Cleavage of Polystyrene-*b*-Poly(ethylene oxide) Block Copolymers with a Trithiocarbonate Linkage in Solutions

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ABSTRACT: In this work, the polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO) block copolymers with a trithiocarbonate group between the blocks were prepared by polymerization of styrene in the presence of a trithiocarbonate reversible addition fragmentation chain transfer (RAFT) agent connected with PEO. Decomposition of the trithiocarbonate group by UV irradiation was investigated in three different types of solvent: tetrahydrofuran (THF, common solvent for both blocks), cyclohexane/dioxane mixture (selective solvent for the PS block) and *N*,*N*-dimethylformamide (DMF)/ethanol mixture (selective solvent for the PEO block). It is found that cleavage of the block copolymers can take place in all these three solvents and the cleavage ratio ranges from 76 to 86%. The micellar morphologies in selective solvents before and after cleavage were examined. It is observed that the size of the micelles is reduced after cleavage and sometimes aggregation of the micelles occurs due to removal of the corona of micelles. It shows that this work provides a facile and general method for synthesis of cleavable block copolymers. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 3834–3840, 2010

KEYWORDS: block copolymer; cleavage; living radical polymerization; photochemistry; RAFT; trithiocarbonate

INTRODUCTION Block copolymer can form various nano-ordered structures due to microphase separation, thus block copolymer thin films are frequently used as template to fabricate nano-devices. During fabrication, one of the blocks needs to be removed selectively or both blocks need to be removed sequentially.[1,2] On the other hand, block copolymer micelles in selective solvent are usually used as drug carrier. For the purpose of controlled release of the drug, block copolymer micelles sometimes need to break down after they reach suitable sites in human body.[3–5] UV irradiation is commonly used to selectively decompose one component in the block copolymer.[6–11] However, this method is only applicable to limited polymers such as poly(methyl methacrylate) and poly(α-methyl styrene). Chemical etching such as hydrolysis under rigorous conditions is also used to degrade one of the blocks in the block copolymers,[12–20] but usually only poly(ε-caprolactone) and poly(L-lactide) are degradable. The ideal and universally applicable method is to cleave the junction between two blocks. Thus synthesis of cleavable block copolymer is the best strategy and some efforts have been made by different researchers. Various cleavable groups or chemical bonds have been introduced into the main chain of the block polymers as the junction of the blocks, including thermounstable multiple hydrogen bonds,[21] trityl ether group scissile in the presence of Brønsted or Lewis acids,[22–24] diphenyl methyl or anthracenyl methyl ether linkage cleavable under mild acidic conditions,[25] acid-liable cyclic *ortho* ester,[26] benzoic-imine group[4] and hydrazone linkage,[3,27] alkali-liable weak ester linkage,[28] decomposable *tert*-butylcarbamate group by trifluoroacetic acid,[29] photocleavable *ortho*-nitrobenzyl group[30–32] and anthracene dimer,[33,34] disulfide bond cleabable by reductants,[5,35–38] and C-ON weak bond cleavable by addition of phenylhydrazine at high temperature.[39]

Dithiocarbonates and trithiocarbonates are frequently used as reversible addition fragmentation chain transfer (RAFT) agents for controlled radical polymerization to synthesize block copolymers.[40,41] Dithiocarbonates and trithiocarbonates RAFT agents can undergo decomposition in the presence of nucleophiles, ionic reductants, oxidant, radical attacker or by thermolysis and by UV irradiation.[42–45] However, during preparation of block copolymers by RAFT process, the dithiocarbonate or trithiocarbonate group is usually located at the end of the polymer chains.

In this work, we first prepared macro-RAFT agent containing poly(ethylene oxide) monomethyl ether (mPEO) and then controlled radical polymerization of styrene was performed.

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As a result, polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO) block copolymers with trithiocarbonate group located between the two blocks were obtained. The advantage of this method lies in the bifunction of the trithiocarbonate RAFT agent: chain transfer agent and cleavable linkage. Herein the PS-*b*-PEO block copolymer solutions were irradiated with UV light and excess 2,2-azobisisobutyronitrile (AIBN) was added into the solutions to intensify the cleavage of trithiocarbonate group. On the one hand, trithiocarbonate RAFT agent will decompose and produce radicals upon UV radiation.[46–48] On the other hand, AIBN can also produce radicals after exposure to UV light,[49,50] which may attack the radicals formed by decomposition of RAFT agent, like termination process in RAFT polymerization. The possible cleavage mechanism of trithiocarbonate group upon UV irradiation in the presence of AIBN is shown in Scheme 1. As the block copolymers may exhibit different aggregation states in different solvents and the solubility of AIBN also varies with solvent, cleavage of PS-*b*-PEO block copolymers carried out in different solvents was investigated.

EXPERIMENTAL

Materials

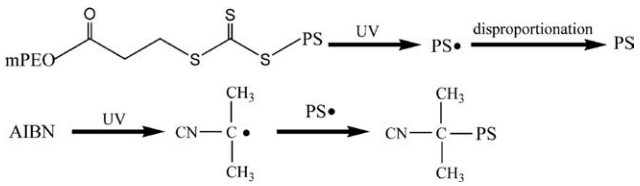
AIBN was purified by twice recrystallization in methanol. Styrene was washed with 5% NaOH solution thrice followed by washing with de-inoized water to neutral, then dried over $CaCl_2$ and distilled under reduced pressure before use. 2-Mercaptopropionic acid (>99%) was purchased from ACROS and used without further purification. Thionyl chloride was freshly distilled before use. Poly(ethylene oxide) monomethyl ethers (mPEO) with $M_n = 2000$ and $M_n = 5000$ were purchased from ACROS. mPEO was distilled with toluene to remove water adsorbed and then dried *in vacuo* at 50 °C for 24 h.

Synthesis of 3-Benzylsulfanylthiocarbonylsufanyl-propionic Acid (BSPA)

Synthesis of BSPA followed a procedure reported in literature.[51,52] Potassium hydroxide (26.0 g) was dissolved in 250 mL water, and then 3-mercaptopropionic acid was added dropwise to the solution. After the dropwise addition of carbon disulfide (30 mL), the orange solution was stirred for 5 h. The mixture was then heated with benzylbromide (39.6 g, 0.23 mol) for 12 h at 80 °C. After cooling, 300 mL of chloroform was added and the reaction mixture was acidified with hydrochloric acid until the organic layer became yellow. The water phase was extracted with chloroform (2 × 100 mL). The combined organic layers were washed with 10% sodium carbonate aqueous solution (2 × 100 mL) and dried over anhydrous sodium sulfate. After evaporation of the solvent, the remaining product was purified by gel column chromatography with a 3:1 hexane/ethyl acetate mixture as an eluent to yield yellow powder. The yellow powder was purified by recrystallization from methylene chloride.

Preparation of Macro-RAFT Agent (mPEO-BSPA)

The macro-RAFT agent (mPEO-BSPA) was synthesized according to reference.[53] Freshly distilled thionyl chloride (10 mL) was slowly dropped into a flask containing 20 mL CH_2Cl_2 and BSPA (20 mmol, 5.46 g) equipped with a condenser at room temperature, then the mixture was refluxed for 2 h. The excess thionyl chloride and solvent were removed by azeotropic distillation. The remaining viscous liquid was 3-benzylsulfanylthiocarbonylsufanyl propionic acid chloride (BSPAC) and was used immediately for the next step. Dry mPEO (2 mmol) was dissolved in 80 mL of CH_2Cl_2 and 10 mmol of anhydrous pyridine was added. The flask containing the solution of mPEO was immersed into an ice-water bath and 10 mmol of BSPAC added dropwise. The temperature was then raised to room temperature and the reaction lasted 12 h. The mixture was extracted thrice with 50 mL of de-ionized water and the organic phase was dried with Na_2SO_4 for 2 h. After filtration the solution was concentrated to about 1/4 of the initial volume and 10-fold of cold diethyl ether was added. The yellow precipitate was washed with excess diethyl ether and the product was dried *in vacuo* at room temperature for 12 h. The obtained yellow powder was stored in dark under N_2 atmosphere.



SCHEME 1 Possible cleavage mechanism of trithiocarbonate group upon UV irradiation in the presence of AIBN.

Synthesis of PS-*b*-PEO Block Copolymers

Styrene, macro-RAFT agent and AIBN were added successively into a schlenk bottle. The mixture was degassed by three freeze-pump-thaw cycles and sealed in nitrogen. The polymerization was carried out at 70 °C for a given time. After polymerization was complete, the schlenk bottle was quenched into liquid nitrogen and precipitated with cold dried *n*-hexane. The product was purified by dissolution/precipitation with tetrahydrofuran (THF)/methanol, and the filtrate product was dried to constant weight *in vacuo* at 40 °C. The obtained PS-*b*-PEO block copolymers were subjected to ^{1}H NMR and GPC characterization. The number-average molecular weight of the PS block was calculated based on ^{1}H NMR spectrum with respect to the molecular weight of the PEO block. The polydispersity index (PDI) of the PS-*b*-PEO block copolymers was determined by GPC. The molecular characteristics of three PS-*b*-PEO block copolymers used in this work were given in Table 1.

Preparation of the Solutions of PS-*b*-PEO Block Copolymers

PS-*b*-PEO block copolymers were dissolved in three different solvents, respectively: THF (common solvent for both PEO and PS blocks), cyclohexane/dioxane mixture (3:1 v/v) (selective solvent for the PS block) and DMF/ethanol mixture (1:1 w/w) (selective solvent for the PEO block). The concentration of the PS-*b*-PEO block copolymers 0.2 w/v %. For THF, the block copolymer was directly dissolved. When cyclohexane/dioxane mixture was used as the solvent, the

TABLE 1 Molecular Characteristics of Three PS-*b*-PEO Block Copolymers

Sample	M_n(PEO)	M_n(PS)	M_n(total)	PDI
PS_{199}-*b*-PEO_{45}	2,000	20,700	22,700	1.18
PS_{158}-*b*-PEO_{113}	5,000	16,400	21,400	1.32
PS_{218}-*b*-PEO_{113}	5,000	22,700	27,600	1.34

PS-*b*-PEO block copolymer was added into the solvent and the solution was heated to 68 °C (higher than the melting temperature of the PEO block) and held for 20 min, then the solution was slowly cooled to room temperature and the micelles with PEO as the core and PS as the corona were formed. As for the solution in DMF/ethanol mixture, PS-*b*-PEO block copolymer was first dissolved in the neat DMF by sonication for 15 min. Ethanol was slowly dropped into the DMF solution under stirring. After the preset amount of ethanol was added, the solution was kept stirring for 10 h to reach equilibrium, and then the micelles with PS as the core and PEO as the coronal were obtained.

Cleavage of PS-*b*-PEO Block Copolymers

AIBN (100-fold of the molar concentration of the trithiocarbonate group in the block copolymers) was added into the solution and the mixture was degassed by three freeze-pump-thaw cycles, and then irradiated by ultraviolet light (wavelength: 232–500 nm, 100 W Mercury lamp) for 45 min. At the polymer concentration of 0.2 w/v %, the 45 min irradiation time is enough to cleave the block copolymer. Extension of irradiation time can hardly enhance the cleavage ratio. When irradiation time is shorter than 45 min, the cleavage ratio increases gradually with irradiation time. At lower concentration the cleavage ratio is unchanged after 45 min UV irradiation but a little longer irradiation time should be used at higher concentration. After UV irradiation, the solution was concentrated and then precipitated with *n*-hexane. The precipitate was obtained by filtration and dried *in vacuo* for 24 h. The dried product was used for GPC characterization. The precipitate was also redissolved and precipitated twice with THF/methanol solvent pair to remove the cleaved PEO block and the obtained product was characterized by ^{1}H NMR.

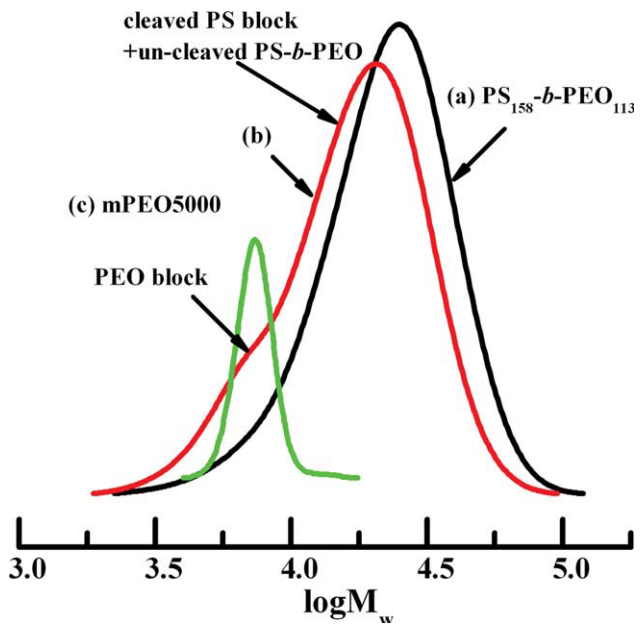


FIGURE 1 GPC curves of PS_{158}-*b*-PEO_{113} before (a) and after (b) cleavage in THF and mPEO with M_n = 5000 (c).

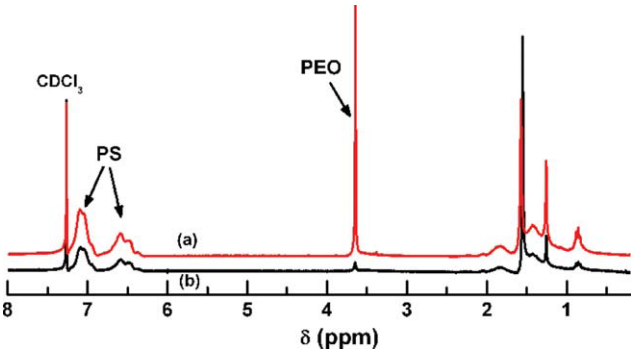


FIGURE 2 ^{1}H NMR spectra of PS_{158}-*b*-PEO_{113} before (a) and after (b) cleavage in THF.

Characterization

^{1}H NMR spectra were recorded on a Bruker AMX-500 spectrometer with $CDCl_3$ as solvent. The chemical shifts of the products in each synthesis step were compared with those reported in literature and the structures were confirmed.[51,52] Molecular weight and molecular weight distribution of the PS-*b*-PEO block copolymers were measured by GPC in a PL 220 GPC instrument (Polymer Laboratories) at 25 °C in THF. Three PLgel 10 μm mixed-B columns were used. Universal calibration against narrow polystyrene standards was adopted. Transmission electron microscopy (TEM) observation was performed on a JEOL JEM-1230EX electron microscope operated at an acceleration voltage of 65 KV. The samples for TEM experiments were prepared by direct dropping a small amount of the micellar solutions onto the copper grids coated with carbon, and then dried at atmospheric pressure at room temperature.

RESULTS AND DISCUSSION

Cleavage in THF

Since THF is the common solvent of both PS and PEO, the solution of PS-*b*-PEO in THF is homogeneous. Figure 1 shows the GPC curves of PS_{158}-*b*-PEO_{113} before and after cleavage in THF. For comparison, the GPC curve of neat mPEO with M_n = 5000 was presented as well. It is observed that a new shoulder peak appears after cleavage. The position of this shoulder peak is similar to that of neat mPEO with M_n = 5000, indicating that it can be attributed to the PEO block after disconnection with the PS block. Moreover, the position of the main peak after cleavage shifts to lower molecular weight when comparing with the peak position of the

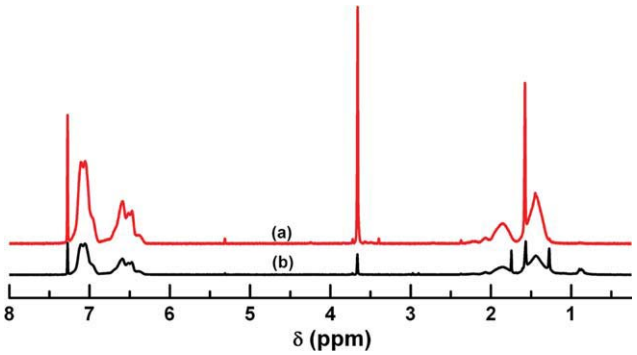


FIGURE 3 ^{1}H NMR spectra of PS_{199}-*b*-PEO_{45} before (a) and after (b) cleavage in 0.2 w/v % solution of cyclohexane/dioxane (3:1 v/v). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

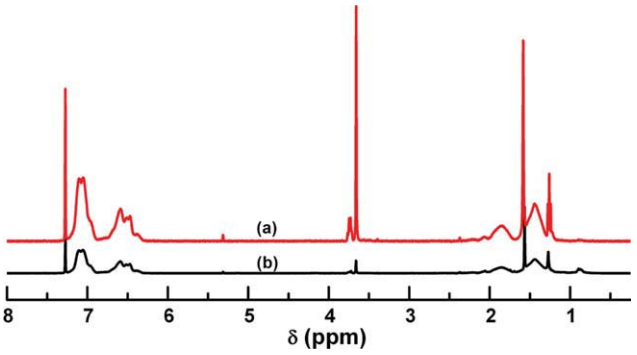


FIGURE 5 ^{1}H NMR spectra of PS_{218}-*b*-PEO_{113} before (a) and after (b) cleavage in 0.2 w/v % solution of in DMF/ethanol (1:1 v/v). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

original PS_{158}-*b*-PEO_{113}. The molecular weight at the peak position after cleavage is about 18,000, not far from that calculated from ^{1}H NMR, thus it can be attributed to the cleaved PS block. There is also a small portion of remaining uncleaved block copolymer in the solution, whose GPC signal may be covered by the GPC signal of the cleaved PS block. One may also notice that the signal of cleaved PEO blocks is very weak when compared with that of the PS blocks in Figure 1. The intensity of GPC signal depends on the concentration as well as the difference of refractive index between the polymer and the eluent. The refractive indices of PEO, PS, and THF are 1.456, 1.59, and 1.404, respectively.[54] As a result, the difference of refractive index between PS and THF is much larger than that between PEO and THF. This may lead to the smaller signal intensity of the cleaved PEO. From the GPC result one can see that cleavage does occur when the PS-*b*-PEO block copolymer connected with a trithiocarbonate group is upon UV irradiation in the presence of AIBN.

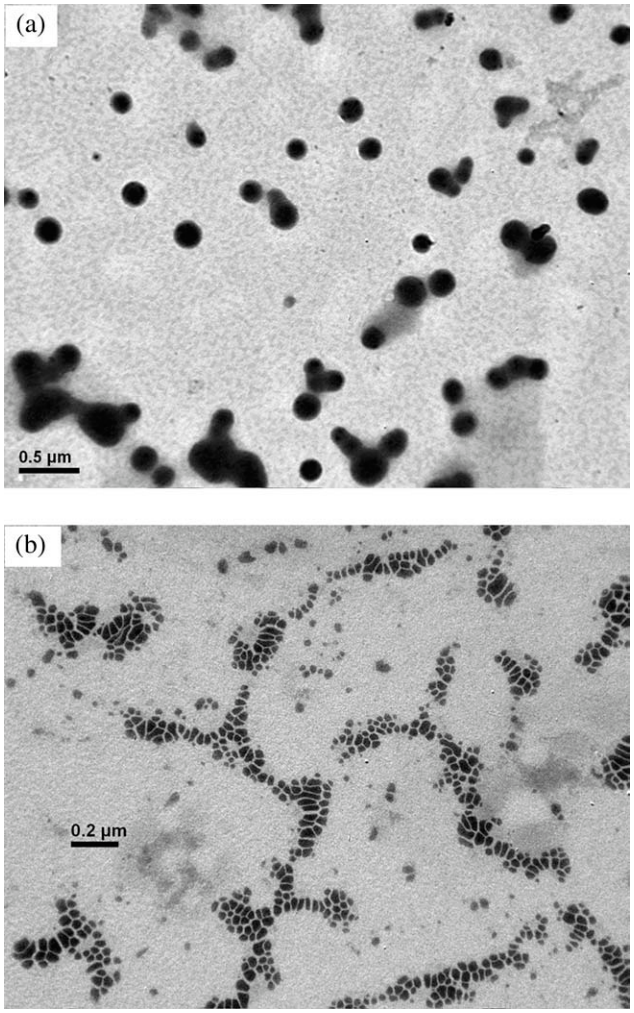


FIGURE 4 TEM images of PS_{199}-*b*-PEO_{45} before (a) and after (b) cleavage in 0.2 w/v % solution of cyclohexane/dioxane (3:1 v/v). The scale bar represents 0.5 μm in (a) and 0.2 μm in (b), respectively.

After cleavage by UV light, the disconnected PEO block was removed by dissolution in methanol and the remaining part was characterized by ^{1}H NMR. Figure 2 shows the ^{1}H NMR spectra of PS_{158}-*b*-PEO_{113} before and after cleavage in THF. One can see from Figure 2 that, the intensity of the CH_2 in the PEO block relatively to the intensity of the phenyl group in the PS block becomes much smaller after cleavage, indicating that most of the PEO blocks are cleaved and removed by methanol. However, the resonance at 3.65 ppm from the PEO blocks can still be observed after cleavage, though the intensity is quite small. This shows that not all the PEO blocks are cleaved and there are some remaining PEO blocks connected with the PS blocks. The cleavage ratio (CR%) can be calculated from the ^{1}H NMR spectra of PS-*b*-PEO block copolymers before and after cleavage based on the following equation:

$$\mathrm{CR}\% = \frac{I_0^{\mathrm{PEO}}/I_0^{\mathrm{PS}} - I_c^{\mathrm{PEO}}/I_c^{\mathrm{PS}}}{I_0^{\mathrm{PEO}}/I_0^{\mathrm{PS}}} \times 100\% \qquad (1)$$

where I_0^{PEO} and I_c^{PEO} are the intensities of the CH_2 peak (3.65 ppm) in the PEO block before and after cleavage, and I_0^{PS} and I_c^{PS} are the intensities of the phenyl peaks (6.20–7.24 ppm) in the PS block before and after cleavage, respectively.

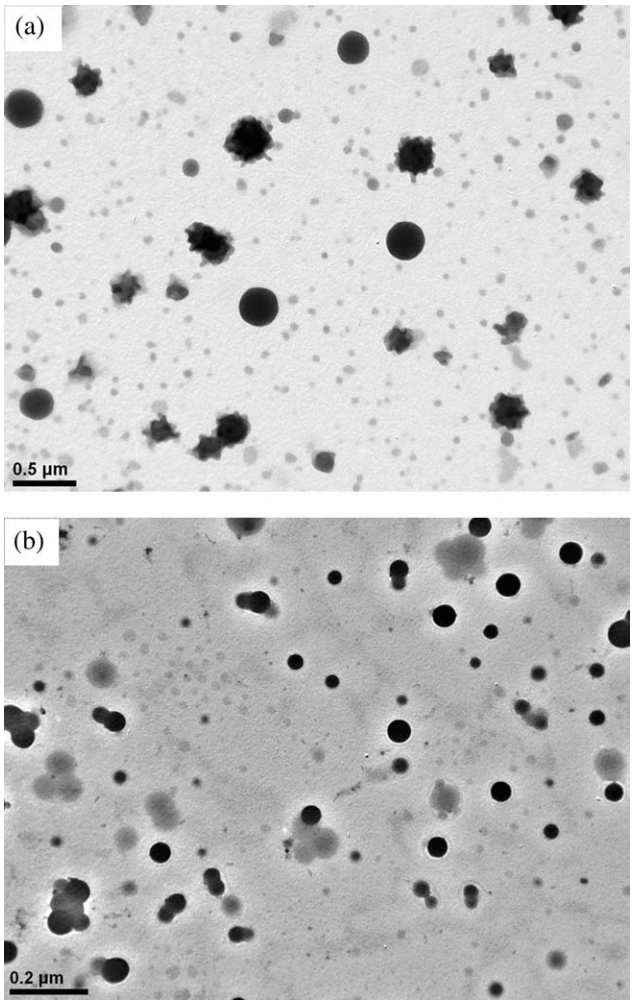


FIGURE 6 TEM images of PS_{218}-*b*-PEO_{113} before (a) and after (b) cleavage in 0.2 w/v % solution of in DMF/ethanol (1:1 v/v). The scale bar represents 0.5 μm in (a) and 0.2 μm in (b), respectively.

It is found that the cleavage ratio is 80% when cleavage is carried out in THF. The incomplete cleavage of the block copolymer by UV irradiation may be a common phenomenon. Nojima et al. observed cleavage ratios ranging from 72 to 88% for the thin films of poly(δ-valerolactone)-*b*-polystyrene (PVL-*b*-PS) block copolymers with a photocleavable *o*-nitrobenzyl group.[31]

Cleavage in Cyclohexane/Dioxane Mixture

In cyclohexane/dioxane mixture, the PS block is soluble but the PEO block is insoluble, thus micelles with PEO as the core and PS as the corona will be formed. Cleavage was carried out under the conditions similar to those in THF solution. Figure 3 shows the ^{1}H NMR spectra of PS_{199}-*b*-PEO_{45} before and after cleavage in cyclohexane/dioxane solution. Like in THF, the resonance intensity from the PEO is very weak after cleavage and the cleavage ratio is 86%, slightly higher than that in THF solution. Since micelles are expected to be formed in cyclohexane/dioxane solution, the micellar morphologies of PS_{199}-*b*-PEO_{45} before and after cleavage were characterized with TEM. As shown in Figure 4, spherical micelles are formed for the original PS-*b*-PEO block copolymer in cyclohexane/dioxane and the diameters of the micelles range from 100 to 200 nm. After cleavage, the morphology becomes irregular and the size is only from 30 to 70 nm. The decrease in size of the micelles verifies the cleavage of the block copolymer. Aggregation is also observed after cleavage. In cyclohexane/dioxane, the core of the micelles is composed of the insoluble PEO block, which is partially crystalline. After cleavage, the protection of the PS block is removed, leading to considerably high specific lateral surface area because of the nano-sized PEO crystals. To reduce free energy, the tiny PEO crystals tend to aggregate after cleavage. Comparing Figure 4(a) with (b), one can see that the number of micelles is not reduced after cleavage. This is due to the solidification effect of the PEO crystals in the core of the micelles, which prevents from reorganization of micelles after cleavage. This leads to only reduction of micellar size, but the number of the micelles is basically unchanged after cleavage.

Cleavage in DMF/Ethanol

In DMF/ethanol mixture, the PEO block is soluble but the PS block is insoluble, thus micelles with PS as the core and PEO as the corona will be formed. Figure 5 shows the ^{1}H NMR spectra of PS_{218}-*b*-PEO_{113} before and after cleavage in DMF/ethanol. Similarly, the resonance of the PEO block becomes very weak after cleavage and the cleavage ratio is about 76%, slightly lower than those in THF and cyclohexane/dioxane mixture. This is possibly due to that ABIN is insoluble in ethanol. The micellar morphologies in DMF/ethanol before and after cleavage were examined and the TEM images are shown in Figure 6. It is found that the size of the micelles changes from 200 to 300 nm before cleavage into 50–75 nm after cleavage. Similarly, we can see from Figure 6 that the number of the micelles is not reduced after cleavage. This is due to the vitrification effect of the PS block, which forms the core of the micelles in DMF/ethanol solution. As the glass transition temperature of the PS block is higher than the room temperature, reorganization of the micelles is forbidden after cleavage, leading to unchanged number of the micelles.

CONCLUSIONS

The result shows that the PS-*b*-PEO block copolymers with a trithiocarbonate group are successfully prepared. When the solutions of the PS-*b*-PEO block copolymers are upon UV irradiation in the presence of AIBN, decomposition of the trithiocarbonate group takes place irrespectively of the common solvent or the selective solvents, leading to cleavage of the block copolymers. In selective solvents micelles are formed and cleavage results in an obvious decrease in the size of the micelles. Aggregation of the micelles may be observed since the protection of the corona of the micelles is removed.

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