Facile Synthesis and Photo-Tunable Properties of a Photosensitive Polymer Whose Chromophores Bound with pH-Labile Cyclic Acetal Linkages

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ABSTRACT: A well-defined photosensitive polymer whose chromophores were bound with pH-labile cyclic acetal linkages, i.e., poly[5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane] (PEMSD), was synthesized via RAFT polymerization of EMSD monomer under a mild visible light radiation at 30 °C. Kinetic studies indicated the well-controlled behavior of this RAFT polymerization. The living character of this RAFT polymerization was confirmed by the well-controlled chain-extending RAFT polymerization using an above-synthesized PEMSD as a macromolecular chain transfer agent under this mild visible light radiation at 30 °C. ^{1}H NMR analysis evidenced the intact cyclic acetal linkages and 100% *E*-cinnamyl chromophores of this PEMSD polymer synthesized under these mild conditions. Isomerization of *E*-cinnamyl chromophores of this polymer was triggered on exposure to UV radiation, particularly in a wave range of 254−365 nm, with strong light intensity dependence. This photoisomerization reached equilibrium at ca. 65% *Z*-cinnamyl formation. On photoisomerization of *E*-cinnamyl chromophores, the maximum absorption wavelength (λ_{max}) of this PEMSD polymer blue-shifted from 252 nm (100% *E*-cinnamyl) to 244 nm (*E*/*Z* = 44:56); accordingly, its molar extinction coefficient at λ_{max} linearly decreased from 1.97×10^4 M^{-1} cm^{-1} to 1.41×10^4 M^{-1} cm^{-1}. Moreover, this photoisomerization improved the irregularity of polymer chains, thus its glass transition temperature linearly decreased from 119 °C (100% *E*-cinnamyl) to 99 °C (*E*/*Z* = 37:63). More importantly, this photoisomerization enhanced the steric hindrance and hydrophobicity of cyclic acetal linkages and shielded the cyclic acetal linkages from the proton attack and hydration. This significantly improved the stability of cyclic acetal linkages neighboring *Z*-cinnamyl chromophores. On the other hand, this photoisomerization improved the irregularity and loose packing of polymer chains, leading to even more labile cyclic acetal linkages neighboring *E*-cinnamyl chromophores than those in 100% *E*-cinnamyl PEMSD polymer. In both 100% *E*-cinnamyl and partially *Z*-cinnamyl-isomerized cases, higher molecular weight of PEMSD polymer led to a slower hydrolysis process of its cyclic acetal linkages. This remarkable phototunable stability of pH-labile cyclic acetal linkages rendered potential applications in photosensors and light-triggered drug delivery.

Introduction

A wide range of biological processes are triggered by light in nature. The vision perception,[1,2] photosynthesis,[3,4] and phototaxis[5,6] are the most fundamental light-controlled mechanisms. The molecular mechanisms of these light-triggered biological processes were extensively studied in recent decades.[4,7,8] One common feature of these systems is the participation of chromophores, particularly those are bound with pH-labile linkages, e.g., Schiff base linkages[9,10] and thiol ester linkages.[6,11] For example, in the visual process, 11-*cis* retinyl chromophores of rhodopsin isomerize to all-*trans* form, leading to the cleavage of their neighboring Schiff base linkages, thus triggering the visual perception.[12,13] Another example is the solar energy conversion process of bacteriorhodopsin in purple membrane of halobacteria. Under solar radiation, all-*trans* retinyl chromophores isomerize to 13-*cis* form, driving their neighboring Schiff base linkages outwardly transport protons from the inner to the outer side of the membrane. This generated potential gradient activates the membrane-bound ATPase for ATP synthesis.[4,14]

In these two photochromic proteins, their retinyl chromophores are bound with pH-labile Schiff base linkages. Through reversible protonation-deprotonation and/or cleavage-regeneration processes, these Schiff base linkages exert precise control over the visual perception or photosynthesis. In bacteriorhodopsin, the light-driven proton transport process requires a reversible deprotonation−reprotonation of Schiff base linkages. This leads to a 160 nm shift of λ_{max} of retinyl chromophores.[4]

Mimicking this particular structural character, we designed a new photosensitive polymer, whose chromophores were bound with pH-labile cyclic acetal linkages, i.e., poly[5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane] (PEMSD). Similar to the hydrolysis of Schiff base, the hydrolysis of cyclic acetal involves a series of reversible intermediate steps, including protonation, hydration, and ring-opening prior to cleavage.[15] More importantly, the cyclic acetal linkages are generally more stable than Schiff base linkages. This facilitates the synthesis of this particular type of photosensitive polymers.

Recently, Zhao and co-workers[16] reported the UV-cleavage of photolabile chromophores from polymer micelles. Most recently, McCoy et al.[17] reported the UV-cleavage of photolabile chromophores from small molecular drug derivatives. However, to the best of our knowledge, the synthesis of a photosensitive polymer, whose chromophores are bound with pH-labile linkages (thereby the stability of these pH-labile linkages being able to be tuned by photoisomerization of their neighboring chromophores), is unprecedented.

Reversible addition−fragmentation chain transfer radical polymerization or RAFT polymerization is a powerful tool for the synthesis of well-defined polymers.[18–22] RAFT polymerization was extensively utilized for the synthesis of pH- or thermosensitive polymers.[23–31] Recently, RAFT polymerization was utilized for the synthesis of azobenzene-containing photosensitive polymers.[32,33]

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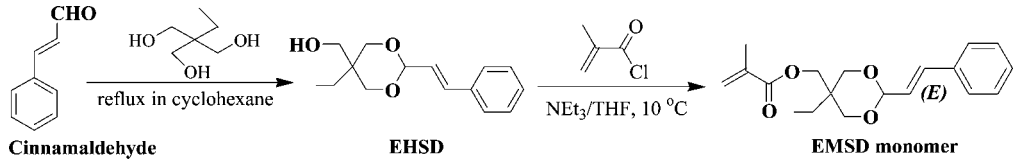
Scheme 1. Schematic Illustration of Synthesis of 5-Ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane (EMSD) Monomer



Enlightened by the pioneer studies of UV-initiating RAFT polymerization separately by Pan and co-workers,[34] Quinn et al.,[35,36] and more recently by Barner and co-workers,[37] our group[38] proposed a rapid and well-controlled ambient temperature RAFT polymerization under a mild long-wave UV−vis radiation. Our studies demonstrated that the living character of this ambient temperature RAFT polymerization strongly depended on the wave range of UV−vis radiation.[39] Moreover, different from what observed in a thermoactivating RAFT polymerization[40] under these mild conditions, decreasing the concentration of chain transfer agent (CTA) and photoinitiator led to a short initialization period and rapid overall polymerization.[41] This approach was successfully utilized for the efficient and facile synthesis of well-defined styrenic-based polymers.[42] Most recently, we reported a rapid and well-controlled ambient temperature RAFT polymerization under a mild solar radiation in a visible wave range over 400 nm.[43] This approach rendered a facile and powerful tool for the synthesis of well-defined photosensitive polymers whose chromophores were bound with cyclic acetal linkages.

This paper described a novel design and facile synthesis of a well-defined photosensitive polymer, whose chromophores are bound with pH-labile cyclic acetal linkages, i.e., poly[5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane]. This polymer was synthesized via RAFT polymerization of 5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane (EMSD) monomer under a mild visible light radiation at 30 °C. The kinetics of this RAFT polymerization was studied using ^{1}H NMR analysis and gel permeation chromatography (GPC) measurements. The living character of this RAFT polymerization was investigated by the chain-extending RAFT copolymerization using an above-synthesized PEMSD polymer macromolecular chain transfer agent under mild visible light radiation at 30 °C. The effect of photoisomerization of *E*-cinnamyl chromophores on the optical properties, glass transition temperature, and stability of cyclic acetal linkages of this PEMSD polymer were studied by UV spectroscopy, differential scanning calorimetry (DSC) measurements, and ^{1}H NMR studies.

Experimental Section

Materials. 2-Cyanoprop-2-yl(4-fluoro)dithiobenzoate (CPFDB) was synthesized according to the literature procedures.[44] (2,4,6-Trimethylbenzoyl)diphenylphosphine oxide (TPO, 97%) was purchased from Runtec Chem. Co. and used as received. Cinnamaldehyde (95%, Shanghai Reagent Co.) was distilled under reduced pressure. 2-Ethyl-2-hydroxymethyl-1,3-propanediol (98%, Shanghai Reagent Co.) was used as received. Poly(ethylene glycol) monomethacrylate (PEGMA, Aldrich, M_n = 475 g mol^{-1}, M_w/M_n = 1.03) was passed through a basic alumina column to remove inhibitor, stored at −20 °C. Glycidyl methacrylate (GMA, Yuanji Chem. Co. Ltd., 98%) was dried over 4 Å molecular sieves overnight, distilled under reduced pressure, and stored at −20 °C. JB400 and JB320 filters were purchased from Yaguang Sci. Edu. Equip. Co., China.

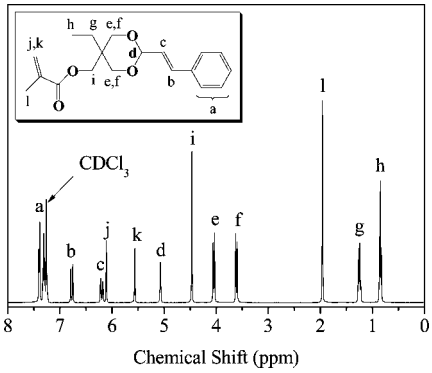


Figure 1. ^{1}H NMR spectrum of 5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane monomer in $CDCl_3$ solution.

Visible Light Radiation Source for Ambient Temperature RAFT Polymerization. A mercury vapor lamp emitting separately at 254, 302, 313, 365, 405,436, 545, and 577 nm, was utilized. JB400 filters were selected to cut off the shorter-wave UV radiation below 400 nm and adjust light intensity. The light intensity was measured on a UV-A radiometer being equipped with a 420 nm sensor. Thus, a visible light radiation source emitting separately at 405, 436, 545, and 577 nm, with a mild intensity of 200 μW cm^{-2} at 420 nm, was obtained for this purpose.

Synthesis of 5-Ethyl-5-hydroxymethyl-2-styryl-[1,3]dioxane (EHSD). 2-Ethyl-2-hydroxymethyl-1,3-propanediol (46.96 g, 0.35 mol), cinnamaldehyde (39.65 g, 0.3 mol), 120 mL cyclohexane, and 0.8 mL of 8.0 mol L^{-1} hydrochloric acid were charged in a 500 mL round-bottom flask being equipped with a water separator. The solution was refluxed for 4 h, and the generated water was removed by azeotropic distillation. The mixture was cooled to room temperature. After filtration, the precipitates were collected, and dissolved in chloroform. The solution was washed by 2 wt % Na_2CO_3 aqueous solution, saturated NaCl aqueous solution, and distilled water until it was neutralized. The solution was dried over anhydrous $MgSO_4$. After filtration, the solvent was removed by rotary evaporation. The crude product was recrystallized in anhydrous ethyl ether at −20 °C to yield white solid product. Weight = 48.5 g, yield = 65%. ^{1}H NMR (δ, in $CDCl_3$, ppm): 0.86 (3H,$CH_2C\underline{H}_3$), 1.24 (2H, $C\underline{H}_2CH_3$), 1.68 (1H, $CH_2O\underline{H}$) 3.58 (2H, two of $OCHOC\underline{H}_2CC\underline{H}_2$ in cyclic acetal), 3.93 (2H, $C\underline{H}_2OH$), 4.03 (2H, two of $OCHOC\underline{H}_2CC\underline{H}_2$ in cyclic acetal), 5.07 (1H, $OC\underline{H}OCH_2CCH_2$ in cyclic acetal), 6.19 (1H, $C_6H_5CH{=}C\underline{H}$), 6.77 (1H, $C_6H_5C\underline{H}{=}CH$), 7.20−7.46 (5H, $C_6\underline{H}_5$).

Synthesis of 5-Ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane (EMSD) Monomer. EHSD (37.20 g, 0.15 mol), triethylamine (20.20 g, 0.20 mol) and 160 mL anhydrous tetrahydrofuran were charged in a 500 mL dried round-bottom flask. The flask was immersed in a cold ice bath at 0 °C. Methacryloyl chloride (17.75 g, 0.17 mol) solution in 80.0 mL anhydrous tetrahydrofuran was added dropwise in the flask over 2 h. The mixture was stirred at 10 °C for 12 h. The white ammonium salt was filtered out. The solution was concentrated by rotary evaporation, washed by 2 wt % Na_2CO_3 solution, saturated NaCl solution, and distilled water until it was neutralized. The solution was dried over anhydrous $MgSO_4$. After filtration, the solvent was removed by rotary evaporation. The crude product was first purified by silica column chroma-

tography, using a mixed petroleum ether and ethyl acetate (9:1, v/v) eluent, and then recrystallized in anhydrous ethyl ether at −20 °C and dried in vacuum at 25 °C to yield white solid product. Weight = 21.68 g, yield = 46%. ^{1}H NMR (δ, in $CDCl_3$, ppm): 0.85 (3H, $CH_2C\underline{H}_3$), 1.25 (2H, $C\underline{H}_2CH_3$), 1.95 (3H, $C\underline{H}_3C{=}CH_2$), 3.60 (2H, two of $OCHOC\underline{H}_2CC\underline{H}_2$ in cyclic acetal), 4.05 (2H, two of $OCHOC\underline{H}_2CC\underline{H}_2$ in cyclic acetal), 4.47 (2H, $COOC\underline{H}_2$), 5.07 (1H, $OC\underline{H}OCH_2CCH_2$ in cyclic acetal), 5.56 and 6.11 (1H, $CH_3C{=}C\underline{H}_2$), 6.20 (1H, $C_6H_5CH{=}C\underline{H}$), 6.77 (1H, $C_6H_5C\underline{H}{=}CH$), 7.22−7.40 (5H, $C_6\underline{H}_5$).

Ambient Temperature RAFT Polymerization of EMSD Monomer under Visible Light Radiation. A protocol for the ambient temperature RAFT polymerization of EMSD monomer under visible light radiation was as follows: EMSD (3.16 g, 10.0 mmol), CPFDB (23.5 mg, 0.1 mmol), TPO (3.5 mg, 0.01 mmol), and 1.40 g anhydrous tetrahydrofuran were charged in a 25 mL round-bottom flask being capped with rubber septa. The solution was deoxygenated by purging with highly pure nitrogen gas for 30 min. The flask was immersed in a thermostatic water bath at 30 °C, under a visible light radiation. Samples were collected using deoxygenated syringes at predetermined intervals, quenched by exposing to air, and adding traces of hydroquinone inhibitor. One portion of sample was diluted in $CDCl_3$ for ^{1}H NMR analysis on a 400 MHz Bruker AV-400 NMR spectrometer. Another portion was diluted in chloroform for GPC measurement. EMSD monomer conversions were assessed by ^{1}H NMR analysis according to eq 1, where $I_{6.77}$ is the integral of proton resonance signal at $\delta = 6.77$ ppm ($C_6H_5C\underline{H}{=}CH$ in both PEMSD polymer and EMSD monomer) and $I_{5.56}$ is the integral of proton resonance signal at $\delta = 5.56$ ppm (one of $C\underline{H}_2{=}CHCH_3$ of EMSD monomer).

$$Conversion = \frac{I_{6.77} - I_{5.56}}{I_{6.77}} \quad (1)$$

64% EMSD monomer conversion was detected under this visible light radiation for 4 h. The resultant PEMSD polymer was precipitated from large excess of anhydrous methanol, dried in vacuum at 25 °C. GPC: $M_n = 13.4$ kg mol^{-1}, $M_w/M_n = 1.17$.

Ambient Temperature RAFT Polymerization of PEGMA Monomer Using a PEMSD Macro-CTA under a Visible Light Radiation. This was carried out as follows. An above-synthesized PEMSD polymer (GPC: M_n =7.9 kg mol^{-1}, $M_w/M_n = 1.17$) was utilized as a macromolecular chain transfer agent (macro-CTA). PEMSD macro-CTA (0.50 g, 0.05 mmol), PEGMA monomer (1.18 g, 2.5 mmol), TPO (1.8 mg, 0.005 mmol), and 0.72 g tetrahydrofuran were charged in a 25 mL round-bottom flask capped with rubber septa. The solution was deoxygenated by purging with highly pure nitrogen gas for 40 min. The flask was immersed in a thermostatic water bath at 30 °C, under a visible light radiation for 40 min. The polymerization was ceased by exposing to air and adding traces of hydroquinone. The resultant PEMSD-*b*-PPEGMA copolymer was precipitated from large excess of diethyl ether, dried in vacuum. ^{1}H NMR: 54% PEGMA monomer conversion. GPC: $M_n = 14.2$ kg mol^{-1}, $M_w/M_n = 1.18$.

The procedures for the synthesis of PEMSD-*b*-PGMA copolymer were similar to what as described above, except for using GMA monomer.

UV−vis Radiations for Photoisomerization of *E*-Cinnamyl Chromophores of PEMSD Polymer. The above-mentioned mercury vapor lamp, without any filtration, was utilized as a full-wave radiation. A long-wave radiation was obtained by using JB320 filters to cut off the shorter-wave UV radiation below 320 nm. A visible light radiation was obtained by using JB400 filters to cut off the shorter-wave UV radiation below 400 nm. The light intensity was measured on a UV-A radiometer being equipped with a 420 nm sensor and a 365 nm sensor.

Photoisomerization of Cinnamyl Chromophores of PEMSD Polymers under Full-Wave Radiation. PEMSD (0.10 g, GPC: M_n =14.1 kg mol^{-1}, $M_w/M_n = 1.17$) polymer was dissolved in 10 mL acetone under stirring in a 25 mL quartz round-bottom flask capped with rubber septa. The solution was deoxygenated by purging with highly pure nitrogen for 30 min. The flask was placed in a thermostatic bath at 30 °C under a full-wave radiation. The samples were collected at predetermined intervals and dried in vacuum at 25 °C prior to ^{1}H NMR analysis. The degrees of *Z*-isomerization of cinnamyl chromophores were assessed according to eq 2, where $I_{6.59}$ is the integral of proton resonance signal at $\delta = 6.59$ ppm ($C_6H_5C\underline{H}{=}CH$ of both *E*- and *Z*-cinnamyl chromophores) and $I_{5.58}$ is the integral of proton resonance signal at $\delta = 5.58$ ppm ($C_6H_5CH{=}C\underline{H}$ of *Z*-cinnamyl chromophores).

$$\text{Degree of } Z\text{-isomerization} = \frac{I_{5.58}}{I_{6.59}} \quad (2)$$

Hydrolysis of Cyclic Acetal Linkages from PEMSD Polymer under Acidic Conditions. 0.1 g PEMSD polymer was dissolved in 10 mL acetone under stirring in a 25 mL round-bottom flask at 30 °C. 0.09 g of 0.25 mol L^{-1} hydrochloric acid was charged into this flask. The solution was stirred at 30 °C. Samples were collected at predetermined intervals, dried in vacuum at 20 °C prior to ^{1}H NMR analysis. The degrees of hydrolysis were assessed according to eq (3), where $I_{3.1-4.5}$ is the integral of proton resonance signal at $\delta = 3.1-4.5$ ppm ($COOC\underline{H}_2$ and $OCHOC\underline{H}_2CC\underline{H}_2$ in EMSD units, $COOC\underline{H}_2$ and $C\underline{H}_2OH$ in the corresponding hydrolyzed units), $I_{5.0}$ is the integral of proton resonance signal of $OC\underline{H}OCH_2CCH_2$ in EMSD units at $\delta = 5.0$ ppm.

$$\text{Degree of hydrolysis} = \frac{I_{3.1-4.5} - 6I_{5.0}}{I_{3.1-4.5}} \quad (3)$$

GPC Measurements. These were performed on a PL-GPC120 setup being equipped with a column set consisting of two PL gel 5 μm MIXED-D columns (7.5 × 300 mm, effective molecular weight range of 0.2−400.0 kg mol^{-1}) using chloroform as the eluent at a flow rate of 1.0 mL min^{-1} at 35 °C. Narrow-distributed polystyrene standards in the molecular weight range of 0.5−750.0 kg mol^{-1} (PSS, Mainz, Germany) were utilized for calibration.

Differential Scanning Calorimetry (DSC) Measurements. These were performed on a Seiko DSC-6200 instrument at a heating rate of 10 °C min^{-1} under nitrogen atmosphere from 40 to 150 °C. The heating/cooling cycle was repeated twice. The heating curves of second cycle were recorded.

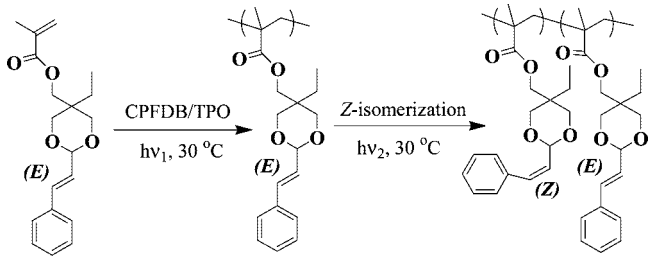
UV Spectroscopic Studies. These were performed on a PerkinElmer Lambda 25 spectrometer in a 10 mm path quartz cell at 25 °C.

Results and Discussion

Synthesis of EMSD Monomer. As shown in Scheme 1, the targeted monomer, 5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane (EMSD) was synthesized via two steps. First, cinnamaldehyde was reacted with 2-ethyl-2-hydroxymethyl-1,3-propanediol to yield a compound, whose cinnamyl chromophore was bound with a cyclic acetal linkage, i.e., 5-ethyl-5-hydroxymethyl-2-styryl-[1,3]dioxane (EHSD). EMSD monomer was synthesized by further esterification of the hydroxyl group of EHSD using methacryloyl chloride.

As shown in Figure 1, the proton resonance signals were in good agreement with the assigned protons of the targeted EMSD

Scheme 2. Schematic Illustration of Ambient Temperature RAFT Polymerization of 5-Ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane (EMSD) Monomer under Mild Visible Light Radiation at 30 °C, and Photoisomerization of *E*-Cinnamyl Chromophores in Its Corresponding PEMSD Polymer



monomer. Their integral ratio was equal to the assigned proton ratio of the targeted monomer. These confirmed the achievement of EMSD monomer. Moreover, the integral of proton resonance signal of $C_6H_5CH{=}C\underline{\mathbf{H}}$ at $\delta = 6.20$ ppm was equal to that of $C_6H_5C\underline{\mathbf{H}}{=}CH$ at $\delta = 6.77$ ppm, suggesting 100% *E*-cinnamyl chromophores in this monomer. Except for the proton resonance signal of $CDCl_3$, no other impurities could be detected. This suggested the high purity of this monomer.

RAFT Polymerization of EMSD Monomer under Visible Light Radiation at 30 °C. As shown in Scheme 2, under visible light radiation emitting separately at 405, 436, 545, and 577 nm with a mild intensity of 200 μW cm^{-2} at 420 nm, RAFT polymerization of EMSD monomer was readily carried out using a 2-cyanoprop-2-yl(4-fluoro)dithiobenzoate (CPFDB) chain transfer agent and a (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TPO) photoinitiator at 30 °C.

As shown in Figure 2, at a feed molar ratio of $[EMSD]_0$:$[CPFDB]_0$:$[TPO]_0 = 100{:}1{:}0.1$ in 30 wt % tetrahydrofuran under this mild visible light radiation at 30 °C, the semilogarithmic kinetic curve linearly evolved up to 64% monomer conversion. This was a typical first-order kinetic character, indicating that the radical concentration was constant and steady during this RAFT polymerization. The initialization period[45,46] of this RAFT polymerization was reasonably short, i.e., 16 min. Under this visible light radiation at 30 °C for 4 h, 64% EMSD monomer conversion was detected.

As shown in Figure 3, on increasing EMSD monomer conversion, GPC traces of PEMSD polymers clearly shifted to the larger molecular weight side. Moreover, these GPC traces were significantly monomodal and reasonably symmetrical.

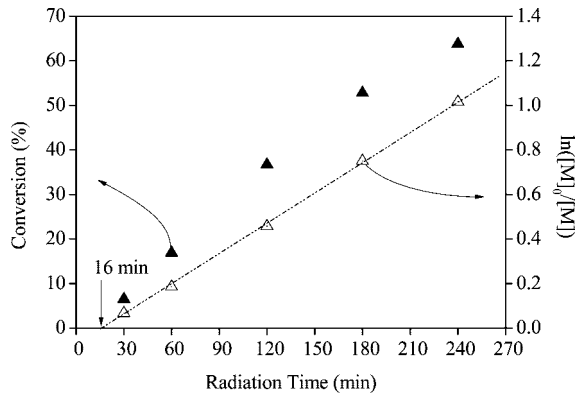


Figure 2. Kinetic curves of RAFT polymerization of 5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3] dioxane (EMSD) monomer, using a 2-cyanoprop-2-yl(4-fluoro)dithiobenzoate (CPFDB) chain transfer agent and a (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TPO) photoinitiator at a $[EMSD]_0$: $[CPFDB]_0$: $[TPO]_0$ of 100:1:0.1 in 30 wt % tetrahydrofuran under a visible light radiation at 30 °C.

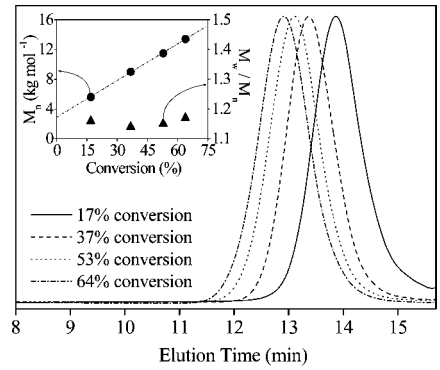


Figure 3. GPC trace evolution of poly[5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane] (PEMSD) polymers as a function of EMSD monomer conversions. Polymerization conditions: using a 2-cyanoprop-2-yl(4-fluoro)dithiobenzoate (CPFDB) chain transfer agent and a (2,4,6-trimethylbenzoyl) diphenylphosphine oxide (TPO) photoinitiator at a $[EMSD]_0$:$[CPFDB]_0$:$[TPO]_0$ of 100:1:0.1 in 30 wt % tetrahydrofuran under a visible light radiation at 30 °C. The inset shows the number-average molecular weights (M_n) and polydispersity indices (M_w/M_n) of poly[5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane] (PEMSD) polymers as a function of EMSD monomer conversions.

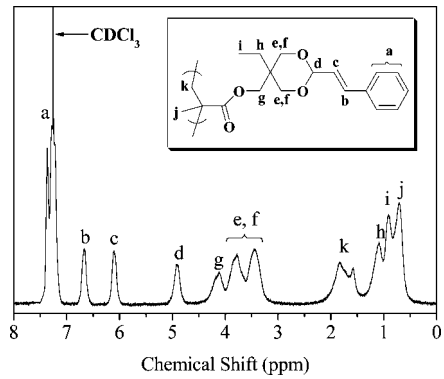


Figure 4. ^{1}H NMR spectrum of a poly[5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane] (PEMSD) polymer synthesized via RAFT polymerization of EMSD monomer using a 2-cyanoprop-2-yl(4-fluoro)dithiobenzoate (CPFDB) chain transfer agent and a (2,4,6-trimethylbenzoyl) diphenylphosphine oxide (TPO) photoinitiator at a $[EMSD]_0$:$[CPFDB]_0$:$[TPO]_0 = 100{:}1{:}0.1$ in 30 wt % tetrahydrofuran under a visible light radiation at 30 °C. ^{1}H NMR: 65% EMSD monomer conversion. GPC: $M_n = 14.1$ kg mol^{-1}, $M_w/M_n = 1.17$.

More importantly, their number-average molecular weights (M_n) linearly increased with monomer conversions. Their polydispersity indices (M_w/M_n) were remarkably narrow at the early stage of RAFT polymerization, e.g., $M_w/M_n = 1.16$ at 17% monomer conversion. This tendency kept up to 64% monomer conversion. These results demonstrated the well-controlled behavior of this RAFT polymerization.

As shown in Figure 4, no signal at $\delta = 5.56$ ppm (one of $C\underline{\mathbf{H}}_2{=}CCH_3$ in EMSD monomer) could be detected, indicating that EMSD monomer was completely removed. The integral ratio of proton resonance signals was equal to the assigned proton ratio of targeted PEMSD polymer, within analysis errors. These confirmed the intact cyclic acetal linkages in this PEMSD polymer. Moreover, the integral of proton resonance signal of $C_6H_5CH{=}C\underline{\mathbf{H}}$ at $\delta = 6.10$ ppm was equal to that of $C_6H_5C\underline{\mathbf{H}}{=}CH$ at $\delta = 6.68$ ppm, suggesting 100% *E*-cinnamyl chromophores in this polymer. This implied that this visible light radiation did not trigger the isomerization of *E*-cinnamyl chromophores during this RAFT polymerization.

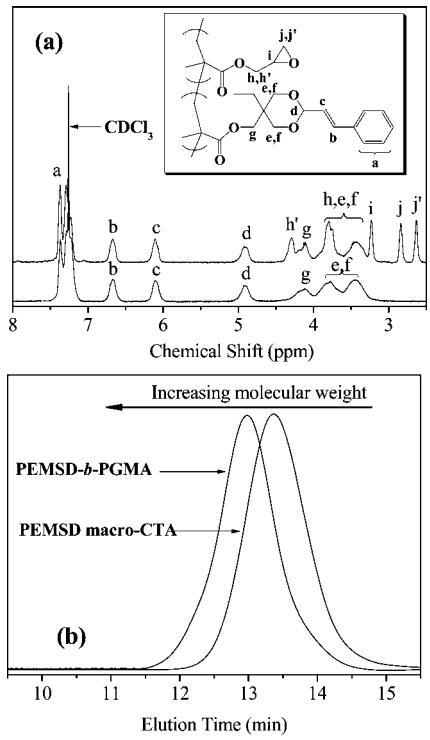


Figure 5. (a) ^{1}H NMR spectra (bottom) of a poly[5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3] dioxane] macromolecular chain transfer agent (PEMSD macro-CTA, GPC: M_n =7.9 kg mol^{-1}, M_w/M_n = 1.17) and (top) its chain-extended block copolymer with poly(glycidyl methacrylate) (PEMSD-*b*-PGMA). (b) GPC traces of PEMSD macro-CTA and its corresponding PEMSD-*b*-PGMA copolymer. Copolymerization conditions: using a (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TPO) photoinitiator at a $[GMA]_0$:$[PEMSD\ macro\text{-}CTA]_0$:$[TPO]_0$ of 100:1:0.1 in 40 wt % tetrahydrofuran under visible light radiation at 30 °C for 90 min. ^{1}H NMR: 36% GMA monomer conversion. GPC: M_n = 10.2 kg mol^{-1}, M_w/M_n = 1.17.

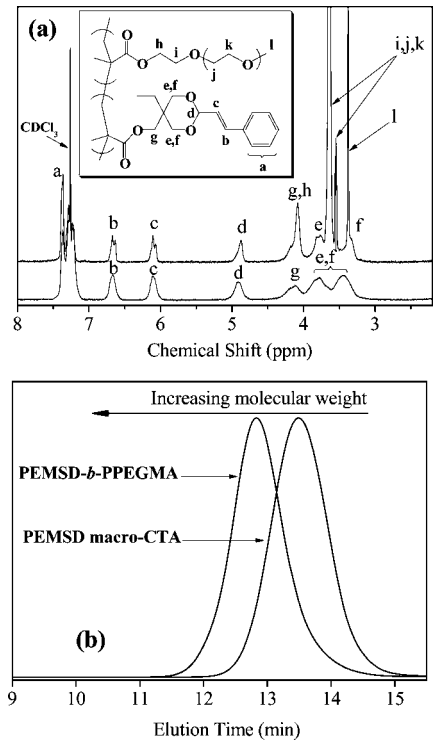


Figure 6. (a) ^{1}H NMR spectra (bottom) of a poly[5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3] dioxane] macromolecular chain transfer agent (PEMSD macro-CTA, M_n = 7.9 kg mol^{-1}, M_w/M_n = 1.17) and (top) its corresponding block polymers with poly[poly(ethylene glycol) monomethacrylate] (PEMSD-*b*-PPEGMA). (b) GPC traces of PEMSD macro-CTA and its corresponding PEMSD-*b*-PPEGMA copolymer (M_n = 14.2 kg mol^{-1}, M_w/M_n = 1.18). Copolymerization conditions: at a $[PEGMA]_0$:$[PEMSD\ macro\text{-}CTA]_0$:$[TPO]_0$ of 50:1:0.1 in 30 wt % tetrahydrofuran under a visible light radiation at 30 °C for 40 min. ^{1}H NMR: 54% PEGMA monomer conversion, where PEGMA is poly(ethylene glycol) monomethacrylate (M_n = 475 g mol^{-1}, M_w/M_n = 1.03).

RAFT Polymerization of Glycidyl Methacrylate (GMA) Monomer using a PEMSD Macro-CTA under a Visible Light Radiation at 30 °C. In order to clarify the living character of above-discussed RAFT polymerization, a chain-extending RAFT copolymerization was carried out using the above-synthesized PEMSD polymer as a macromolecular chain transfer agent (macro-CTA) under visible light radiation at 30 °C. Moreover, glycidyl methacrylate (GMA) was employed as a functional monomer to enhance the properties of this photosensitive PEMSD polymer.[47–49]

As shown in Figure 5a, the distinct chemical environment of $COOCH_2CH$ in GMA units led to the separate proton signals at δ = 4.29 and 3.81 ppm. Moreover, the proton signals at δ = 3.23 ppm ($CHOCH_2$ in oxirane rings) and 2.84 and 2.63 ppm ($CHOCH_2$ in oxirane rings) confirmed the intact oxirane rings in this PEMSD-*b*-PGMA copolymer. Moreover, the integral ratio of I_b:I_c:I_j:$I_{j'}$ was equal to 1:1:1.2:1.2, suggesting 100% *E*-cinnamyl chromophores and a 5:6 molar ratio of EMSD units to GMA units in this PEMSD-*b*-PGMA copolymer.

Based on ^{1}H NMR analysis, 36% GMA monomer was polymerized under this visible light radiation at 30 °C for 90 min. As shown in Figure 5b, the GPC trace of PEMSD-*b*-PGMA copolymer clearly shifted to the larger molecular weight side. It was significantly monomodal and reasonably symmetrical, with a narrow polydispersity index (M_w/M_n) of 1.17. These indicated a living character of this RAFT polymerization.

RAFT Polymerization of Poly(ethylene glycol) Monomethacrylate (PEGMA) Monomer Using a PEMSD Macro-CTA under a Visible Light Radiation at 30 °C. As shown in Figure 6a, the proton signal of OCH_3 in PEGMA units appeared at δ = 3.37 ppm. The methylene protons of $COOCH_2CH_2$ and CH_2CH_2O in PEGMA units appeared at δ = 3.55 and 3.64 ppm. The integral ratio of I_b:I_c:[($I_{g,h}$ − 2I_b)/2] was equal to 1:1:1 within analysis errors, suggesting 100% *E*-cinnamyl chromophores and approximately 1:1 molar ratio of EMSD units to PEGMA units in this PEMSD-*b*-PPEGMA copolymer.

Based on ^{1}H NMR analysis, 54% PEGMA monomer was polymerized under visible light radiation at 30 °C for 40 min. As shown in Figure 6b, the GPC trace of PEMSD-*b*-PPEGMA copolymer clearly shifted to the larger molecular weight side. Moreover, it was significantly monomodal and reasonably symmetrical, with a narrow M_w/M_n of 1.18. These indicated a living character of this ambient temperature RAFT polymerization.

This amphiphilic PEMSD-*b*-PPEGMA copolymer could form micelles in aqueous solution. Moreover, PPEGMA blocks impart excellent biocompatibility[50] and nonadhesive characterisitics to proteins.[51,52] It is reasonable to expect that this photosensitive PEMSD-*b*-PPEGMA copolymer would be of interest in biomedical or pharmaceutical applications.

Photoisomerization of *E*-Cinnamyl Chromophores in a PEMSD Polymer. As discussed above (see Figure 4), 100% *E*-cinnamyl PEMSD polymers were synthesized via RAFT polymerization of *E*-cinnnamyl EMSD monomer under this mild visible light radiation at 30 °C. As shown in Figure 7, a long-wave radiation in a wave range of 365−577 nm could not trigger the isomerization of *E*-cinnamyl chromophores. However, a full-wave radiation in a wave range of 254−577 nm triggered the isomerization of *E*-cinnamyl chromophores. This suggested that

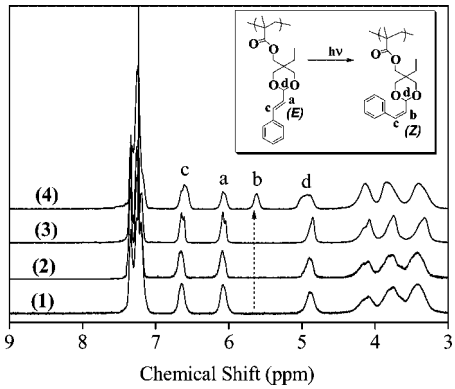


Figure 7. ^{1}H NMR spectra of a poly[5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane] (PEMSD, M_n = 14.1 kg mol^{-1}, M_w/M_n = 1.17, 10 mg mL^{-1} PEMSD polymer solution in acetone): (1) initial PEMSD polymer, (2) on exposure to a visible light radiation with an intensity of 460 μW cm^{-2} at 420 nm at 30 °C for 4 h, (3) on exposure to a long-wave radiation with an intensity of 510 μW cm^{-2} at 365 nm and 460 μW cm^{-2} at 420 nm at 30 °C for 4 h, and (4) on exposure to a full-wave radiation with an intensity of 700 μW cm^{-2} at 365 nm and 460 μW cm^{-2} at 420 nm at 30 °C for 4 h.

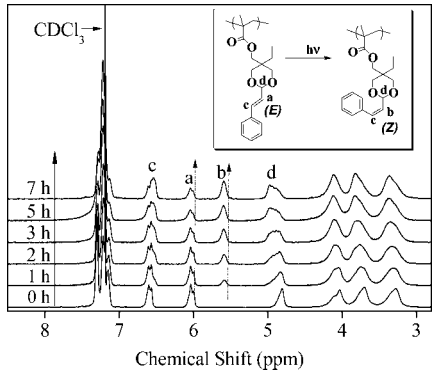


Figure 8. ^{1}H NMR spectrum evolution of a poly[5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3] dioxane] (PEMSD, M_n = 14.1 kg mol^{-1}, M_w/M_n = 1.17, 10 mg mL^{-1} solution in acetone) on exposure to a full-wave radiation with an intensity of 1300 μW cm^{-2} at 365 nm and 810 μW cm^{-2} at 420 nm at 30 °C.

this isomerization was sensitive to UV radiation in a wave range of 254−365 nm.

As shown in Figure 8, under a full-wave radiation with a large intensity of 1300 μW cm^{-2} at 365 nm at 30 °C, a proton signal at δ = 5.58 ppm appeared, leading to the decrease of integral of proton signal at δ = 6.03 ppm ($C_6H_5CH{=}C\underline{H}$ in *E*-cinnamyl EMSD units). Moreover, the integral combination of proton signals at δ = 5.58 and 6.03 ppm was equal to the proton signal integral of $C_6H_5C\underline{H}{=}CH$ at δ = 6.59 ppm. This suggested that the proton signal at δ = 5.58 ppm was attributed to $C_6H_5CH{=}C\underline{H}$ in *Z*-cinnamyl units. In addition, this isomerization led to the proton signal of $C_6H_5C\underline{H}{=}CH$ slightly shifted to high field and that of $OC\underline{H}OCH_2CCH_2$ in cyclic acetal linkages slightly shifted to low field.

As shown in Figure 9, this isomerization was clearly accelerated by increasing the light intensity of full-wave radiation. For example, under a full-wave radiation with a large intensity of 1300 μW cm^{-2} at 365 nm for 7 h, 64% *E*-cinnamyl chromophores were isomerized to *Z*-form, whereas only 44% *Z*-cinnamyl formation was observed under a full-wave radiation with a low intensity of 400 μW cm^{-2} at 365 nm for 7 h. Similar to the small molecular analogues,[53] the phototriggered *Z*-isomerization of cinnamyl chromophores in this PEMSD polymer reached equilibrium at ca. 65% *Z*-cinnamyl formation.

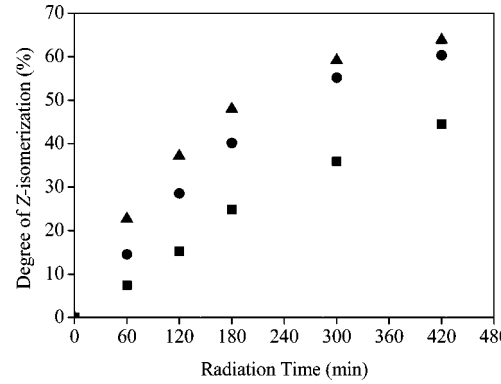


Figure 9. Degree of *Z*-isomerization of a 100% *E*-cinnamyl poly[5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane] (M_n = 14.1 kg mol^{-1}, M_w/M_n = 1.17, 10 mg mL^{-1} solution in acetone) under a full-wave radiation: (▲) 1300 μW cm^{-2} at 365 nm, (●) 700 μW cm^{-2} at 365 nm, and (■) 400 μW cm^{-2} at 365 nm at 30 °C.

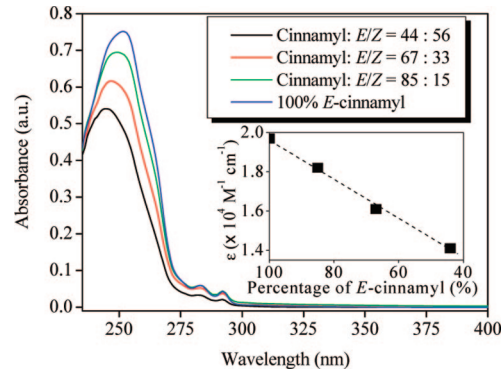


Figure 10. UV spectra of 12.0 mg L^{-1} poly[5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane] (PEMSD; GPC: M_n = 14.1 kg mol^{-1}, M_w/M_n = 1.17) polymer solutions in tetrahydrofuran. Inset shows the molar extinction coefficient (ϵ) at λ_{max} as a function of percentage of *E*-cinnamyl chromophores in this PEMSD polymer.

Effect of Photoisomerization on Optical Properties of a PEMSD Polymer. As shown in Figure 10, on photoisomerization of *E*-cinnamyl chromophores of a PEMSD polymer, the maximum absorption wavelength (λ_{max}) of this PEMSD polymer blue-shifted from 252 nm (100% *E*-cinnamyl) to 244 nm (*E*/*Z* = 44:56); accordingly, its molar extinction coefficient (ϵ) at λ_{max} linearly decreased from 1.97 × 10^4 M^{-1} cm^{-1} to 1.41 × 10^4 M^{-1} cm^{-1} (see inset of Figure 10). This phenomenon was also observed in small molecular cinnamic acid derivatives[54] and azobenzene-based photosensitive polymers.[55]

Effect of Photoisomerization on Glass Transition Temperature of a PEMSD Polymer. As shown in Figure 11, on photoisomerization of *E*-cinnamyl chromophores, the glass transition temperature (T_g) of this PEMSD polymer linearly decreased from 119 °C (100% *E*-cinnamyl) to 99 °C (*E*/*Z* = 37:63). This indicated the enhanced segmental mobility and loose packing of these polymer chains, which were caused by the improved chain irregularity on partially *Z*-isomerization of cinnamyl chromophores. These effects facilitated the proton attack and hydration of cyclic acetal linkages under acidic conditions.

Effect of Photoisomerization on Stability of Cyclic Acetal Linkages in a PEMSD Polymer. ^{1}H NMR spectra of a 100% *E*-cinnamyl PEMSD polymer hydrolyzed in acidic acetone solution at predetermined intervals are summarized in Figure 12-1. When stirred at 30 °C for 0.5 h, strong proton signals of small molecular cinnamaldehyde at δ = 9.47 ppm ($C_6H_5CH{=}CHC\underline{H}O$) and 6.70 ppm ($C_6H_5CH{=}C\underline{H}CHO$) ap-

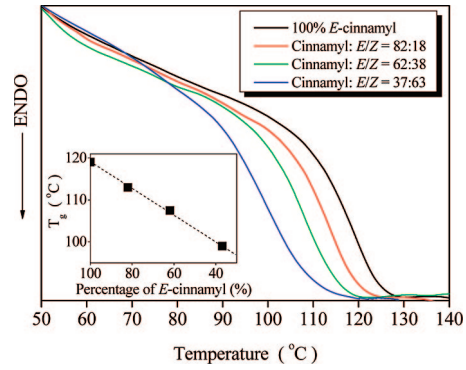


Figure 11. Differential scanning calorimetry (DSC) curves of a poly[5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane] (PEMSD, M_n = 14.1 kg mol^{-1}, M_w/M_n = 1.17) at various *E/Z* cinnamyl ratios. The inset shows the glass transition temperature (T_g) of this PEMSD polymer as a function of its corresponding percentage of *E*-cinnamyl chromophores.

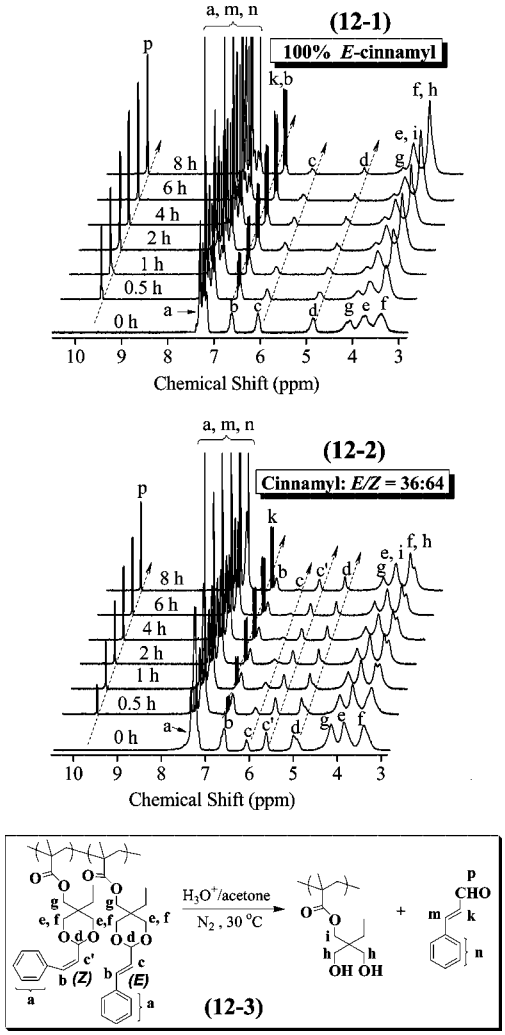


Figure 12. ^{1}H NMR spectra of a poly[5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane] (PEMSD) polymer (M_n = 14.1 kg mol^{-1}, M_w/M_n = 1.17): (**Upper**) 100% *E*-cinnamyl, (**Middle**) at an *E/Z* cinnamyl ratio of 36:64, as a function of hydrolysis time. Hydrolysis conditions: adding 90 mg of 0.25 mol L^{-1} hydrochloric acid in 7.0 mL of 10 mg mL^{-1} PEMSD polymer solution in acetone, stirring the solution in nitrogen atmosphere at 30 °C.

peared, indicating a rapid cleavage of cyclic acetal linkages from this polymer. In addition, the proton signal of C**H**$_2$OH of 2-ethyl-2-hydroxymethyl-1,3-propanediol at δ = 3.47 ppm was negligible, suggesting the negligible hydrolysis of ester linkages from this polymer under these conditions. Thus, this hydrolysis was illustrated in Figure 12-3.

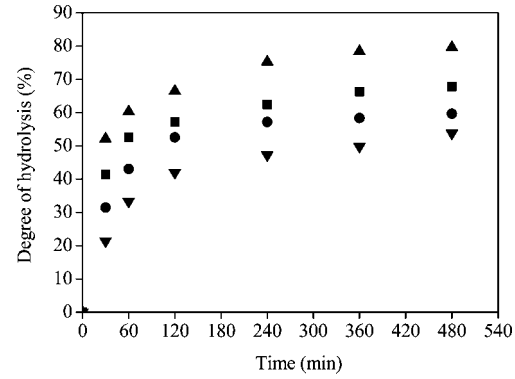


Figure 13. Kinetic data for hydrolysis of a poly[5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane] (PEMSD, M_n = 14.1 kg mol^{-1}, M_w/M_n = 1.17): (▲) 100% *E*-cinnamyl, (■) at an *E/Z* cinnamyl ratio of 73:27, (●) at an *E/Z* cinnamyl ratio of 54:46, and (▼) at an *E/Z* cinnamyl ratio of 36:64. Hydrolysis conditions: adding 90 mg of 0.25 mol L^{-1} hydrochloric acid in 7.0 mL of 10 mg mL^{-1} PEMSD polymer solution in acetone, stirring the solution in nitrogen atmosphere at 30 °C.

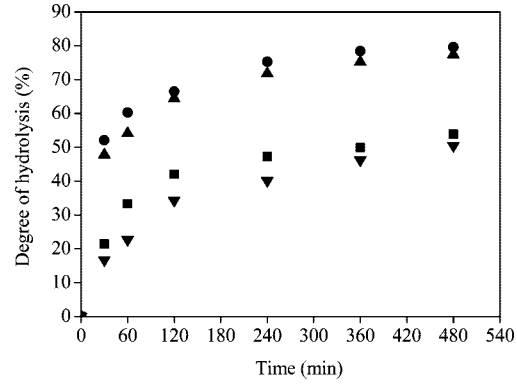


Figure 14. Kinetic data for hydrolysis of a poly[5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane] polymers: (●) M_n = 14.1 kg mol^{-1}, M_w/M_n = 1.17, 100% *E*-cinnamyl; (▲) M_n = 25.8 kg mol^{-1}, M_w/M_n = 1.23, 100% *E*-cinnamyl; (■) M_n = 14.1 kg mol^{-1}, M_w/M_n = 1.17, at an *E/Z* cinnamyl ratio of 36:64; (▼) M_n = 25.8 kg mol^{-1}, M_w/M_n = 1.23, at an *E/Z* cinnamyl ratio of 36:64. Conditions: addition of 90 mg of 0.25 mol L^{-1} hydrochloric acid to 7.0 mL of 10.0 mg mL^{-1} PEMSD polymer solution in acetone with stirring of the solution in nitrogen atmosphere at 30 °C.

On photoisomerization this 100% *E*-cinnamyl PEMSD polymer to an *E/Z* cinnamyl ratio of 36:64, the hydrolysis kinetics of this polymer was quite different from the former under the same conditions. As shown in Figure 12-2, under stirring at 30 °C for 0.5 h, the proton signals of cinnamaldehyde at δ = 9.47 and 6.70 ppm attenuated much more slowly than those in 100% *E*-cinnamyl PEMSD polymer, suggesting a slower cleavage process of cyclic acetal linkages from this partially *Z*-isomerized PEMSD polymer than that from its corresponding 100% *E*-cinnamyl PEMSD polymer.

As shown in Figure 12-2, in striking contrast to the slow attenuation of proton signal of $C_6H_5CH{=}C\underline{H}$ (c′) in *Z*-cinnamyl EMSD units, the proton signal of $C_6H_5CH{=}C\underline{H}$ (c) in *E*-cinnamyl EMSD units attenuated much more rapidly than the former. This indicated that the significantly more labile cyclic acetal linkages neighboring *E*-cinnamyl chromophores than those neighboring *Z*-cinnamyl chromophores.

The degrees of hydrolysis of cyclic acetal linkages from PEMSD polymers, with various *E/Z* cinnamyl ratios at prede-

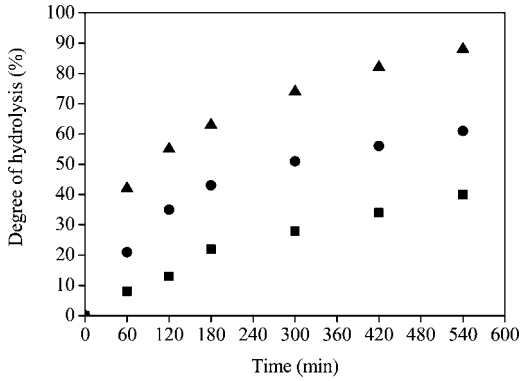


Figure 15. Kinetic data for hydrolysis of poly[5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane]-*block*-poly[poly(ethylene glycol) monomethacrylate] (PEMSD-*b*-PPEGMA) copolymer (^{1}H NMR: approximately 1:1 molar ratio of EMSD units to PEGMA units; GPC: M_n = 14.2 kg mol^{-1}, M_w/M_n = 1.18): (▲) 100% *E*-cinnamyl; (●) at an *E/Z* cinnamyl ratio of 62:38; (■) at an *E/Z* cinnamyl ratio of 40:60. Conditions: addition of 90 mg of 0.25 mol L^{-1} hydrochloric acid to 7.0 mL of 10 mg mL^{-1} PEMSD-*b*-PPEGMA copolymer solution in acetone with stirring of the solution in nitrogen atmosphere at 30 °C.

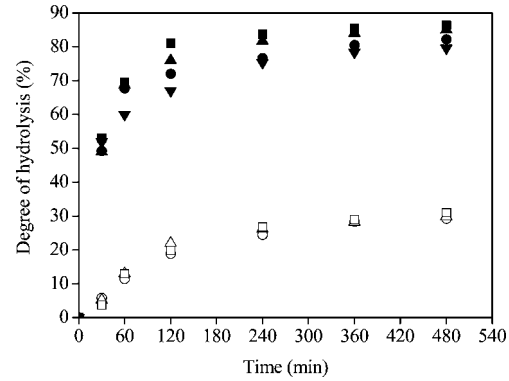


Figure 16. Kinetic data for hydrolysis of poly[5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane] (M_n = 14.1 kg mol^{-1}, M_w/M_n = 1.17): (▼) in 100% *E*-cinnamyl form; (●) *E*-cinnamyl and (○) *Z*-cinnamyl units of this polymer at an *E/Z* cinnamyl ratio of 73:27; (▲) *E*-cinnamyl and (Δ) *Z*-cinnamyl units of this polymer at an *E/Z* cinnamyl ratio of 54:46; (■) *E*-cinnamyl and (□) *Z*-cinnamyl units of this polymer at an *E/Z* cinnamyl ratio of 36:64. Conditions: addition of 90 mg of 0.25 mol L^{-1} hydrochloric acid to 7.0 mL of 10 mg mL^{-1} PEMSD polymer solution in acetone with stirring the solution in nitrogen atmosphere at 30 °C.

termined intervals, are summarized in Figure 13. In all cases, this hydrolysis proceeded rapidly at the early stage up to 2 h and then slowed down. More importantly, the higher percentage of *Z*-cinnamyl chromophores led to a slower cleavage process of cyclic acetal linkages. For example, under stirring at 30 °C for 0.5 h, over 52% cyclic acetal linkages were hydrolyzed from a 100% *E*-cinnamyl PEMSD polymer whereas just 21% cyclic acetal linkages were hydrolyzed from its corresponding PEMSD polymer at an *E/Z* cinnamyl ratio of 36:64.

As shown in Figure 14, in both 100% *E*-cinnamyl and partially *Z*-cinnamyl-isomerized cases, increasing the molecular weight of PEMSD polymer did not change the hydrolysis tendency but slowed down the hydrolysis process of cyclic acetal linkages.

As shown in Figure 15, at the early stage of hydrolysis, the cyclic acetal linkages of a 100% *E*-cinnamyl PEMSD-*b*-PPEGMA copolymer were hydrolyzed more slowly than those of its corresponding 100% *E*-cinnamyl PEMSD homopolymer. For example, under stirring at 30 °C for 1 h, 42% cyclic acetal linkages were hydrolyzed from a 100% *E*-cinnamyl PEMSD-*b*-PPEGMA copolymer whereas over 60% cyclic acetal linkages were hydrolyzed from its corresponding 100% *E*-cinnamyl PEMSD polymer under the same conditions. When stirred at 30 °C for 9 h, the degree of hydrolysis increased up to 88%.

As shown in Figure 15, partially *Z*-cinnamyl PEMSD-*b*-PPEGMA copolymers exhibited a slower hydrolysis process, but the hydrolysis tendency was similar to that of its corresponding 100% *E*-cinnamyl PEMSD-*b*-PPEGMA copolymer. Similar to its corresponding PEMSD homopolymer, higher percentage of *Z*-cinnamyl chromophores led to a slower hydrolysis process of their cyclic acetal linkages from this copolymer.

As shown in Figure 16, higher percentage of *Z*-cinnamyl chromophores of a PEMSD polymer led to a more rapidly hydrolysis process of the cyclic acetal linkages neighboring *E*-cinnamyl chromophores. For example, increasing the degree of *Z*-isomerization of cinnamyl chromophores from 0% to 27% to 46% and finally to 64% increased the degree of hydrolysis of cyclic acetal linkages neighboring *E*-cinnamyl chromophores from 67% to 72% to 76% and finally to 81%, respectively, under stirring at 30 °C for 2 h. This was attributed to the enhanced segmental mobility and loose chain packing of polymer chains on *Z*-isomerization of cinnamyl chromophores, which facilitated

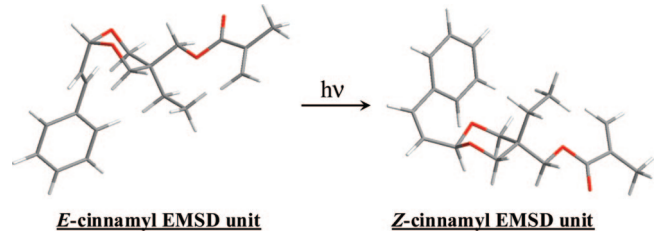


Figure 17. Schematic illustration of the geometry configurations of *E*-cinnamyl EMSD unit and its corresponding photoisomerized *Z*-cinnamyl EMSD unit.

the proton attack and hydration of cyclic acetal linkages under acidic conditions.

Strikingly, as shown in Figure 16, *Z*-isomerization of cinnamyl chromophores led to a significantly slow cleavage process of cyclic acetal linkages of neighboring *Z*-cinnamyl chromophores, e.g., ca. 20% cyclic acetal linkages neighboring *Z*-cinnamyl chromophores were hydrolyzed in 2 h.

As illustrated in Figure 17, photoisomerization of *E*-cinnamyl chromophores enhanced the steric hindrance and hydrophobicity of cyclic acetal linkages and shielded the cyclic acetal linkages from the proton attack and hydration. On the other hand, the hydrolysis of cyclic acetal involved a series of intermediate steps, including a rate-determining step of carbonium ion−alcohol pair formation.[15] B3LYP/6−31G* simulation demonstrated that the carbonium ion−alcohol pair intermediate of neighboring *Z*-cinnamyl chromophores were more stable than those of the neighboring *E*-cinnamyl chromophores at a ΔE of −27.04 kJ mol^{-1}. These effects significantly suppressed the hydrolysis of cyclic acetal linkages of neighboring *Z*-cinnamyl chromophores under acidic conditions.

Interestingly, this phenomenon was also observed in the light-triggered cleavage of pH-labile Schiff base linkages from rhodopsin in the visual process.[12,13] On exposure to light, 11-*cis* retinyl chromophores of rhodopsin isomerized to all-*trans* retinyl, leading to a rapid cleavage of neighboring Schiff base linkages. This remarkable phototunable stability of pH-labile cyclic acetal linkages is desirable for the applications in photosensors and light-triggered drug delivery.

Conclusion

This paper described a novel design and facile synthesis of a photosensitive polymer, whose chromophores were bound with

pH-labile cyclic acetal linkages, i.e., poly[5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane] (PEMSD). This polymer was readily synthesized via RAFT polymerization of 5-ethyl-5-methacryloyloxymethyl-2-styryl-[1,3]dioxane monomer using a CPFDB chain transfer agent and a TPO photoinitiator under a mild visible light radiation at 30 °C. The kinetic studies suggested a well-controlled behavior of this RAFT polymerization. The living character of this RAFT polymerization was confirmed by the well-controlled ambient temperature RAFT polymerization using a PEMSD macro-CTA under this mild visible light radiation. This rendered the facile synthesis of well-defined PEMSD-based block copolymers with PGMA block or PPEGMA block.

^{1}H NMR analysis confirmed the intact cyclic acetal linkages and 100% *E*-cinnamyl chromophores of PEMSD polymers synthesized under these mild conditions. UV radiation, particularly in a wave range of 254−365 nm, triggered *Z*-isomerization of cinnamyl chromophores in a 100% *E*-cinnnamyl PEMSD polymer. This isomerization was dependent on the light intensity, which reached equilibrium at ca. 65% *Z*-cinnamyl formation.

On photoisomerization of *E*-cinnamyl chromophores, the maximum absorption wavelength (λ_{max}) of this PEMSD polymer blue-shifted from 252 nm (100% *E*-cinnamyl) to 244 nm (*E*/*Z* = 44:56); accordingly, its molar extinction coefficient at λ_{max} linearly decreased from 1.97×10^4 M^{-1} cm^{-1} to 1.41×10^4 M^{-1} cm^{-1}. Moreover, this photoisomerization led to the enhanced chain irregularity, thus the glass transition temperature of this polymer linearly decreased from 119 °C (100% *E*-cinnamyl) to 99 °C (*E*/*Z* = 37:63).

More importantly, this photoisomerization enhanced the steric hindrance and hydrophobicity of cyclic acetal linkages and shielded the cyclic acetal linkages from the proton attack and hydration, thus significantly suppressing the hydrolysis of cyclic acetal linkages of neighboring *Z*-cinnamyl chromophores under acidic conditions. However, this photoisomerization enhanced segmental mobility and loose chain packing of this polymer, thus facilitating the proton attack and hydration of cyclic acetal linkages of neighboring *E*-cinnamyl chromophores, leading to even more rapid hydrolysis of cyclic acetal linkages of neighboring *E*-cinnamyl chromophores from this partially *Z*-cinnamyl PEMSD polymer than that of cyclic acetal linkages from 100% *E*-cinnamyl PEMSD polymer. In both 100% *E*-cinnamyl and partially *Z*-cinnamyl-isomerized cases, higher molecular weight of PEMSD polymer led to a slower hydrolysis process of its cyclic acetal linkages. This remarkable phototunable stability of pH-labile cyclic acetal linkages render the materials as potential for applications in photosensors and light-triggered drug delivery.

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