

## PS-*b*-PMMA 블록공중합체 마이셀의 방사선 영향 평가

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### Effects of Radiation on PS-*b*-PMMA Block Copolymer Micelles

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**초록:** 본 연구의 목적은 다이옥산/메탄올 혼합물에서 형성된 PS-*b*-PMMA 블록공중합체 마이셀의 감마선에 대한 영향을 평가하는 것이다. DLS 측정결과, 감마선으로 조사된 마이셀은 PS 블록의 가교구조 형성으로 인해 PS와 PMMA 블록 모두에 용해도가 높은 톨루엔 용매에서 감마선으로 조사되지 않은 마이셀에 비해 안정성이 향상됨을 확인하였다. 또한 조사된 PS-*b*-PMMA 마이셀과 조사되지 않은 PS-*b*-PMMA 마이셀의 상대적 크기와 구조는 TEM을 이용하여 비교 관찰하였다.

**Abstract:** The purpose of this study is to investigate the effects of gamma-ray radiation on PS-*b*-PMMA block copolymer micelles formed in a mixture of dioxane/methanol. It was found by DLS measurement that the irradiated micelles were more stable in a good solvent (toluene) for both PS and PMMA blocks compared to non-irradiated micelles due to the cross-linking of PS blocks. TEM was used to observe and compare the relative size and structure of the PS-*b*-PMMA micelles before and after irradiation.

**Keywords:** cross-linking, micelle, PS-*b*-PMMA, block copolymer, radiation.

### Introduction

Block copolymers are composed of two or more polymer blocks linked together by a covalent bond. It is well known that many block copolymers are attractive as self-organizing materials for nanotechnology because they can spontaneously self-assemble in selective solvents to form micelles or nanostructures (spherical micelles, worm-like micelles, cylindrical micelles, and vesicles) with sizes ranging from tens to several hundreds of nanometers, depending on the molecular weight, block length, ratio, and chemical composition.<sup>1-10</sup>

Micelles are generally obtained by dissolving a block copolymer in a solvent that has high solubility for one of the blocks. Additionally, the micellization process of the block copolymer

depends mainly on the critical micelles temperature (CMT) and critical micelle concentration (CMC). If the CMT and CMC are not reached, self-assembly of the block copolymer will not occur. Consequently, the stability of the micelles produced by a block copolymer strongly depends on external conditions such as the solvent, temperature, and concentration.<sup>9-12</sup>

Among the block copolymers, amphiphilic diblock copolymers exhibit excellent self-assembly capabilities due to their unique chain structure, which includes both hydrophilic and hydrophobic blocks. Above their CMT or CMC, the micelles from an amphiphilic diblock copolymer are composed of an inner core part formed from one block and an outer corona part formed from the other block. Self-assembled micelles produced from amphiphilic diblock copolymers have received considerable attention because they have potential applications in the fields of biotechnology, drug delivery, the fabrication of nanoparticles, and so on.<sup>9,10,12-17</sup> However, these self-assembled

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micelles have a drawback that arises from their inherent low physical stability, which often limits their practical applications. The micelles formed by non-covalent interaction can easily lose their self-assembled structure due to changes in environmental conditions such as solvent polarity, pH, concentration, and temperature. According to previous studies, one of the effective ways to stabilize block copolymer micelles is to induce a cross-linked network in the micellar core or corona by introducing relatively strong and robust covalent bonding. The morphological structure of the cross-linked micelles is expected to preserve their structure in the face of environmental change.<sup>9,10,18-21</sup>

Among amphiphilic diblock copolymers, PS-*b*-PMMA (polystyrene-*b*-poly(methyl methacrylate)) has been widely used to fabricate self-assembled nanostructured materials including polymeric micelles. Several studies have reported that UV and electron beam (EB) are effective tools for the selective cross-linking of one block (PS) or the selective removal of the other block (PMMA). It is known that PS and PMMA have different reaction patterns under a radiation environment. Generally, when PS chains are exposed to radiation a cross-linking reaction predominantly occurs, whereas a chain scission reaction predominantly occurs in the case of PMMA chains.<sup>8,22-25</sup>

Recently, Fayad *et al.* reported the effect of UV exposure on PS-*b*-PMMA micelles in a solution. In their work, it was also observed that a cross-linking reaction was produced in the micellar core part (PS), whereas a degradation reaction occurred in the micellar corona part (PMMA) upon UV irradiation. In addition, the results indicate that the size of the micelles decreased with UV exposure as a result of PMMA degradation, and the morphology of the micelles was changed from star-like to crew-cut micelles.<sup>26</sup> In this study, we investigated the effect on PS-*b*-PMMA block copolymer micelles using a gamma-ray irradiation method, because gamma-ray irradiation has several advantages compared to UV irradiation, including high reactivity, deep penetration ability, high energy, and a fast processing time. Among them, the deep penetration ability of gamma-ray irradiation is very useful, especially when a thicker material has to be treated evenly from the surface to the inner core. Therefore, in this experiment, gamma-ray irradiation was used to treat the vials containing PS-*b*-PMMA micelles. The morphological changes of the block copolymer micelles produced by gamma-ray irradiation were evaluated by dynamic light scattering (DLS) and transmission electron microscopy (TEM) measurements.

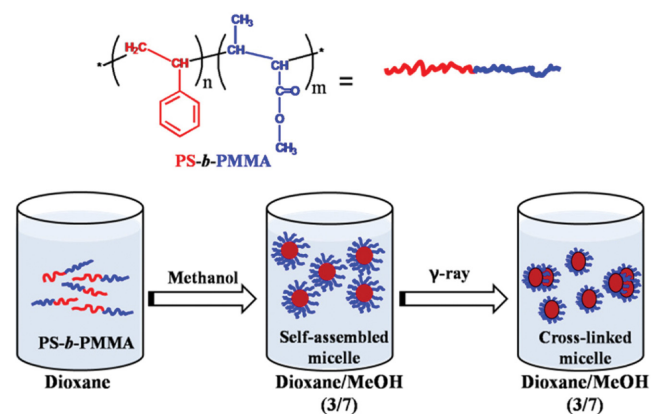
## Experimental

**Materials.** Styrene (99% pure) and methyl methacrylate (99% purity) were purchased from Sigma-Aldrich Co. LLC. and were purified by vacuum distillation in the presence of calcium hydride or/and sodium just before use. *sec*-Butyllithium was purchased from Rockwood Lithium Inc. and used as received. Lithium chloride (anhydrous, > 99% purity) was purchased from Sigma-Aldrich Co. LLC. and used as received. Tetrahydrofuran (THF) was purchased from Fisher Scientific international Inc. and was then distilled from a sodium benzophenone ketal. Other solvents including 1,4-dioxane (99% purity), methanol (99.8% purity), and toluene (99.5% purity) were purchased from Showa Chemical Co. Ltd. and used without further purification.

**Synthesis of PS-*b*-PMMA.** PS-*b*-PMMA copolymer was synthesized by anionic polymerization using *sec*-butyllithium as the initiator with a sequential addition of styrene and methyl methacrylate in THF at -78 °C in the presence of LiCl under purified atmosphere. The molecular weight ( $M_w$ ) and polydispersity of the PS<sub>437</sub>-*b*-PMMA<sub>455</sub> copolymer were 91000 and 1.18, respectively.

**Micelle Preparation.** The preparation scheme of the PS<sub>437</sub>-*b*-PMMA<sub>455</sub> copolymer solution is illustrated in Scheme 1. PS<sub>437</sub>-*b*-PMMA<sub>455</sub> copolymer was completely dissolved in 1,4-dioxane in concentrations of 2.6, 5.3, and 10.6 mg/mL by shaking the solution at room temperature for 12 h using a Roller shaker (Roller 6 basic, IKA®). The PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelles were formed by the slow addition of 70% v/v methanol to the stock solution at 30 °C under magnetic stirring.<sup>22</sup>

**Gamma-ray Irradiation.** The PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelle solution prepared was placed in a 10 mL glass vial and then



**Scheme 1.** Preparation of cross-linked PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelles by gamma-ray irradiation.

irradiated at room temperature using a gamma-ray from a  $^{60}\text{Co}$  source at irradiation doses ranging from 2.5 to 30 kGy with a dose rate of 5 kGy/h.

**Characterization.** The diameters and dispersion patterns of the preformed  $\text{PS}_{437}\text{-}b\text{-PMMA}_{455}$  micelle solutions and the irradiated solutions were determined by DLS measurements (Delsa Nano C, Beckman Coulter). The DLS measurements of the irradiated micelle solutions were performed within 1 h after the gamma-ray irradiation experiments. The morphology and dimensional stability of the irradiated micelles against the addition of toluene were studied using TEM (JEOL, JEM 2200-FS TEM). The irradiated micelle solutions were mixed with toluene within 1 h after the gamma-ray irradiation experiments. To observe the TEM image, the micelle solutions were dripped onto support films, ultrathin carbon film/holey carbon, 400 mesh copper grids and then dried at room temperature for 1 day.

## Results and Discussion

$\text{PS-}b\text{-PMMA}$  block copolymer is known to spontaneously self-assemble to form micelles in selective solvents including a solvent mixture of dioxane/methanol. In this study, the formed  $\text{PS-}b\text{-PMMA}$  micelles were subjected to gamma-ray irradiation to investigate the effect of radiation on the micelle (Scheme 1). According to previous studies by Duhamel *et al.*,<sup>22</sup> the solvent composition is a key factor in the micelle formation of  $\text{PS-}b\text{-PMMA}$  block copolymer. As is well known, both PS and PMMA blocks are well-dissolved in dioxane, whereas only the PMMA block is well-dissolved in methanol. In their work, it was found that  $\text{PS-}b\text{-PMMA}$  micelles were well-formed in a 3/7 volume percent mixture of dioxane/methanol. A higher methanol content leads to aggregation, and a lower methanol content prevents the self-assembly of the block copolymer into micelles.

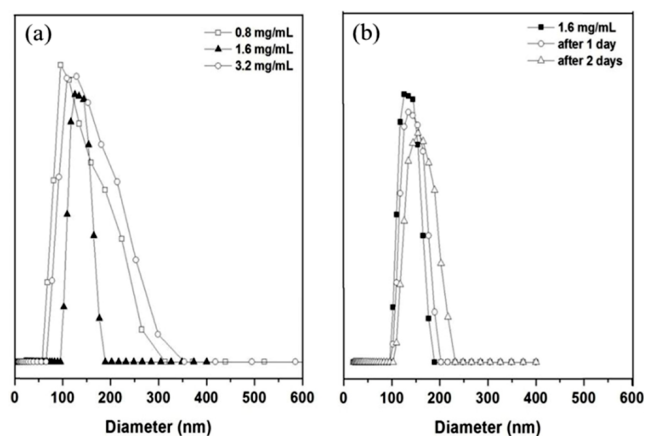
The  $\text{PS}_{437}\text{-}b\text{-PMMA}_{455}$  block copolymer was prepared using the standard anionic polymerization method. The molecular weight ( $M_w$ ) and polydispersity of the prepared  $\text{PS-}b\text{-PMMA}$  block copolymer were 91000 and 1.18, respectively. In this study, three different  $\text{PS-}b\text{-PMMA}$  block copolymers, with  $\text{PS}_{92}\text{-}b\text{-PMMA}_{382}$ ,  $\text{PS}_{437}\text{-}b\text{-PMMA}_{455}$ , and  $\text{PS}_{638}\text{-}b\text{-PMMA}_{166}$  were synthesized through anionic polymerization. It was observed that the  $\text{PS-}b\text{-PMMA}$  block copolymers with a relatively larger or shorter PMMA block ( $\text{PS}_{92}\text{-}b\text{-PMMA}_{382}$  and  $\text{PS}_{638}\text{-}b\text{-PMMA}_{166}$ ) formed larger aggregates instead of well-dispersed micelles in a mixture of dioxane/methanol (3/7). In

contrast, the  $\text{PS}_{437}\text{-}b\text{-PMMA}_{455}$  polymer successfully formed well-dispersed micelles in the solvent.

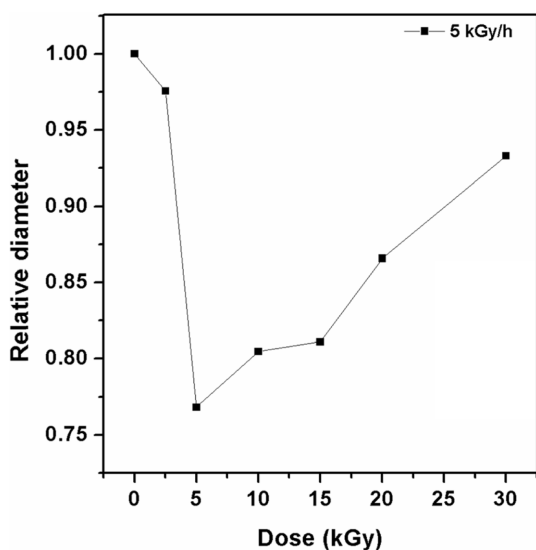
The size distributions of the  $\text{PS}_{437}\text{-}b\text{-PMMA}_{455}$  micelles prepared with different concentrations (0.8, 1.6, and 3.2 mg/mL) in a mixture of dioxane/methanol (3/7) were determined by DLS, and the results are shown in Figure 1. The DLS is a very useful tool for estimating the hydrodynamic diameter of a block copolymer micellar system. As shown in Figure 1(a), the average hydrodynamic diameters at 0.8, 1.6, and 3.2 mg/mL were measured to be 118, 134, and 126 nm, respectively. No significant difference in the average hydrodynamic diameters of the micelles was observed within the concentration range. However, the size distribution of the micelles formed at 1.6 mg/mL was relatively narrow compared to the others. The hydrodynamic diameter ranged from 102.5 to 176.7 nm at 1.6 mg/mL, whereas that of the other micelles ranged from 68.5 to 264.8 nm at 0.8 mg/mL and from 78.2 to 299.2 nm at 3.2 mg/mL.

Figure 1(b) demonstrates the changes in the size distribution of micelles formed at 1.6 mg/mL as a function of time. It was observed that the size distribution and the average hydrodynamic diameter of the micelles slightly increased with an increase in time of up to 2 days. This result implies that the micelles which are formed at a concentration of 1.6 mg/mL are relatively stable. Therefore, in this study,  $\text{PS}_{437}\text{-}b\text{-PMMA}_{455}$  polymer micelles were prepared in a mixture of dioxane/methanol (3/7) with a concentration of 1.6 mg/mL and used to investigate the radiation effects of the micelles induced by gamma-ray irradiation.

As mentioned earlier, it was reported that when the  $\text{PS-}b\text{-}$



**Figure 1.** Size distributions and diameters of the  $\text{PS}_{437}\text{-}b\text{-PMMA}_{455}$  micelles as the function of (a) concentrations; (b) time at 1.6 mg/mL at 25 °C.

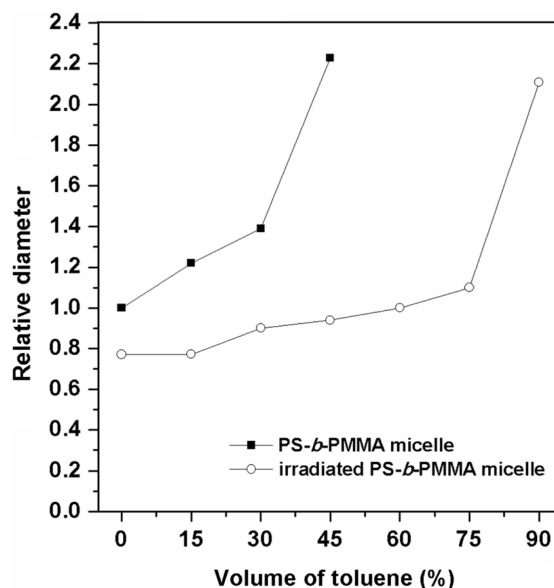


**Figure 2.** Relative diameters of the gamma-ray irradiated PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelles.

PMMA micelles were exposed by UV irradiation a cross-linking reaction occurred at the micellar core part (PS block) whereas a degradation reaction occurred at the micellar corona part (PMMA block). Figure 2 illustrates the relative average hydrodynamic diameters of the PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelles obtained after their exposure to gamma-ray at various doses. The relative diameters were found to significantly decrease when the dose was increased up to 5 kGy and then gradually increased up to 30 kGy. This result is similar to those previously reported for UV irradiation.<sup>26</sup> Therefore, it can be assumed that the PMMA block of the micellar corona is degraded through a chain scission by gamma-ray irradiation, and the morphology of the micelles is changed from star-like to crew-cut micelles. The crew-cut micelles, having a relatively shorter micellar corona, begin to aggregate into micelle groups due to the lack of a PMMA corona to protect them.

As mentioned earlier, a cross-linking reaction occurs predominantly when PS chains are exposed to radiation.<sup>23-25</sup> Thus, it is expected that the PS blocks of the PS-*b*-PMMA block copolymer are also mainly cross-linked through gamma-ray irradiation. The stabilizing effect on the micelles obtained by the cross-linking of the PS block was investigated by adding toluene into the micelle solution since toluene is a good solvent for both blocks (PS and PMMA) and can induce the demicellization of the block copolymer micelles.<sup>10,14,26</sup>

Figure 3 shows the relative diameters of the PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelles and the gamma-ray irradiated PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelles in accordance with toluene addition. The

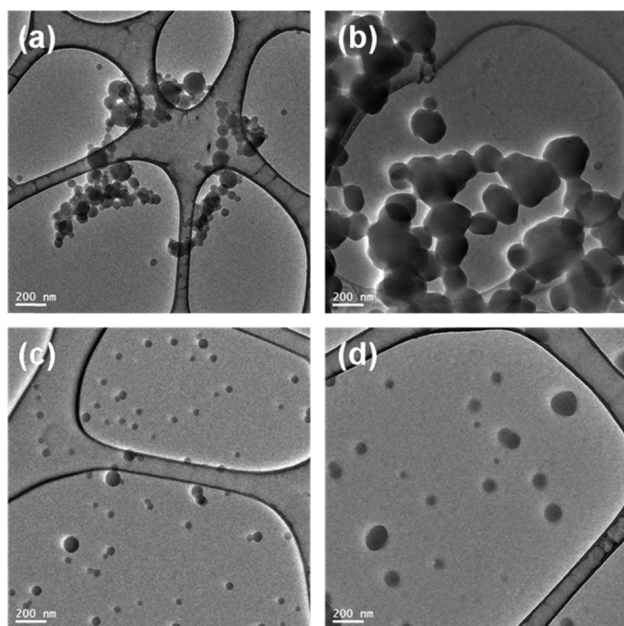


**Figure 3.** Relative diameters of the PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelles and the gamma-ray irradiated PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelles in accordance with toluene addition.

relative diameter of the non-irradiated PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelles was found to significantly increase with the increasing addition of toluene, and above a 45% relative volume fraction of toluene the micelles eventually lost their self-assembled structure. However, the relative diameter of the gamma-ray irradiated PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelle slowly increased with the increasing addition of toluene until the relative volume of toluene reached 75%. These results indicate that the gamma-ray irradiated micelles are more stable and resistant to demicellization produced by the addition of toluene, compared to non-irradiated micelles, owing to the cross-linking by gamma-ray irradiation of PS chains in the micellar core.<sup>26</sup>

Furthermore, the increased stability of gamma-ray irradiated PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelles as a result of the cross-linking of PS chains in the micellar core part was also confirmed by direct observation with TEM. Figure 4 shows TEM images of the PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelles and gamma-ray irradiated PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelles before and after toluene addition (15%). From the TEM images of the PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelles (Figure 4(a) and 4(b)), it was observed that the diameters of micelles are ranged from 30 to 142 nm and from 114 to 457 nm before and after the addition of toluene, respectively. As mentioned above, the addition of toluene leads to the swelling of the micelles, and then the dimensions of the micelles finally increase.

On the other hand, the diameters of the gamma-ray irra-



**Figure 4.** TEM images of (a) PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelles; (b) PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelles after toluene addition (15%); (c) gamma-ray irradiated PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelles; (d) gamma-ray irradiated PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelles after toluene addition (15%).

diated PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelles (Figure 4(c) and 4(d)) were only slightly changed after the addition of toluene (the diameters were measured to be ranged from 30 to 114 nm before the addition of toluene and from 30 to 171 nm after the addition of toluene). Although the dimensions of the gamma-ray irradiated micelles slightly increased, the morphology of the micelles was not significantly changed with the addition of toluene. Therefore, the TEM results also confirmed that the gamma-ray irradiated micelles had become more stable due to the cross-linking of the PS chains.

In this study, we demonstrated that gamma-ray irradiation can be effectively utilized for stabilizing the self-assembled PS-*b*-PMMA micelles by inducing a cross-linked network in the PS block in the core part of the block copolymer micelles.

## Conclusions

This study investigated the effects of gamma-ray irradiation on PS<sub>437</sub>-*b*-PMMA<sub>455</sub> block copolymer micelles formed in a mixture of dioxane/methanol. Measurements indicated that the relative diameter of the PS<sub>437</sub>-*b*-PMMA<sub>455</sub> micelles decreased significantly at the beginning of the irradiation and then increased slowly with an increase in the irradiation dose. This was understood to occur because the PMMA block of the

micellar corona is degraded via chain scission due to gamma-ray irradiation, and then a relatively shorter micellar corona begins to aggregate into micelle groups. The stabilization of the micelles by the radiation cross-linking of the PS block was also investigated by adding toluene into the irradiated micelle solution. It was observed that the irradiated micelles were more stable and resistant to the demicellization induced by the addition of toluene compared to non-irradiated micelles, due to the cross-linking by gamma-ray irradiation of the PS chains located in the micellar core. These results suggest that gamma-ray irradiation can be effectively utilized for stabilizing self-assembled PS-*b*-PMMA micelles by introducing a cross-linked network into the PS block in the core part of the block copolymer micelles.

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