

Article

Controlled Synthesis and Photoresponsive Properties of Spiropyran End-Functionalized Poly(vinyl ether)s

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Abstract: Due to the need to develop smart materials for a variety of applications such as catalysts and drug delivery, the development of photoresponsive polymers is receiving increasing attention. In particular, the photoisomerization of spiropyran (SP), unlike many other photoresponsive compounds, has attracted attention because it dramatically changes not only the molecular structure but also the polarity of the molecule. However, in most cases where SP is used as a photoresponsive functional group, SP is introduced in the side chain of the polymer, and few cases have been reported in which SP is introduced at the end of the polymer chain. Therefore, we designed a new amphipathic poly(vinyl ether) with an SP moiety at the end of the polymer chain. First, an initiator having an SP moiety was synthesized and used for living cationic polymerization to synthesize a poly(vinyl ether) bearing an SP moiety at the end of the polymer chain. Furthermore, we investigated the photoresponsive properties of the obtained polymers, we found that self-assembly of the amphiphilic polymers could be controlled by photoirradiation.



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Keywords: spiropyran; end-functionalized polymer; living cationic polymerization; photoresponsive polymer

1. Introduction

The development and research of stimulus-responsive polymers are gaining increasing attention as smart materials need to be developed for a variety of applications such as catalysts [1,2] and drug delivery [3–6]. In particular, the response by photostimulation is a very powerful tool among various stimulations [6,7]. This is because there is no need to add chemical reagents externally, and in addition, local irradiation of the sample is possible. For this reason, many photoresponsive compounds have been used in stimulus-responsive materials. For example, azobenzene [8,9] is the most widely used compound for cis-trans isomerization, and compounds with unique photoreactivity such as spiropyran [10–12] for heterolytic cleavage and diarylethene [13,14] for electrocyclic reactions are also used. It is noteworthy that the photo heterolytic cleavage of spiropyran (SP), unlike many other photoresponsive compounds, dramatically changes not only the molecular structure of the compound but also the polarity of the molecule. Therefore, polymers containing SP species are very attractive as effective stimulus-responsive materials for drug delivery and controlled release systems due to the dramatic change in solubility with photoirradiation [15–17]. However, almost the reported studies using photoresponsive SP moieties have been classified into pendant-functionalized SP-carrying polymers, and a few have possessed an SP moiety at the end of a polymer chain. The SP end-capped polymers so far reported have been synthesized via living radical polymerization, and the synthesis of such polymers by living ionic polymerization has not yet been reported. This is because the nitrobenzene group in SP moiety deteriorates the livingness of cationic polymerization [18]. We attempted the living cationic polymerization of a VE having a pendant SP moiety (SPVE)

but failed to achieve controlled polymerization. We, therefore, expected the potential ability of the SPVE derivative (SPVE-TFA) as an initiator for living cationic polymerization of vinyl ethers (VEs) because the concentration of the nitro groups in the polymerization system is sufficiently suppressed to make it possible to synthesize well-defined SP end-capped polyVEs through a living polymerization process. SPVE-TFA can be readily prepared by the addition of TFA to SPVE. Thus, we studied the synthesis of a series of SP end-capped polyVEs by living cationic polymerization with SPVE-TFA as an initiator. An advantage of the synthetic strategy developed in this study is that one can design a wide variety of SP end-capped polymers by living cationic polymerization of functionalized VEs. We have succeeded in synthesizing poly(vinyl ether)s (polyVEs) having a π -conjugated functional group at the end of the polymer chain by using an initiator having a π -conjugated molecule [19–24]. Furthermore, as a result of investigating the self-assembling behavior of amphipathic polyVE having C_{60} at the terminal, we found that it self-assembles to form polymeric micelle-like aggregates due to intermolecular hydrophobic interactions between the C_{60} moieties of polyVE. In addition, the external addition of γ -CD induced the dissociation of the polymer aggregates into molecularly dispersed free polymers [20]. This means that the self-assembly behavior of polymers can be controlled by a slight change in the solubility of the terminal group. This unexpected observation prompted us to synthesize a new amphiphilic polyVE having an SP moiety at the polymer terminus (Figure 1). First, we investigate the living cationic polymerization behavior of isobutyl vinyl ether (IBVE) as a VE monomer with a new SP-appended initiator (SPVE-TFA) (Scheme 1). Subsequently, an amphipathic vinyl ether monomer (2-methoxyethyl vinyl ether; MOVE) was used in the same polymerization system for the synthesis of a target amphiphilic polyVE having an SP moiety at the polymer terminus (SP-PMOVE). Furthermore, the self-assembly behavior of SP-PMOVE and the photoresponsive properties were investigated in detail. We expect that such polymers induce macroscopic changes in the state due to changes in the chemical structure of the terminal molecules, allowing the on/off switching of aggregate formation by using photoirradiation.

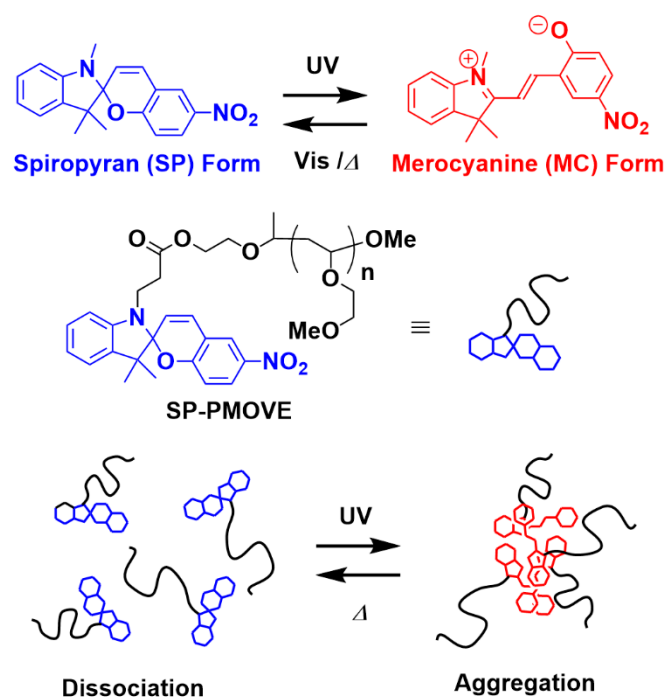
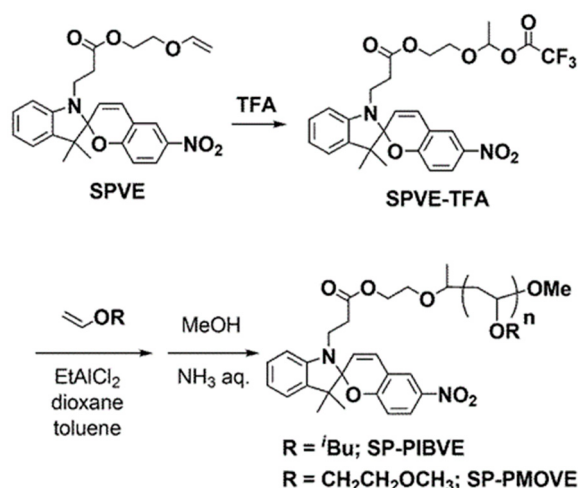


Figure 1. Schematic representation of the formation and deformation of aggregates of SP-PMOVE in EtOH upon photoirradiation.



Scheme 1. Synthetic route of a novel SP-appended initiator and SP end-functionalized polymers via living cationic polymerization.

2. Materials and Methods

2.1. Chemicals and Reagents

Unless otherwise stated, all commercial reagents were used as received. 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (WSCl; Tokyo Chemical Industry Co., Ltd., Tokyo, Japan, 98%), 4-dimethylaminopyridine (DMAP; FUJIFILM Wako Pure Chemical Corporation, Osaka, Japan, 98%), trifluoroacetic acid (TFA; FUJIFILM Wako Pure Chemical Co., Osaka, Japan, 98%), ethylaluminum dichloride (EtAlCl_2 , 1.0 M in n-hexane; FUJIFILM Wako Pure Chemical Co., Osaka, Japan), dehydrated dimethylacetamide (FUJIFILM Wako Pure Chemical Co., Osaka, Japan, 99.5%) and 2-hydroxyethyl vinyl ether (Maruzen Petrochemical Co., Ltd., Tokyo, Japan, 99.4%) were used as received. Isobutyl vinyl ether (IBVE; Sigma-Aldrich Co., LLC., St. Louis, MO, USA, 99%) and 2-methoxyethyl vinyl ether (MOVE; Maruzen Petrochemical Co., Ltd., Tokyo, Japan, 99.9%) were dried overnight over KOH pellets and distilled twice over CaH_2 . SPCO_2H was prepared according to the literature [25].

2.2. Methods

^1H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker model AC-500 spectrometer (Bruker, Billerica, MA, USA), operating at 500 and 125 MHz, respectively, where chemical shifts (δ in ppm) were determined with respect to non-deuterated solvent residues as internal standards. Preparative gel permeation chromatography (SEC) was performed at 25 °C by using 21.5 mm $\times$ 300 mm polystyrene gel columns (TOSOH TSKgel G2000H, G2500H, and G3000H) on a TOSOH model CCPE equipped with RI-8022 RI detector (TOSOH, Tokyo, Japan). Analytical size exclusion chromatography (SEC) was performed in tetrahydrofuran (THF) at 40 °C, using 8.0 mm $\times$ 300 mm gel columns (Shodex KF-804 $\times$ 2) on a TOSOH model DP-8020 with a RI-8022 RI detector. The number-average molecular weight (M_n) and polydispersity ratio (M_w/M_n) were calculated from the chromatographs with respect to 15 polystyrene standards (Scientific Polymer Products, Inc.; M_n = 580–670,000, M_w/M_n = 1.01–1.07). UV-vis spectra were recorded using a quartz cell of 1 cm path length on a SHIMADZU Type UV-2550 spectrometer (SHIMADZU, Kyoto, Japan). Dynamic light scattering (DLS) analysis was performed on the solutions of the SP end-functionalized polymers with the concentration of 2.0 wt% at 25 °C using a Malvern Instruments model Zetasizer Nano-ZS instrument equipped with a green laser (λ = 532 nm) (Malvern Panalytical Ltd., Malvern Worcestershire, UK). A scattering angle of 173 ° was used in all measurements.

2.3. Synthesis of SPVE

To solution of SPCO_2H [25] (890 mg, 2.0 mmol), DMAP (50 mg, 0.42 mmol) and 2-hydroxyethyl vinyl ether (0.20 mL, 2.4 mmol) in CH_2Cl_2 (50 mL) was added WSCI (0.5 g, 2.4 mmol) at 25 °C and the mixture was stirred for 15 h at 25 °C under N_2 . The reaction mixture was washed with water, dried over Na_2SO_4 and evaporated to dryness. The residue was subjected to column chromatography (ethyl acetate/hexane = 1/1, *v/v*) on SiO_2 to allow isolation of SPVE as a yellowish oil (830 mg, 1.8 mmol) in 92% yield.

^1H NMR (500 MHz, CDCl_3 δ): 8.00 (m, 2H), 7.19 (m, 1H), 7.08 (m, 1H), 6.91 (m, 2H), 6.74 (m, 1H), 6.61 (d, J = 2.4 Hz, 1H), 6.43 (m, 1H), 5.87 (d, J = 10.4 Hz, 1H), 4.25 (t, J = 2.6 Hz, 2H), 4.17 (d, J = 2.4 Hz, 1H), 3.95 (m, 1H), 3.83 (t, J = 2.6 Hz, 2H), 3.64 (m, 2H), 2.67 (m, 2H), 1.26 (s, 3H), 1.15 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3 δ): 171.7, 159.4, 151.3, 146.3, 141.1, 136.0, 128.4, 127.8, 125.9, 122.8, 122.0, 121.9, 119.9, 118.7, 115.6, 106.8, 106.7, 87.2, 65.6, 62.8, 52.9, 39.2, 33.6, 25.8, 19.

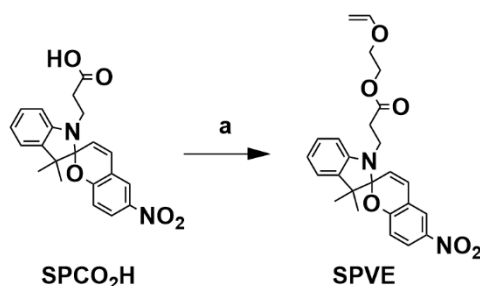
2.4. Cationic Polymerization of Vinyl Ether Monomers with SPVE-TFA

The preparation of SPVE-TFA and polymerization of vinyl ether monomers (IBVE and MOVE) were carried out under a dry nitrogen atmosphere in baked glass tubes equipped with a three-way stopcock. A typical example of the polymerization procedure is given below. To a toluene solution (19.8 mL) of SPVE (225 mg, 500 μmol) was added 1 equivalent TFA (2 mol L^{-1} in toluene; 0.25 mL, 500 μmol) at 0 °C under N_2 , and the mixture was stirred for 4 h at 0 °C under N_2 . And then, to the reaction mixture were added of vinyl ether monomer (IBVE; 0.66 mL, 5.0 mmol, MOVE; 0.62 mL, 5.0 mmol), dioxane (0.39 mL, 4.5 mmol) and EtAlCl_2 (in hexane, 1.0 mol L^{-1} ; 0.1 mL, 100 μmol) at 0 °C under N_2 . After stirring for 90 or 30 min, the polymerization was quenched with an excess amount of prechilled MeOH (1 mL) containing a small amount of NH_3 aq. The monomer conversion was determined by GC measurement. The quenched reaction mixture was poured into toluene and then washed with dil. HCl and water to remove the aluminum-containing residues, and evaporated to dryness under reduced pressure. The residue was subjected to preparative SEC, where the first band was collected and evaporated to dryness to give SP-PIBVE or SP-PMOVE as pearl yellow oil.

3. Results and Discussion

3.1. Synthesis of SPVE-TFA

We have succeeded in the synthesis of various types of end-functionalized polyVEs bearing terminal fullerene [19,20], phenylacetylene [21], thiophene [22] moieties, and so on at α -end by living cationic polymerization with the corresponding functionalized initiators in combination with EtAlCl_2 and an added base such as dioxane. The key compound in the present study is a newly designed SP derivative (SPVE) with a VE group, which can be readily derivatized to the initiator (SPVE-TFA) for living cationic polymerization by the quantitative addition reaction of trifluoroacetic acid (TFA) to the VE moiety of SPVE. As shown in Scheme 2, the synthesis of SPVE was carried out by condensation of 2-hydroxyethyl vinyl ether with SPCO_2H , which was synthesized according to a previous report [25], and unambiguously characterized by ^1H NMR (Figure 2a) and ^{13}C NMR. Subsequent treatment of SPVE with an equimolar amount of TFA in toluene at 0 °C under dry N_2 for 4 h led to SPVE-TFA (Scheme 1). ^1H NMR spectroscopy of SPVE-TFA (Figure 2b) showed that the vinyl protons of the precursor SPVE (peaks a, b, and c) completely disappeared, and all the signals are consistent with those of the expected structure of the TFA addition product (peaks A and B), indicating the quantitative formation of SPVE-TFA from SPVE. The solution of SPVE-TFA was employed as prepared for the subsequent living polymerization.



a: 2-Hydroxyethyl vinyl ether, DMAP, WSCI, CH₂Cl₂, 25 °C.

Scheme 2. Synthesis of SPVE.

3.2. Cationic Polymerization of IBVE Monomer with SPVE-TFA

We first attempted to synthesize a polyVE having pendant SP moieties by living cationic polymerization of SPVE in CH₂Cl₂ at 0 °C for 12 h under dry N₂. The ¹H NMR spectroscopy of the reaction mixture showed complete disappearance of the vinyl protons of SPVE; however, the SEC chromatogram showed only an oligomer peak at the low molecular weight region ($M_n = 1900$, $M_w/M_n = 1.52$), and as a result, no polymer peaks were observed. This was probably due to side reactions such as chain transfer and termination reactions induced by the interaction of the carbocationic species and nitro groups in the pendant moieties of SPVE [18]. This result prompted us to synthesize polyVEs having an SP moiety at the end of the polymer chain by using SPVE-TFA as an initiator for living cationic polymerization. We need to investigate adequate initiating systems for the controlled polymerization of VEs with SPVE-TFA as an initiator. Isobutyl vinyl ether (IBVE) was then polymerized with SPVE-TFA in combination with EtAlCl₂ and dioxane as an activator and added base, respectively, [19,21,22] in toluene at 0 °C under dry N₂ ($[SPVE-TFA]_0/[IBVE]_0/[EtAlCl_2]_0/[dioxane]_0 = 1/100/2/90$). After 90 min, IBVE was consumed completely, and the reaction was quenched with an excess of prechilled MeOH containing a small amount of NH₃ aq. The resulting polymer (SP-PIBVE) was analyzed by SEC with refractive index (RI) and UV (254 nm) dual detectors in THF. The SEC curve of the resulting SP-PIBVE showed a unimodal peak with narrow molecular weight distribution (MWD) ($M_n = 10,000$ g mol^{−1}, $M_w/M_n = 1.12$, as estimated using polystyrene standards), and the SEC curves obtained by RI and UV detectors, were almost identical, indicating that the resulting polymers have the terminal chromophoric SP moiety, regardless of molecular weight (Figure 2d). The formation of the target SP end-functionalized polymer (SP-PIBVE) was confirmed by ¹H NMR measurement in CDCl₃ (Figure 2c). All the key signals arising from the SP moiety (8.0 and 7.2 – 5.9 ppm) at the α-terminus and IBVE repeating units (0.9 and 3.1 – 3.6 ppm) were able to characterize the expected structure for the SP-PIBVE. The number-average degree of polymerization (DP_n) of SP-PIBVE was determined by the peak intensity ratio of the isobutyl protons (peak f) based on the terminal aromatic protons (peak d', e'), and the evaluated DP_n value was 126. In order to investigate the detailed polymerization behavior of the cationic polymerization of IBVE using SPVE-TFA, we analyzed the products at various polymerization times (Figure 3). As shown in Figure 3a, the SEC curves of the product polymers shifted to the high molecular weight region as the reaction time increased with relatively narrow MWD ($M_w/M_n < 1.2$). Figure 3b shows the time–conversion curve obtained for the polymerization of IBVE, showing that the polymerization proceeded smoothly without an induction phase and then reached over 90% conversion within 90 min. The first-order kinetic plot for the polymerizations of IBVE revealed a linear relationship, indicating the concentration of the carbocationic species is kept constant throughout the polymerization. The proportional relationship was shown between the conversion of the IBVE monomer and M_n of the obtained IBVE polymers (SP-PIBVEs) (Figure 3c), indicating that the present polymerization proceeded in a controlled manner. These results achieved precisely controlled cationic polymerization of IBVE by using the SPVE-TFA/EtAlCl₂/dioxane initiation system. In other words, the growth of

polyIBVE chains from the SPVE-TFA initiator allowed the functionality of the SP moiety at the α -terminus to nearly quantitative.

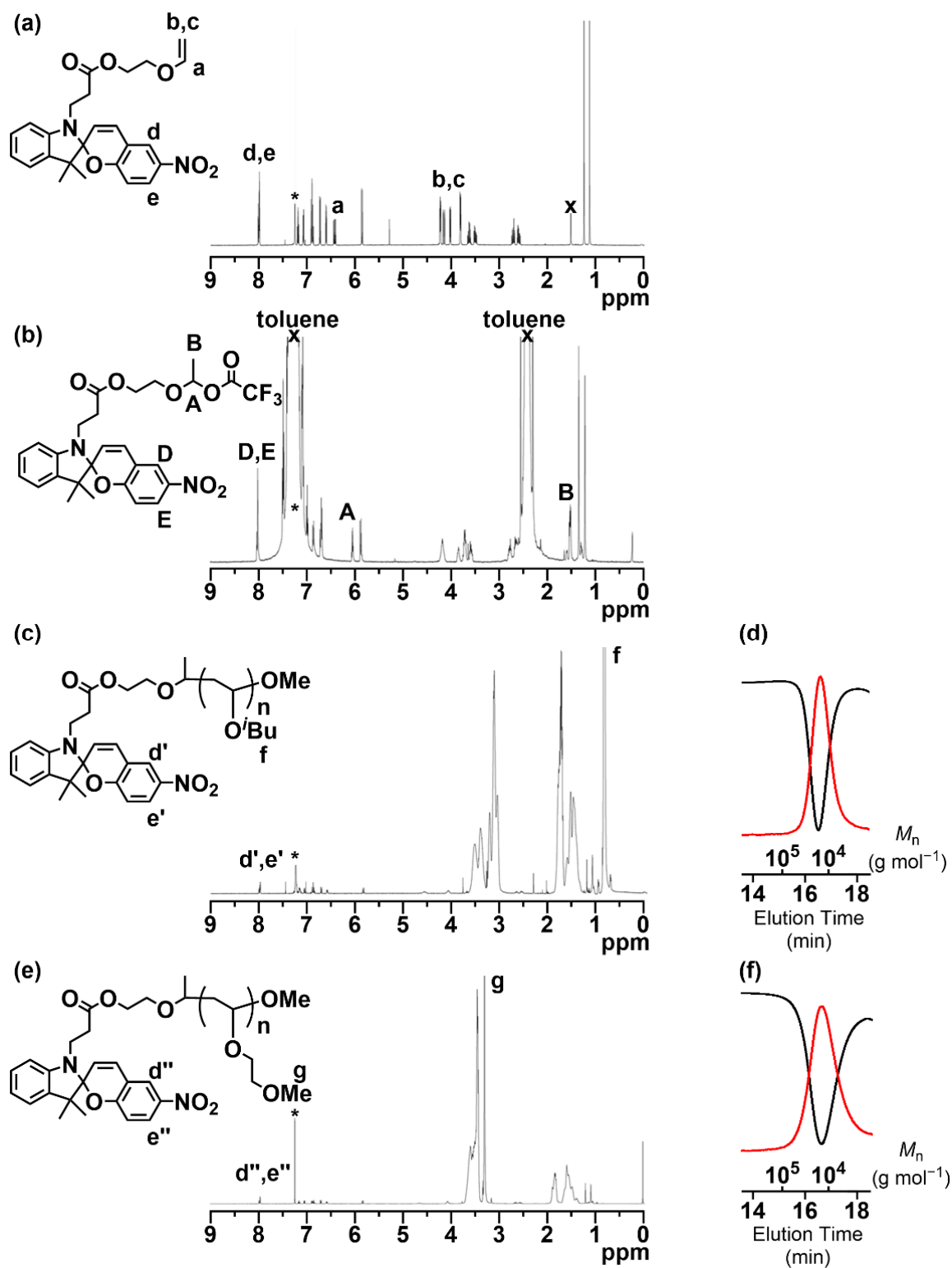


Figure 2. ^1H NMR spectra of (a) SPVE, (b) SPVE-TFA, (c) SP-PIBVE, and (e) SP-PMOVE in CDCl_3 (asterisk and x indicate remaining CHCl_3 and other solvents, respectively). RI (red line) and UV (254 nm, black line) detected SEC curves of (d) SP-PIBVE, and (f) SP-PMOVE using THF as the eluent.

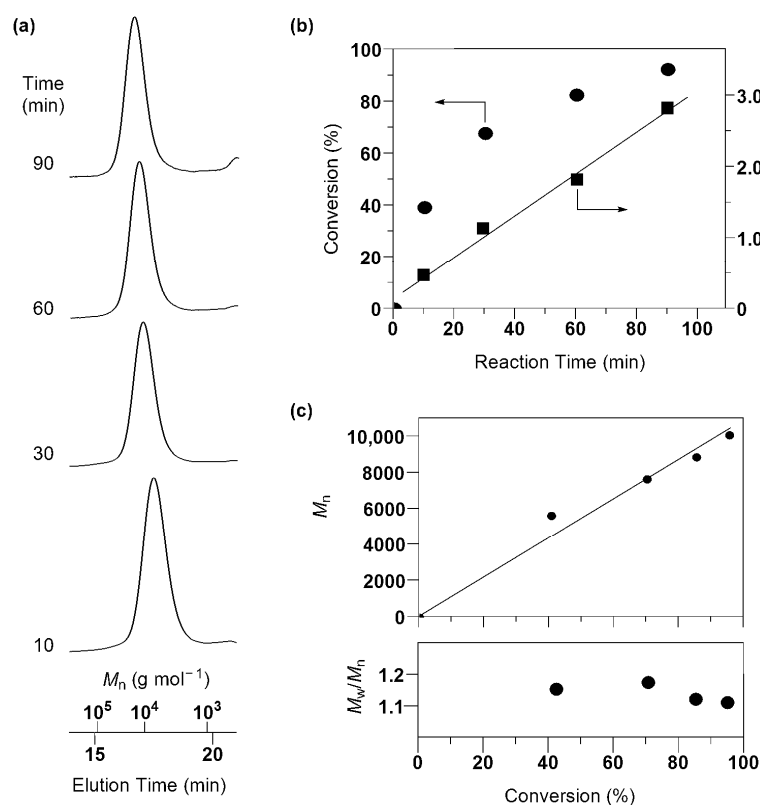


Figure 3. (a) SEC curves of SP-PIBVE measured in THF, (b) a time-conversion curve and first-order kinetic plot for the polymerization of IBVE, and (c) M_n and M_w/M_n values of SP-PIBVE plotted against monomer conversion. Polymerization was conducted with SPVE-TFA/EtAlCl₂/dioxane in toluene at 0 °C ([IBVE]₀ = 1000 mmol L⁻¹, [EtAlCl₂]₀ = 20 mmol L⁻¹, [dioxane]₀ = 900 mmol L⁻¹, [SPVE-TFA]₀ = 10 mmol L⁻¹).

3.3. Synthesis of SP-PMOVE

The living cationic polymerization with the SPVE-TFA initiating system was further investigated to explore its potential ability to synthesize an amphiphilic SP end-functionalized polymer having controlled architecture. Thus, 2-methoxyethyl vinyl ether (MOVE), representative amphiphilic vinyl ether, was applied to the present polymerization system. The RI-detected SEC curve of the polymerization product shows a unimodal peak with a relatively narrow molecular weight distribution ($M_n = 6300$, $M_w/M_n = 1.25$, as estimated using polystyrene standards), indicating the exclusive formation of well-defined SP-PMOVE (Figure 2f). The obtained SP-PMOVE was soluble in common organic solvents, even polar ones such as EtOH and MeOH. The ¹H NMR spectrum of the obtained polymer displayed peaks at 8.0 and 7.2 – 5.9 ppm assignable to the SP moiety at the α-terminus, and the peak intensities of the SP moiety (peak d'', e'') and pendant methoxy protons in polyMOVE chain (peak g) indicated that the DP_n of SP-PMOVE was 80 (Figure 2e). Figure 4b shows the time-conversion curve and first-order kinetic plot obtained for the polymerization of MOVE, showing that the polymerization proceeded smoothly without an induction phase and then reached 100% conversion within 1 h. The SEC curves obtained for the polymers shifted to higher molecular weight regions as the reaction time increased (Figure 4a). In Figure 4c, the values of M_n and M_w/M_n for the polymers are plotted against monomer conversions. A linear increase in M_n against conversion as well as maintaining of narrow molecular weight distribution ($M_w/M_n < 1.32$) of the polymers indicate that the polymerization of MOVE proceeded in a controlled manner.

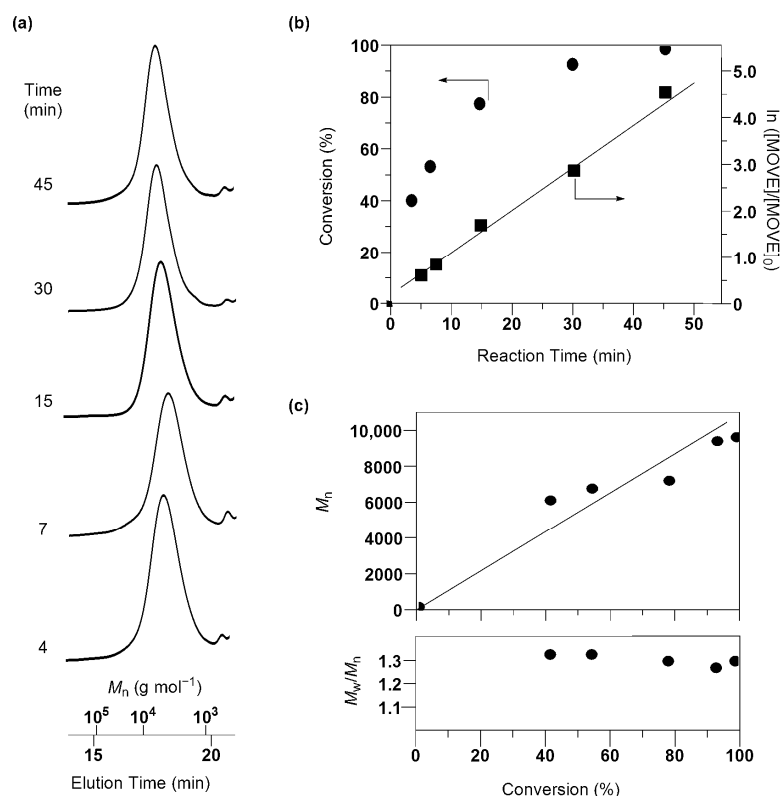


Figure 4. (a) SEC curves of SP-PMOVE measured in THF, (b) a time-conversion curve and first-order kinetic plot for the polymerization of MOVE, and (c) M_n and M_w/M_n values of SP-PMOVE plotted against monomer conversion. Polymerization was conducted with SPVE-TFA/EtAlCl₂/dioxane in toluene at 0 °C ($[MOVE]_0 = 1000 \text{ mmol L}^{-1}$, $[EtAlCl_2]_0 = 20 \text{ mmol L}^{-1}$, $[dioxane]_0 = 900 \text{ mmol L}^{-1}$, $[SPVE-TFA]_0 = 10 \text{ mmol L}^{-1}$).

3.4. Photoresponsive Properties of SP-PMOVE

SP derivatives are known to exhibit reversible photoisomerization and dramatically change the polarity of the compound (Figure 1). Upon irradiation with UV, SP, which is a relatively low polarity compound, changes to merocyanine (MC) form. Then, MC, which is a zwitterionic form and high polarity compound, returns to SP by irradiation of visible light or heat. To investigate the photoresponsive behavior, we measured UV-vis absorption spectra in isopropanol (iPrOH), EtOH, and MeOH. Figure 4a shows the UV-vis absorption spectra of the SP-PMOVE solution (0.1 mmol L^{-1}) prepared in the dark and under UV irradiation (150 W high-pressure mercury arc lamp) for 5 min. Without UV irradiation, all the solutions were colorless and showed no absorption in the 400–700 nm range. Upon UV irradiation, the SP-PMOVE solutions became colored and showed strong absorptions in the range of 400–700 nm (Figure 5). At that time, the peak top of the absorption spectrum changed depending on the solvent; $\lambda_{\text{max}} = 560 \text{ nm}$ in iPrOH, $\lambda_{\text{max}} = 554 \text{ nm}$ in EtOH, and $\lambda_{\text{max}} = 542 \text{ nm}$ in MeOH. From this result, under UV irradiation, SP moieties at the terminus of the polyMOVE chain undergo the heterolytic cleavage of the C–O bond and the ring-opening to produce the MC form. On the other hand, at room temperature even under dark conditions, the colored solutions returned to their colorless state, but the time required for the recovery process also varied depending on the solvent: the recovery process took about 12, 35, and 90 min for iPrOH, EtOH, and MeOH, respectively. The phenomena that the absorption properties and the recovery rate are solvent dependent are consistent with the results for spiropyran derivatives [26,27]. This is because increasing the polarity of the solvent stabilizes the MC form, which is a zwitterionic structure [28].

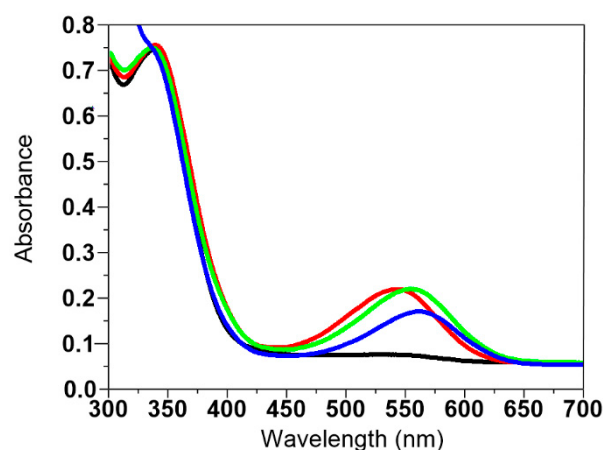


Figure 5. Absorption spectra of solutions of SP-PMOVE (0.1 mM) without UV irradiation (black line) and SP-PMOVE (0.1 mM) in iPrOH (blue line), EtOH (green line) and MeOH (red line) at 25 °C upon UV irradiation for 2 min.

3.5. Self-Assembly of SP-PMOVE via Photoirradiation

When we experiment with UV light irradiation to EtOH solution of SP-PMOVE (2 wt%), we found that the polymer solution showed strong Tyndall scattering observable with the naked eye by using a green laser pointer. Therefore, it means that the self-assembled aggregates grew by UV irradiation. We further evaluated the size of the self-assembled aggregates of SP-PMOVE upon UV irradiation formed in EtOH by dynamic light scattering (DLS) analysis at 25 °C. DLS measurement of an EtOH solution of SP-PMOVE prior to UV irradiation showed the presence of nearly uniform-sized nanoparticles with an average diameter of ca. 1.6 nm (Figure 6a). The EtOH solution after exposure to UV irradiation showed significant differences, showing polymer aggregates with an average size of approximately 50 nm in the DLS profile (Figure 6b). After that, after standing it in the dark for 20 min at room temperature, the polymer solution changed from magenta to colorless, and as a result of DLS measurement again, the size of the nanoparticles recovers to the original size of ca. 1.6 nm (Figure 6c). These results suggest that photoisomerization of the terminal SP moiety of SP-PMOVE induced aggregation and dissociation of SP-PMOVE and that the aggregations were able to control by photoirradiation.

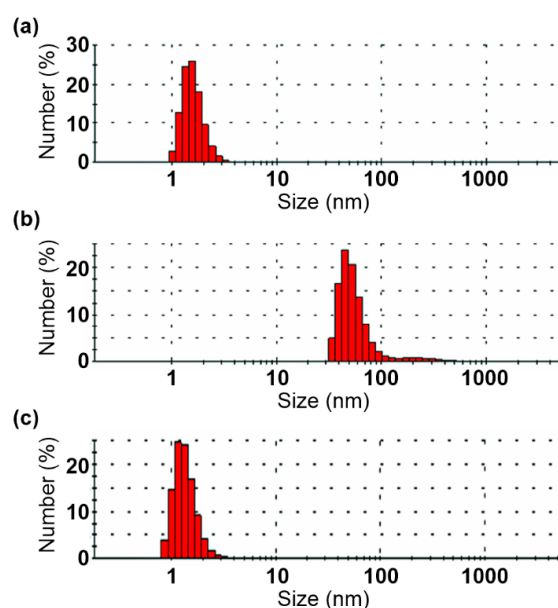


Figure 6. Size distributions of SP-PMOVE in EtOH (a) without UV irradiation, (b) upon UV irradiation for 5 min, and (c) after standing of the sample in the dark for 20 min determined by DLS.

4. Conclusions

In conclusion, we have demonstrated that a novel SP derivative (SPVE-TFA) acts as an initiator for living cationic polymerization of functionalized vinyl ethers in combination with EtAlCl_2 and an added base such as dioxane, and efficiently affords SP end-functionalized polymers with no byproducts. It should be emphasized that this approach is very useful for quantitatively synthesizing SP end-functionalized polymers having an SP moiety at the α -terminus. Furthermore, SP-PMOVE can be reversibly self-assembled and dissociated by UV irradiation due to the photoisomerization of the terminal SP moiety. This finding contributes to the development of new photoresponsive polymers as advanced materials serving as drug delivery systems.

Author Contributions: Conceptualization, J.M. and M.M.; methodology, J.M. and M.M.; validation, J.M.; formal analysis, A.F.; investigation, J.M.; resources, J.M. and M.M.; data curation, A.F. and J.M.; writing—original draft preparation, J.M.; visualization, J.M.; supervision, M.M.; project administration, J.M.; funding acquisition, J.M. and M.M. All authors have read and agreed to the published version of the manuscript.

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