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ARTICLE

A Facile Strategy for the Synthesis of Block Copolymers Bearing an Acid-Cleavable Junction

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Post-cleavable block copolymers is crucially important for nanoporous structures fabrications from self-assembly of block copolymers by selective etching of one block. Here, we present a facile and inexpensive approach to get block copolymers bearing an acid-cleavable junction. Difunctional inifer containing an acetal group is synthesized for sequential reversible addition-fragmentation transfer (RAFT) polymerization of *tert*-butyl methacrylate and sequentially atom transfer radical polymerization (ATRP) of styrene. Moreover, the polymerization sequence of the monomers can be altered. The acetal juncture in the resultant block copolymers can be readily cleaved by acid at ambient conditions. Aldehyde or monoglyceride end groups are left at the end of PS residue, which can be used as binding site for future application.

1. Introduction

Block copolymers can self-assemble into various ordered nanostructures (spherical, cylindrical, gyroidal, lamellar) as the function of volume fraction, Flory-Huggins interaction of the blocks.[1,2] This offers promising applications in fields of nanoscience and nanotechnology, such as capacitors,[3,4] surface patterning,[5-7] separation membrane,[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 for nanodots,[12-15] nanowires,[16-18] etc.

In the past years, many efforts have been focused on the synthesis of cleavable block copolymers and creation of nanoporous structures. UV etching techniques have been widely used. UV degradation of polymethyl methacrylate (PMMA) in the PMMA based block copolymers leads to ordered nanoporous thin film.[19,20] Also, photochemically sensitive groups, such as *ortho*-nitrobenzyl group,[21-24] photodimer of anthracene,[25] triphenylmethyl ether,[26,27] etc. are installed as a linker. Although the UV-etching technique has advantages of easy operation and free of contamination, the target samples are always limited in submicrometer thickness. Further, deep UV exposure may cause unexpected side reaction with the other constituent blocks.

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

In this contribution, we put a kind of acid-cleavable juncture, an acetal linkage, into block copolymers. It is known that the acetal groups have been widely used in the protection/deprotection strategies of aldehydes and ketones. The acetal groups are stable under neutral and basic conditions, while instable under acidic condition.[36-43] We synthesized heterofunctional inifer containing an acetal group (see Scheme 1). The agents we used here are all cheap and of easy preparation. 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 residue 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. Extensive monomers have been successfully polymerized by 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 also tolerance of wide scope of monomers.[46,47]
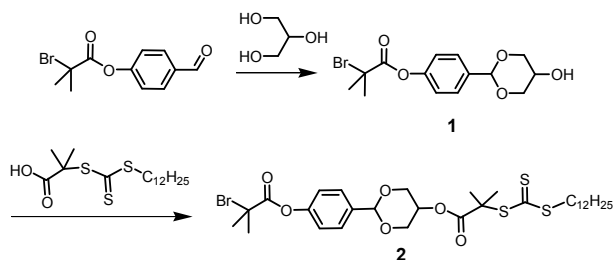
Scheme 1. Synthesis of the acid-cleavable initiator with ATRP initiator group and RAFT agent.

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.) were 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'', N''-Pentamethyldiethylenetriamine (PMDETA, 99.5%, TCI), 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] and the RAFT CTA agent was synthesized followed by the previous method.[49]

Measurements

All of the characterization methods such as ^1H NMR spectroscopy, 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 benzene flask equipped with an oil-water separator. Catalyst amount of 4-methylbenzene-1-sulfonyl chloride was added. The mixture was reflux for 12 h. then, the mixture was washed with 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 get 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 difunctioanl initiator 2 1.10 g of compound **1** (3.19 mmol), 1.45 g of CTA (3.98 mmol), 1.53 g of EDC (7.97mmol), and 0.0973 g of DMAP (0.797mmol) were added into 50 mL of CH_2Cl_2, stirring 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/e): 691 ([M+1]$^+$).

RAFT Polymerization of P*t*BA 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), 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 added, precipitated in 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 39900, 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), 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 added, precipitated into methanol, the polymer was filtered and dried under vacuum. The product was a canary yellow solid (3.5 g, yielding 43.8%). $M_{n,PS}$=26400, PDI=1.21.

General Procedure for P*t*BA-*b*-PS with P*t*BA-Br Macroinitiator In a typical procedure, 0.70 g of P*t*BA macroinitiator (M_n=39.9 kg/mol, 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), 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, precipitated into methanol. The block copolymer was filtered and dried under vacuum. The product was a canary yellow solid.

General Procedure for PS-*b*-P*t*BA with PS-Br Macroinitiator In a typical procedure, 0.7 g of PS macroinitiator (M_n=26.4 kg/mol , 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) , 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, precipitated into methanol. The block copolymer was filtered and dried under vacuum. The product was a canary yellow solid ($M_{n,PS-b-PtBA}$=36400, PDI=1.20). The monomer conversion is around 22% calculated from the ^1H NMR.

Acid-cleavage of P*t*BA-*b*-PS 50 mg P*t*BA-*b*-PS-1 was dissolved in 2 mL CH_2Cl_2, 0.5 mL TFA was added, stirring for 8 h. Precipitating into methanol , the product was filtered and dried under vacuum. (M_n=10100，PDI=1.13) .
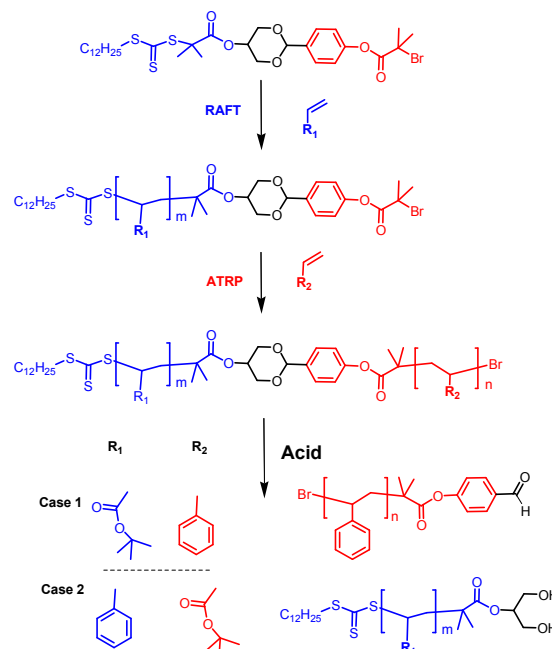
Scheme 2. Synthetic procedure of block copolymers containing PtBA and PS with an acid-cleavable junction between the blocks by ATRP and RAFT processes, and acid degradation of the block copolymer.

3. Results and discussion

Firstly, 2-bromoisobutyrate group derived benzaldehyde is condensed with glycerol to form acetals. The application of glycerol is crucial, because the resultant product has hydroxyl end group for further modification. It is worth to note that the product acetals are approximately equimolar amounts of five- and six-number rings.[50] The content of six-number-ring acetals is about 53.5% calculated from ^{1}H NMR. The 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 cost and product lost. Considering that the acetal linkage is ready to cleaved, both the five- and six-number-ring acetals are exclusively degraded by acid without selectivity. We are not going to isolate the isomers (For clarity, only six-number-ring acetals are shown in the molecular formula). The remaining hydroxyl group in the acetals is esterified with RAFT agent containing carboxylic acid group. Heterofunctional inifer is obtained. All the synthetic procedures are easy prepared, and the yields are high.
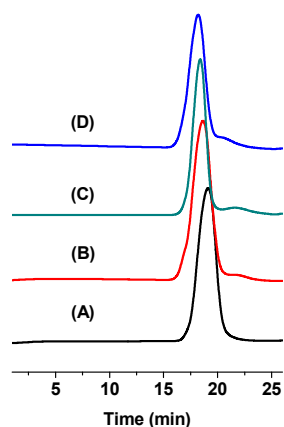
Sample					
PtBA$_{169}$-b-PS$_{28}$	23300	1.15	26800	1.13	11.7
PtBA$_{169}$-b-PS$_{339}$	23300	1.15	53800	1.33	62.0

[a] determined by GPC.
[b] determined by ^{1}H NMR.

To demonstrate the feasibility and controllability of our inifer, a series of diblock copolymers are synthesized. Firstly, the PtBA macrointiators are synthesized by RAFT. The advantage of choosing PtBA is that PtBA can be easily removed under the same acidic condition as acetal groups degradation. Then ATRP of styrene is carried on by using the PtBA macroinitiator. From the GPC curves, we can see that obvious shifts to the higher molecular weight occur, retaining monomodal shapes. The characterizations 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. Taken the polymerization sequence as an example, PS is firstly polymerized by RAFT and PtBA sequentially polymerized by ATRP. Figure 2 shows the PS macroinitiator, and the subsequent PS-b-PtBA. The slight shoulder on the left side of the GPC curve is ascribed to coupling reaction of the polymeric radicals.
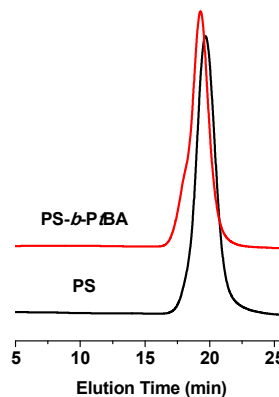

Figure 1. GPC curves of the PtBA macroinitior (A, M_n=39900, PDI=1.17) and the successive block copolymers PtBA$_{300}$-b-PS$_{111}$ (B), PtBA$_{300}$-b-PS$_{140}$ (C), PtBA$_{300}$-b-PS$_{161}$ (D), indicating the well-controlled polymerization of block copolymers.

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 %(PS)[b]
PtBA$_{300}$-b-PS$_{111}$	39900	1.17	51900	1.22	23.1
PtBA$_{300}$-b-PS$_{140}$	39900	1.17	61000	1.15	27.5
PtBA$_{300}$-b-PS$_{-161}$	39900	1.17	67900	1.21	30.4

Figure 2. GPC curves of PS macroinitiator and the successive PS$_{250}$-b-PtBA$_{66}$.

^{1}H NMR and ^{13}C NMR measurements were used to confirm the structures and to calculate chemical compositions of the block copolymers. The ^{1}H NMR spectrum of PtBA$_{300}$-b-PS$_{111}$ is shown in Figure 3A. The characteristic peak at δ=1.4 ppm was assigned to the methylene protons in the PtBA blocks. While the peaks, located in the range of δ from 6.3 to 7.2 ppm, are ascribed to PS, suggesting incorporation of PS blocks. Due to the molecular weight is high, the content of buried mid-acetal groups is very low. Thus, the peaks around δ~4 ppm in the inset of Figure 3A, corresponding to the acetal groups, are qualitatively the evidence of the acetal existence. The error is relatively large if quantitatively as the calculating reference. From the ^{13}C NMR spectrum, we can see the typical chemical shifts from the PS blocks and PtBA blocks (Figure 3B). The apearance of typical peaks of aromatic carbon from PS and the tertiary carbon from PtBA blocks provids more evidence for the sucessful block polymerization. The inset in Figure 2A shows the peaks of acetal

hydrogen, indicating the success of introduction of acid-cleavable group. The above results strongly demonstrate that precise block copolymer was prepared using the combination of RAFT and ATRP processes with acid cleavable acetal junction.
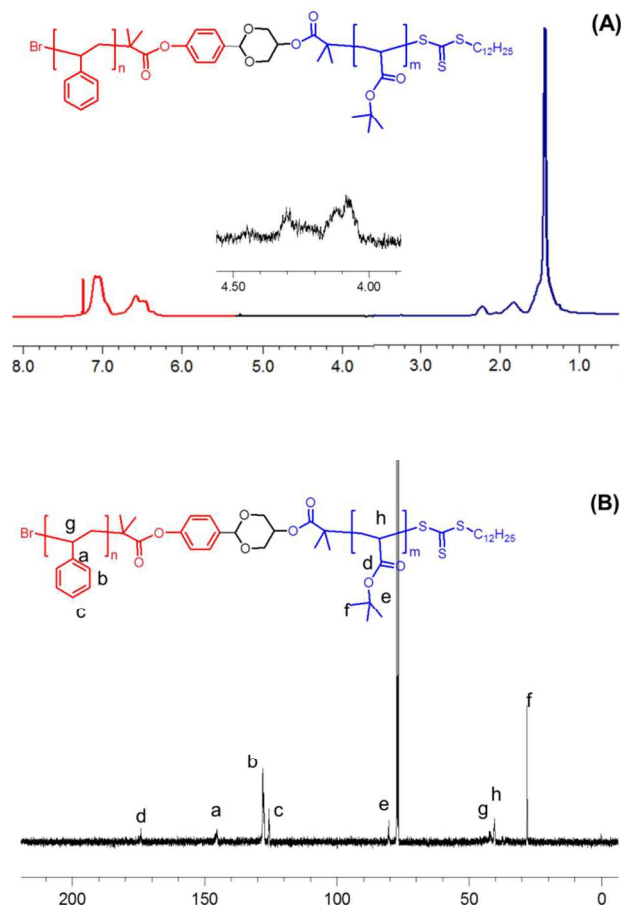

Figure 3. ^{1}H NMR (A) and ^{13}C NMR (B) of block copolymer PtBA$_{300}$-b-PS$_{111}$, indicating the successful polymerization of block copolymer and introduction of acid-cleavable atctal junction.

The next step is to demonstrate the acid-cleavage of the obtained block copolymers by acid. Solutions of the block copolymer PtBA$_{300}$-b-PS$_{111}$ and PS$_{250}$-b-PtBA$_{66}$ in dichloromethane were added with trifluoroacetic acid (TFA). The acetal group was degraded, as well as the *tert*-butyl groups. The remaining PS block was collected. Figure 4A shows the contrastive GPC curves of PtBA macroinitiator, PtBA$_{300}$-b-PS$_{111}$ before and after TFA cleavage. After TFA cleavage, the peak of the BCP is no longer observed. Instead, a new peak is visible with lower molecular weight (M_n=10100, PDI=1.13). Figure 4B shows the contrastive GPC curves of PS macroinitiator, PS$_{250}$-b-PtBA$_{66}$ before and after TFA cleavage. After TFA cleavage, the peak shifts to lower molecular weight, and the peak has the same elution time as that of PS macroinitiators. These results indicate that the acetal group junction holding the two blocks together can be efficiently cleaved under the mild condition.
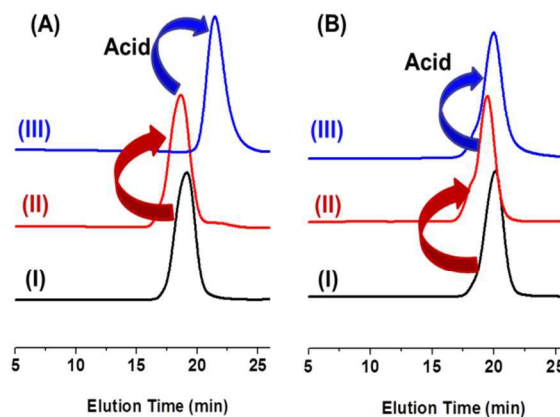

Figure 4. (A) GPC curves of the PtBA macroinititior (I), block copolymers PtBA$_{300}$-b-PS$_{111}$ (II), and PS residue after acid degradation (III), and (B) GPC curves of the PS macroinititor (I), block copolymers PS$_{250}$-b-PtBA$_{66}$ (II), and PS residue after acid degradation (III), indicating successful degradation of block copolymers.

The acid cleaved process was also confirmed by SEM. We chose the PS dominated sample PtBA$_{169}$-b-PS$_{339}$. The sample was spin coated onto 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 (Figure 5).
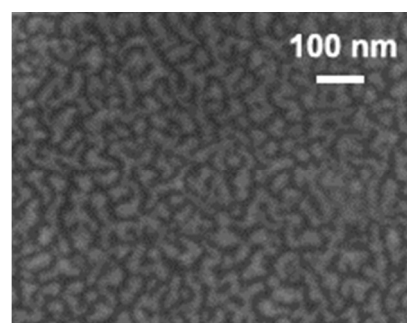

Figure 5. The SEM image of PtBA$_{169}$-b-PS$_{339}$ after acid-cleavage, indicating the successful cleavage of PtBA block.

Moreover, another advantage of our strategies is that the end groups of the residue can be controlled. The ^{1}H NMR of degradation product from PtBA$_{300}$-b-PS$_{111}$ shows that the typical peaks of PtBA disappear, and the PS peaks remain. From the inset of Figure 6, we can see a peak appears at the chemical shift of 9.9, corresponding to the aldehyde group from the degradation of acetal linkage. If we choose the PS-b-PtBA block copolymers to degrade, the other part of acetal group is left on the residue end. From the inset in Figure 7, we can see that the monoglyceride group, with the chemical shift around δ~4 ppm, is left when PS$_{250}$-b-PtBA$_{66}$ block copolymers are acid-cleaved. Compared to other works, the advantage of our strategies is that the end groups of the residues after degradation is controllable, and can be chosen between aldehyde group and monoglyceride group. Both the remaining end groups are very useful in the future chemical modification.
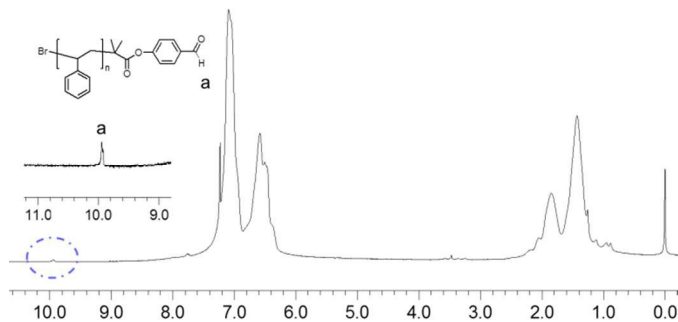
Figure 6. The ^{1}H NMR of PS residue after acid-cleavage of PtBA$_{300}$-b-PS$_{111}$, indicating the successful acid etching of block copolymer. The inset shows the characteristic peak of aldehyde end group.

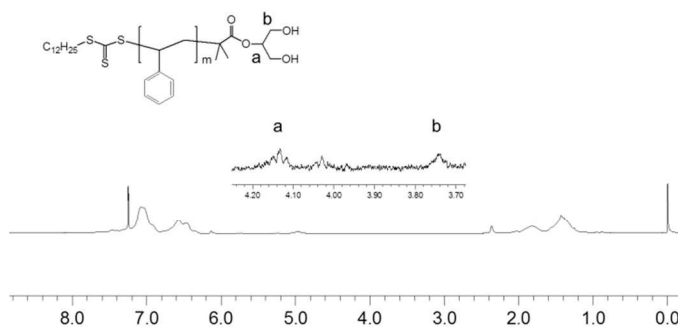Figure 7. The ^{1}H NMR of PS residue after acid-cleavage of PS$_{250}$-b-PtBA$_{66}$, indicating the successful acid etching of block copolymer. The inset shows the characteristic peak of monoglyceride end groups.

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 are synthesized, as well as PS-b-PtBA. The acid-cleavage of acetal junction occurs under mild conditions, as well as 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.

Acknowledgements

Notes and references

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