copolymers containing PtBA and PS with an acid-cleavable junction between the blocks using ATRP and RAFT processes and acid degradation of the block copolymer.

precipitated in methanol. The block copolymer was filtered and dried under vacuum. The product was a canary yellow solid ($M_{n,PS-b-PtBA} = 36\,400$, PDI = 1.20). The monomer conversion is around 22%, as calculated from the ^1H NMR spectrum.

Acid-cleavage of PtBA-*b*-PS. 50 mg of PtBA-*b*-PS-1 was dissolved in 2 mL of CH_2Cl_2 . 0.5 mL of TFA was added and the mixture was stirred for 8 h. The product was precipitated into methanol, filtered and dried under vacuum ($M_n = 10\,100$, PDI = 1.13) (Scheme 2).

3. Results and discussion

Firstly, the 2-bromoisobutyrate group derived benzaldehyde is condensed with glycerol to form acetals. The use of glycerol is crucial because the resultant product has a hydroxyl end group for further modification. It is worth noting that the acetal products have approximately equimolar amounts of five- and six-membered rings.⁵⁰ The contents of six-membered-ring acetals was about 53.5%, as calculated from the ^1H NMR spectrum. Isolation of the isomer mixture was carried out by gas chromatography on a small scale,⁵¹ or separation of the converted derivatives,^{52,53} resulting in expensive purification costs and product loss. Considering that the acetal linkage is ready to be cleaved, both the five- and six-membered-ring acetals are exclusively degraded by acid without any selectivity. We did not isolate the isomers (for clarity, only six-membered-ring acetals are shown in the molecular formula). The remaining hydroxyl groups in the acetals were esterified with the RAFT agent containing a carboxylic acid group. A heterofunctional inifer was

obtained. All the synthetic procedures were easy to carry out and the yields were high.

To demonstrate the feasibility and controllability of our inifer, a series of diblock copolymers were synthesized. Firstly, the PtBA macroinitiators were synthesized by RAFT. The advantage of choosing PtBA is that PtBA can be easily removed under the same acidic conditions as used for the acetal group degradation. Then, ATRP of styrene was carried out using the PtBA macroinitiator. From the GPC curves (Fig. 1), we can see that obvious shifts to higher molecular weight occur, retaining the monomodal shapes. The characterization of the block copolymers are summarized in Table 1. The advantage of our heterofunctional inifer is that the choice of monomers and polymerization sequence is arbitrary. Taking the polymerization sequence as an example, PS is firstly polymerized by RAFT and PtBA is sequentially polymerized by ATRP. Fig. 2 shows the GPC curves of the PS macroinitiator and the subsequent PS-*b*-PtBA copolymer. The slight shoulder on the left side of the GPC curve is ascribed to the coupling reaction of the polymeric radicals.

^1H NMR and ^{13}C NMR measurements were used to confirm the structures and to calculate the chemical compositions of the block copolymers. The ^1H NMR spectrum of PtBA₃₀₀-*b*-PS₁₁₁ is shown in Fig. 3A. The characteristic peak at $\delta = 1.4$ ppm is

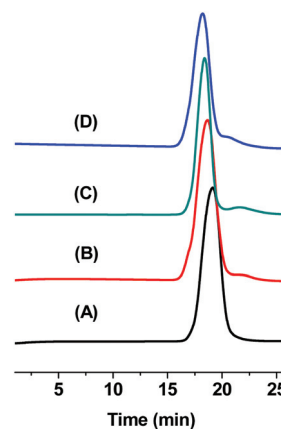


Fig. 1 GPC curves of the PtBA macroinitiator (A, $M_n = 39\,900$, PDI = 1.17) and the subsequent block copolymers PtBA₃₀₀-*b*-PS₁₁₁ (B), PtBA₃₀₀-*b*-PS₁₄₀ (C), and PtBA₃₀₀-*b*-PS₁₆₁ (D), indicating the well-controlled polymerization of the block copolymers.

Table 1 The chemical structures of the PtBA and the PtBA-*b*-PS block copolymers

Samples	$M_{n, PtBA}^a$	PDI ^a	M_n^a	PDI ^a	wt% ^b (PS)
PtBA ₃₀₀ - <i>b</i> -PS ₁₁₁	39 900	1.17	51 900	1.22	23.1
PtBA ₃₀₀ - <i>b</i> -PS ₁₄₀	39 900	1.17	61 000	1.15	27.5
PtBA ₃₀₀ - <i>b</i> -PS ₁₆₁	39 900	1.17	67 900	1.21	30.4
PtBA ₁₆₉ - <i>b</i> -PS ₂₈	23 300	1.15	26 800	1.13	11.7
PtBA ₁₆₉ - <i>b</i> -PS ₃₃₉	23 300	1.15	53 800	1.33	62.0

^a Determined by GPC. ^b Determined by ^1H NMR spectroscopy.

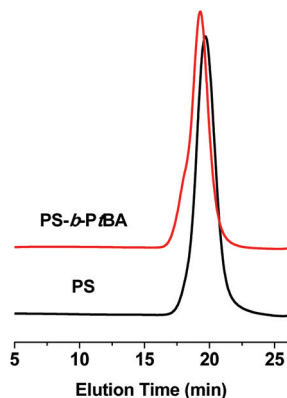


Fig. 2 GPC curves of the PS macroinitiator and the subsequent PS₂₅₀-*b*-PtBA₆₆ copolymer.

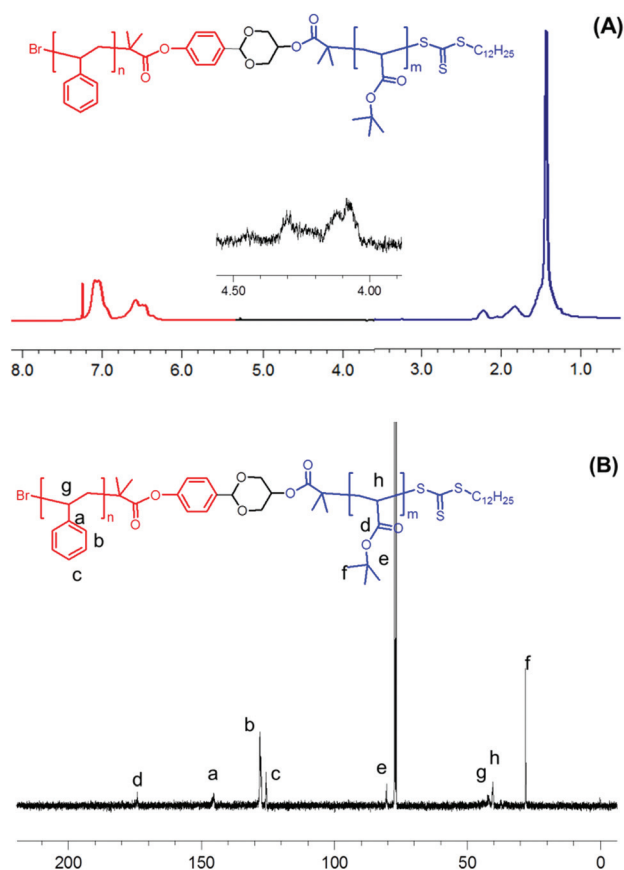


Fig. 3 ¹H NMR (A) and ¹³C NMR (B) spectra of block copolymer PtBA₃₀₀-*b*-PS₁₁₁, indicating the successful polymerization of the block copolymer and the introduction of the acid-cleavable acetal junction.

assigned to the methylene protons in the PtBA blocks. The peaks located in the range of δ 6.3 to 7.2 ppm are ascribed to PS, suggesting incorporation of PS blocks. As the molecular weight is high, the intensity of the buried mid-acetal groups is very low. Thus, the peaks around δ 4 ppm in the inset of Fig. 3A, corresponding to the acetal groups, are qualitatively

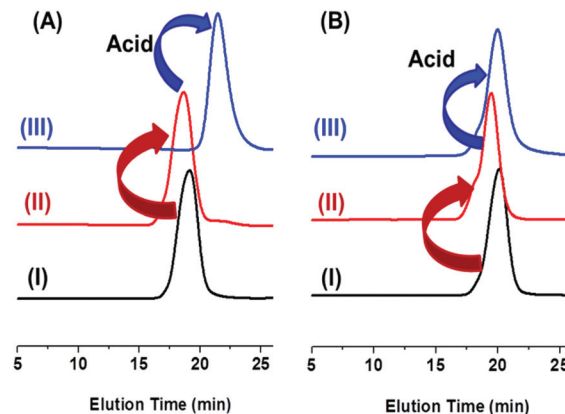


Fig. 4 (A) GPC curves of the PtBA macroinitiator (I), block copolymer PtBA₃₀₀-*b*-PS₁₁₁ (II), and PS residue after acid degradation (III), and (B) GPC curves of the PS macroinitiator (I), block copolymer PS₂₅₀-*b*-PtBA₆₆ (II), and PS residue after acid degradation (III), indicating the successful degradation of the block copolymers.

the evidence for the existence of the acetal groups. The error is relatively large if calculating quantitatively. From the ¹³C NMR spectrum, we can see typical chemical shifts for the PS blocks and PtBA blocks (Fig. 3B). The appearance of typical aromatic carbon peaks from PS blocks and tertiary carbon peaks from PtBA blocks provides more evidence for the successful block polymerization. The inset in Fig. 3A shows the peaks for the acetal hydrogen atoms, indicating the successful introduction of the acid-cleavable group. The above results strongly demonstrate that a precise block copolymer was prepared using a combination of RAFT and ATRP processes with an acid cleavable acetal junction.

The next step was to demonstrate the acid-cleavage of the obtained block copolymers by acid. Solutions of the block copolymers PtBA₃₀₀-*b*-PS₁₁₁ and PS₂₅₀-*b*-PtBA₆₆ in dichloromethane were added to trifluoroacetic acid (TFA). The acetal group was degraded, as well as the *tert*-butyl groups. The remaining PS block was collected. Fig. 4A shows the contrasting GPC curves of the PtBA macroinitiator, and PtBA₃₀₀-*b*-PS₁₁₁ before and after TFA cleavage. After TFA cleavage, the peak of the block copolymer is no longer observed. Instead, a new peak is visible with a lower molecular weight ($M_n = 10\,100$, PDI = 1.13). Fig. 4B shows the contrasting GPC curves of the PS macroinitiator, and PS₂₅₀-*b*-PtBA₆₆ before and after TFA cleavage. After TFA cleavage, the peak shifts to a lower molecular weight, and the peak has the same elution time as that of the PS macroinitiator. These results indicate that the acetal group junction holding the two blocks together can be efficiently cleaved under the mild conditions.

The acid cleaved process was also confirmed by SEM. We chose the PS dominated sample PtBA₁₆₉-*b*-PS₃₃₉. The sample was spin coated onto a silicon wafer, then the sample film was treated with TFA, and washed with methanol. The PS block was left on the silicon wafer. From the SEM image, we can see the ravine-like surface topologies of the sample after acid cleavage (Fig. 5).

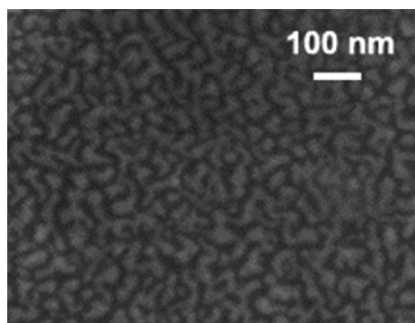


Fig. 5 The SEM image of PtBA₁₆₉-*b*-PS₃₃₉ after acid-cleavage, indicating the successful cleavage of the PtBA block.

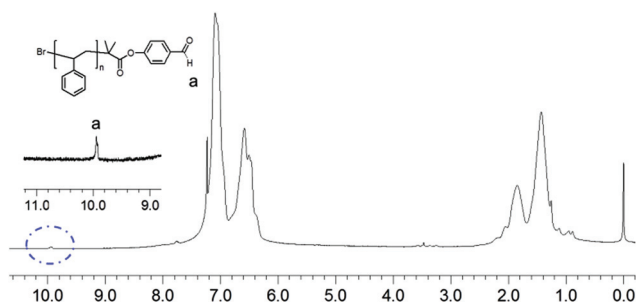


Fig. 6 The ¹H NMR spectrum of the PS residue after acid-cleavage of PtBA₃₀₀-*b*-PS₁₁₁, indicating the successful acid etching of the block copolymer. The inset shows the characteristic peak of aldehyde end groups.

Moreover, another advantage of our strategy is that the end groups of the residue can be controlled. The ¹H NMR spectrum of the degradation product from PtBA₃₀₀-*b*-PS₁₁₁ shows that the typical peaks of PtBA disappear, and the PS peaks remain (Fig. 6). From the inset in Fig. 6, we can see that a peak appears at the chemical shift of 9.9, corresponding to the aldehyde group from the degradation of the acetal linkage. If we choose the PS-*b*-PtBA block copolymer to degrade, the other part of the acetal group is left on the residue end. From the inset in Fig. 7, we can see that the monoglyceride group, with a chemical shift around δ 4 ppm, is left when the PS₂₅₀-*b*-PtBA₆₆

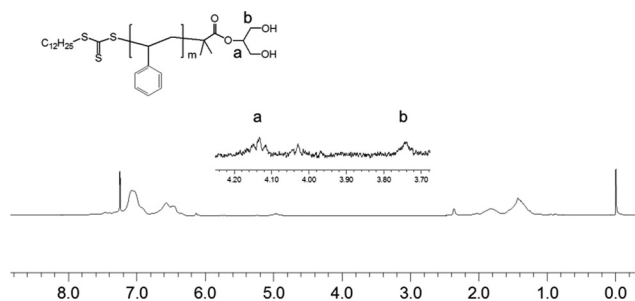


Fig. 7 The ¹H NMR spectrum of the PS residue after acid-cleavage of PS₂₅₀-*b*-PtBA₆₆, indicating the successful acid etching of the block copolymer. The inset shows the characteristic peak of monoglyceride end groups.

block copolymer is acid-cleaved. Compared to other work, the advantage of our strategy is that the end groups of the residues after degradation are controllable, and can be chosen to be either aldehyde groups or monoglyceride groups. Both the remaining end groups are very useful for future chemical modification.

4. Conclusions

In conclusion, we have presented an inexpensive and facile strategy to prepare block copolymers bearing an acid-cleavable acetal junction. PtBA-*b*-PS block copolymers have been synthesized, as well as PS-*b*-PtBA block copolymers. The acid-cleavage of the acetal junction occurs under mild conditions, as well as the degradation of the PtBA blocks. The PS blocks are fully conserved after acid etching. Moreover, the residue PS blocks bear a functional aldehyde group or monoglyceride group, and this gives opportunities to perform further chemistry.

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