

Synthesis of block copolymer with photo-decomposable polyurethane and its photo-initiated domino decomposition



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ABSTRACT

A block copolymer consisting of a photo-decomposable polyurethane and poly(methyl methacrylate) (PMMA) was developed. The end-functionalized polyurethane (**P2**) was synthesized by polycondensation with the end-functionalization reagents. **P2** possesses the photosensitive *o*-nitrobenzyl group and the 2-bromoisobutyryl group as the initiator of the atom transfer radical polymerization (ATRP). The block copolymer (**P2-*b*-PMMA**) was synthesized by the ATRP of methyl methacrylate (MMA) with **P2** as the macroinitiator. The **P2** block in **P2-*b*-PMMA** was decomposed by photo-irradiation at 365 nm by the initiation of the photo-fries rearrangement of the urethane linkage and the subsequent domino reaction consistent with the elimination of the aza-quinone methide and decarboxylation. The photo-initiated decomposition of the **P2** segment in the thin-film state was accomplished.

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1. Introduction

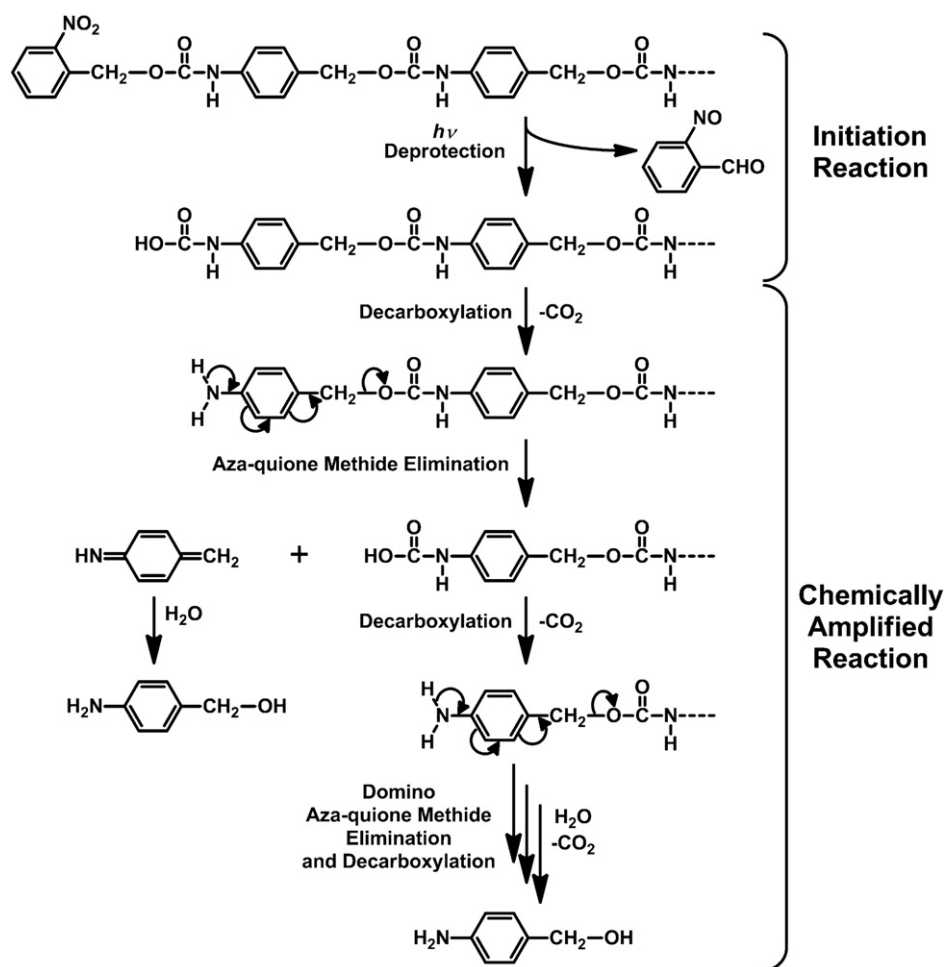
Block copolymers consist of two or more chemically different polymer chains covalently bonded at the chain ends and possess the ability to self-assemble because of the segregation between each block segment [1,2]. The microphase-separated structure via the self-assembly of the block copolymer in the bulk is typically applied as thermoplastic elastomers consistent with the plastic polymer domain as the physical cross-linking point in the elastomer matrix [3,4]. The block copolymer thin film also provides potential applications for lithographic materials [5–8], solar cells [9], etc. [10–12]. The change in the self-assembled structure by external stimuli in the bulk or thin-film state is based on the shift in the volume fraction between each block segment. A cylindrical structure-forming block copolymer containing poly(*tert*-butyl methacrylate) as the minor domain, which thermally decomposes to generate poly(methacrylic acid) or poly(methacrylic anhydride) and formed a spherical morphology by thermal annealing because of the decrease in the volume fraction of the poly(*tert*-butyl methacrylate) domain in the block copolymer thin film [13]. By using area-selective stimuli such as the photo-irradiation of the photosensitive block copolymer, different microphase-separated structures were obtained in the exposed and unexposed areas. Bothworth et al. reported that poly(α -methylstyrene)-*b*-poly(4-hydroxystyrene) (P α MS-*b*-PHOST) with a photo-acid generator and cross-linker, which produced a spherical and cylindrical microphase-separated structure at the exposed and unexposed areas, respectively [14].

To induce a significant magnitude of change in the self-assembled structure by a stimulus, a reaction system including an initiation reaction followed by a catalytic or domino reaction is a promising method, because a large number of reactions are caused by a single initiation reaction. A chemically amplified photoresist is one of the most efficient stimuli-responsive systems such that the catalytic reaction drastically changes the solubility of the polymers even for a short photo-irradiation for catalyst generation [15,16]. Furthermore, decomposition of the polymer main chain is one of the biggest and irreversible changes in the chemical structure of the polymer and is suitable for the high magnitude change of stimuli-responsive materials.

The “self-immolative polymer,” labeled by Shabat, is a class of polymers decomposed by various stimuli [17–20]. The polymer main chain can be decomposed by a domino reaction initiated by the deprotection of the chain-end protection group. The protection group is designed by the target stimuli, and a wide variety of stimuli such as pH [21], enzyme [22], and photo-irradiation [23], have been used. Most of these decomposable polymer main chains are consistent with the aromatic polyurethane based on the 4-aminobenzyl alcohol. The polyurethanes are decomposed by repeating the aza-quinone methide elimination and the subsequent decarboxylation from the 4-aminobenzyloxy group at the chain end as shown in Scheme 1. Furthermore, Wilhelm et al. reported the photo-fries rearrangement of the aromatic polyurethane to generate the 4-aminobenzyl derivatives in the main chain [24]. To develop a more efficient stimuli-responsive system, in this study, we used the photo-fries rearrangement as the initiation reaction of the domino decomposition. In this system, the initiation reaction occurs at any polyurethane linkage, and each photo-fries rearrangement was amplified to a number of main chain decompositions in the domino

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Scheme 1. Chemically amplified decomposition of polyurethane initiated by photo-deprotection at the chain end.

reaction mode (Scheme 2). Furthermore, one of the challenging issues in the domino decomposition system is controlling the self-assembled structure in the block copolymer system. There are only a few reports dealing with a block copolymer including the domino decomposition system, while the decomposition of one of the block segments can induce a large amplitude of change in the self-assembled structure. Gillies et al. reported the controlled release of a dye from a block copolymer micelle consistent with a decomposable polyurethane and an inert polyethylene glycol catalyzed by trifluoromethyl acetic acid in an aqueous solution [25]. Compared with this system, photo-irradiation is a substantially cleaner system and can induce change without any addition. Furthermore, the domino decomposition behavior in the polymer bulk and thin film is essential for inducing the change in the self-assembled structure in these states.

In this study, we synthesized a block copolymer including a photo-decomposable polyurethane as one block segment that decomposed in the domino reaction mode. The block copolymer was synthesized by polycondensation to obtain the end-functionalized polyurethane with a photo-decomposable end and a 2-bromoisobutyl group as the atom transfer radical polymerization (ATRP) initiator, which was followed by the subsequent ATRP of methyl methacrylate (MMA) using the polyurethane as a macroinitiator [26]. The polyurethane segment can be decomposed by the chemically amplified system consistent with the initiation reaction and domino decomposition. The photo-initiation reactions include the photo-deprotection of the *o*-nitrobenzyl group at the chain end and the photo-fries rearrangement of the urethane linkage in the main chain. The generated 4-aminobenzoyloxy chain end causes the elimination of the aza-quinone methide and decarboxylation in the domino reaction mode.

2. Experimental

2.1. Materials

MMA and dimethyl sulfoxide (DMSO) were purchased from Tokyo Kasei Kogyo Co. Ltd. (Tokyo, Japan) and used after distillation over CaH₂. Copper (I) bromide (CuBr) was purchased from Wako Pure Chemical Industries, Ltd. (Kyoto, Japan) and purified by dissolving in aq. 1 M HBr, precipitated in H₂O, and then stored under nitrogen. All of the other reagents and solvents were used as received.

2.2. Measurements

The ¹H NMR spectra were recorded by a JEOL JNM-ECA-500 instrument at 500 MHz. CDCl₃ and DMSO-*d*₆ were used as the solvents with tetramethylsilane (TMS) as the internal standard. The infrared (IR) spectra were recorded by a JASCO FT/IR-4100 spectrometer. The number- and weight-average molecular weights (*M*_n and *M*_w, respectively) were estimated by gel permeation chromatography (GPC) analysis with GPC 101 (Shodex Inc) using RI detectors eluted with tetrahydrofuran (THF) at a flow rate of 1 mL/min and calibrated by standard polystyrene samples. The MALDI-TOF-MS spectra were recorded by a Shimadzu/Krotos Axima curved field reflectron (CFR) in the reflectron ion mode using a laser ($\lambda = 337$ nm). A sample solution of the polymer with dithranol as the matrix and potassium trifluoroacetate as the cationization agent was prepared in THF. Differential scanning calorimetry (DSC) analyses were performed on a HITACHI X-DSC 7000 (Hitachi High-Tech Science Corporation, Tokyo, Japan) at heating and cooling rates of 10 °C/min under nitrogen flow (see supplementary data). The

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