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Preparation and reversible photo-crosslinking/photo-cleavage behavior of 4-methylcoumarin functionalized hyperbranched polyester

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ABSTRACT

A novel hyperbranched polymer endcapped with 4-methylcoumarin group (MCTH40) was prepared via thiol–ene addition reaction of thiol-modified hyperbranched polyester (fully thioglycolic acetate of Boltorn™ H40, TAH40) with a vinyl monomer (7-(4-vinyl-benzyloxyl)-4-methylcoumarin, VBMC), and characterized with ^{1}H NMR and FT-IR spectroscopies. Its reversible photo-crosslinking/photo-cleavage behavior was evaluated based on the UV–vis spectroscopic analysis, and compared with the linear polymer, poly(7-(4-vinyl-benzyloxyl)-4-methylcoumarin (PVBMC)). The absorbance at 319 nm in the UV–vis spectrum gradually decreased under UVA irradiation ($\lambda_{max} = 365$ nm), and then rapidly recovered under UVC irradiation ($\lambda_{max} = 254$ nm). The fluorescence intensity of MCTH40 ($\lambda_{max} = 469$ nm) recovered to 85.2% of original level after photo-cleavage under UVC irradiation, higher than 83.5% of PVBMC ($\lambda_{max} = 472$ nm). The UV–vis analysis results indicated that MCTH40 performs more rapid photo-response than linear PVBMC under the same conditions. Furthermore, the average doses of UVA irradiation for the maximum degree of photo-crosslinking were 22.08 J cm^{-2} for MCTH40 and 28.29 J cm^{-2} for PVBMC. The average UVC doses of complete photo-cleavage were 9.44 J cm^{-2} for MCTH40 and 9.58 J cm^{-2} for PVBMC. The GPC analysis indicated that the average molecular weight and its PDI of MCTH40 showed a slight increase after three reversible cycles.

1. Introduction

Coumarin-containing polymers have been well studied and widely applied in many fields, such as biochemicals, electro-optical materials, organic–inorganic hybrid materials, liquid crystalline materials and light harvesting/energy transferring materials [1–8]. Moreover, their reversible photo-crosslinking and photo-cleavage behavior have been widely investigated for the application of photo-response materials [9–12]. Under UVA irradiation ($\lambda = 320$–400 nm), the [2 + 2] cycloaddition of a couple of coumarin moieties takes place to form a cyclobutane ring. After irradiated under UVC light ($\lambda = 200$–280 nm), the coumarin photodimers can be cleaved and regenerate the former coumarin moieties. Therefore, the polymers containing coumarin structural units perform quick photo-response and effective photo-reversibility with alternative irradiation of UV light of different wavelength.

However, most reported coumarin-containing polymers were linear polymers. And the coumarin functional group was introduced as a pendent group or terminal group of the polymer chain [13–17]. Compared with the linear one, coumarin-containing hyperbranched polymer shows a new direction of research and application for photo-responsive materials. They are relatively easy for preparation and tailored modification. So it is a facile way to prepare photo-responsive materials based on tailoring-made coumarin-containing hyperbranched polymers. Boltorn™ H40 is a commercial hyperbranched aliphatic polyester polyol based on 2,2-bis(hydroxymethyl) propionate structure and owns 64 terminal hydroxyl groups that can be easily modified. Moreover, the thiol–ene addition has been proved to be a reaction with very high conversion under mild conditions [18,19], and introduced into tailored terminal modification of various polymers, even so called as “thiol-click reaction” [20,21]. Therefore, it is effective to apply the thiol–ene addition reaction for modifying hyperbranched polymers.

In this work, a new photo-responsive hyperbranched polymer was prepared by linking a vinylbenzyl ether derivative of 4-methylcoumarin (VBMC) onto the surface of thiol-modified hyperbranched aliphatic polyester (fully thioglycolic acetate of Boltorn™ H40, named as TAH40) via thiol–ene addition under mild conditions. The molecular structure of coumarin endcapped hyperbranched polymer (MCTH40) was characterized with ^{1}H NMR and FT-IR spectroscopies. Furthermore, the photo-reversible behaviors of photo-crosslinking under UVA irradiation ($\lambda_{max} = 365$ nm) and photo-cleavage under UVC irradiation ($\lambda_{max} = 254$ nm) were

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investigated by using UV–vis and fluorescence analyses. Furthermore, a linear polymer of the vinyl monomer as above, PVBMC, which possessed the same level of average molecular weight and degree of polymerization of MCTH40, was synthesized via RAFT polymerization for comparison. The determination of UV absorbance at 319 nm was repeated for three UVA/UVC irradiation cycles to investigate the photo-reversibility of MCTH40 and PVBMC.

2. Experimental

2.1. Materials

The hyperbranched aliphatic polyester polyol, Boltorn™ H40 (H40), supplied by Perstorp Specialty Chemicals AB (Sweden), possesses the molecular weight of 5100 g/mol and a PDI of 1.8. Resorcinol (99%), 4-methoxyphenol (99%), 4-vinylbenzyl chloride (90%) and thioglycolic acid (98%) were purchased from Aldrich Chemical Co. Azobisisobutyronitrile (AIBN), ethyl acetoacetate, styrene, sodium methoxide, elemental sulfur, anhydrous potassium carbonate, 4-dimethylaminopyridine, *p*-toluenesulfonic acid and other reagents were purchased from Shanghai first Reagent Co. (China) with analytical grade purity. H40 was refined with fractional precipitation. Azobisisobutyronitrile was recrystallized from hot ethanol for three times to obtain pure white needle-like crystal. Ethyl acetoacetate, styrene and 4-vinylbenzyl chloride were distilled prior to use. And other reagents were used as-received without further purification.

2.2. Synthesis

2.2.1. Thioglycolic acetate of H40 (TAH40)

As H40 was a commercial hyperbranched polyester, it is necessary to refine the raw material with fractional precipitation method to remove the component of low molecular weight [22]. The modified method was followed as reported by Ornatska et al. [23]: 25 g H40 was added into 50 mL of toluene and refluxed for 4 h to remove the moisture in polyol. After toluene evaporated, the dry H40 was added into 250 mL of dry 1,4-dioxane at room temperature, and stirred vigorously until the polyol was completely dissolved. And then the solution was dropwise added into 200 mL of ethyl ether. The suspension was stirred overnight, and then the white precipitate was filtered, washed with the mixture of acetone and ethyl ether (1:1) and dried in a vacuum oven. The fractionalized H40 was obtained as a wax-like solid and kept in a desiccator.

4-Dimethylaminopyridine *p*-toluenesulfonate (DPTS) as a catalyst for esterification was synthesized according to the method reported by Moore and Stupp [24]. In a typical synthesis, thioglycolic acid (5.54 g, 60 mmol), H40 (5.72 g, 0.78 mmol, 50 mmol of –OH) and DPTS (0.32 g, 3 wt%) were added in 100 mL of toluene in a three-neck flask with a Dean–Stark trap. Then the mixture was kept under refluxing overnight at 110 °C under nitrogen atmosphere. Thereafter, toluene was removed under reduced pressure. The crude product was diluted with 50 mL of CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ and distilled water, and then dried with anhydrous $MgSO_4$. After removal of $MgSO_4$ by filtration, CH_2Cl_2 was evaporated under vacuum. Colorless viscous oil was obtained, named as TAH40, and kept in a vacuum desiccator (8.43 g, yield 89%).

2.2.2. 7-Hydroxyl-4-methylcoumarin

The typical procedure was taken according to early literature [25]. Resorcinol (22.0 g, 0.2 mol) was dissolved in freshly distilled ethyl acetoacetate (26.0 g, 0.2 mol), and dropped slowly into a 100 mL of concentrated H_2SO_4 cooled in ice bath. The reaction was kept stirring under 10 °C for 2 h, and then overnight at room temperature. The suspension was poured into 500 mL of icy distilled water to obtain a white precipitate. Thereafter, the filtered white solid was washed with saturated aqueous $NaHCO_3$ (100 mL × 3) and then cold distilled water (100 mL × 3). After dried in a vacuum oven and recrystallized from 99% ethanol for three times, a white crystalline powder was obtained with a yield of 94% and kept in a dark bottle wrapped with an aluminum foil.

^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 2.41 (s, 3H), 6.14 (s, 1H), 6.82 (d, 1H), 6.87–6.90 (dd, 1H), 7.48–7.51 (d, 1H).

2.2.3. 7-(4-Vinyl-benzyloxyl)-4-methylcoumarin (VBMC)

In a typical procedure, 7-hydroxyl-4-methylcoumarin (8.76 g, 0.05 mol) was firstly dissolved in 50 mL of DMF and stirred intensively with the addition of finely ground anhydrous potassium carbonate (6.91 g, 0.05 mol). Then 4-vinylbenzyl chloride (7.63 g, 0.05 mol) with the addition of 4-methoxyphenol (0.08 g, 1 wt%) was dropped into the suspension, and kept refluxing at 60 °C overnight. Thereafter, the precipitate was removed by filtration and the organic phase was poured into 150 mL of 5% HCl. The suspension was extracted with 50 mL of CH_2Cl_2. The organic phase was washed with distilled water (100 mL × 3) and dried over anhydrous $MgSO_4$. After removal of $MgSO_4$ by filtration and evaporation of CH_2Cl_2 under reduced pressure, the product was obtained as yellowish powder, kept away from light, named as VBMC (yield 87%).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.41 (s, 3H), 5.09 (s, 2H), 5.17–5.25 (dd, 1H), 5.73–5.77 (dd, 1H), 6.16 (s, 1H), 6.65–6.73 (m, 1H), 6.86–6.87 (d, 1H), 6.89–6.93 (dd, 1H), 7.27–7.48 (m, 5H).

2.2.4. 4-Methylcoumarin terminal functionalized H40 (MCTH40)

In a typical procedure of thiol–ene addition, VBMC (1.87 g, 6.4 mmol) and TAH40 (1.20 g, 0.1 mmol) were dissolved in 20 mL of THF and stirred at 60 °C for 8 h. The degree of addition reaction was monitored with thin layer chromatographic method (TLC, ethyl acetate/$CH_2Cl_2 = 1:4$, v/v). The reactant was stirred until the trace of vinyl monomer ($R_f \sim 0.75$) was finally absent, and then for additional 30 min. The solution was dropped into methanol. A yellowish precipitate was collected by filtration and dried in a vacuum oven. The crude product was further recrystallized with acetone/methanol (5:1) to afford a white solid (yield 93%), named as MCTH40.

2.2.5. Poly(7-(4-vinyl-benzyloxyl)-4-methylcoumarin) (PVBMC) via RAFT polymerization

1-Phenylethyl dithiobenzoate (PEDB) was synthesized as a chain transfer agent according to literature [26]. The synthesized monomer above, VBMC (2.92 g, 10 mmol), PEDB (25.8 mg, 0.1 mmol) and AIBN (1.6 mg, 0.01 mmol) as an initiator were successively added into a dry glass tube with a magnetic bar, and degassed through three vacuum/dry nitrogen cycles. Thereafter, the tube was sealed under vacuum and heated with an oil bath at 110 °C for 24 h. The polymerization was quenched by freezing with liquid nitrogen. The crude product was dissolved in dry THF and precipitated from methanol for three cycles to obtain a purified product, named PVBMC. The conversion was calculated based on the ^{1}H NMR result of the crude product.

2.3. Measurements

The ^{1}H NMR spectroscopic analysis was performed on a Bruker 300 MHz nuclear magnetic resonance instrument (Bruker Bio-Spin Co., Switzerland). The FT-IR spectra were recorded on a Perkin–Elmer Spectrum 2000 Fourier transform infrared spectrometer (Perkin–Elmer Instruments, USA). The UV–vis analysis was performed on a Shimadzu UV-2401PC ultraviolet–visible spectrometer (Shimadzu Corporation, Japan). The fluorescence spectra were recorded on a Perkin–Elmer LS-55 Fluorescence Spectrometer (Perkin–Elmer, USA). The gel permeation chromatographic (GPC) analysis was performed on a GPC apparatus (Waters, USA) at 25 °C.

THF was used as an eluent with an elution rate of 1.0 mL/min. The standard PSt was used for the calibration of samples. The polymer solution was ultrafiltered with a 220 nm PTFE filter prior to GPC analysis. The sample was irradiated with a BHG-250 UV-spotcure system (Mejiro Precision Co., Japan) for photo-crosslinking ($\lambda_{max} = 365$ nm, 9.2 mW cm^{-2} at the sample cell). Then the sample was irradiated with an EF-140C UV system (Spectronics, USA) equipped with a UVC lamp ($\lambda_{max} = 254$ nm, 8.6 mW cm^{-2} at the sample cell) for photo-cleavage.

2.4. General procedure for photo-crosslinking/photo-cleavage

Both the MCTH40 and the PVBMC were processed with the same procedure as follows. The polymer dissolved in chloroform (0.05 mmol L^{-1} for MCTH40 and 0.03 mmol L^{-1} for PVBMC) in a quartz sample cell was continuously irradiated under UVA light ($\lambda_{max} = 365$ nm) and immediately determined for the UV–vis spectrum for an interval of 5 min. When the minimum value of absorbance at 319 nm in UV-vis spectrum was determined, the sample was irradiated under UVC light ($\lambda_{max} = 254$ nm) and determined for the same interval. The procedure of irradiation and determination was repeated for three cycles as described above in order to investigate the photo-reversibility. After three UVA/UVC irradiation cycles, the resulted polymer was characterized with GPC, FT-IR and fluorescence analyses.

3. Results and discussion

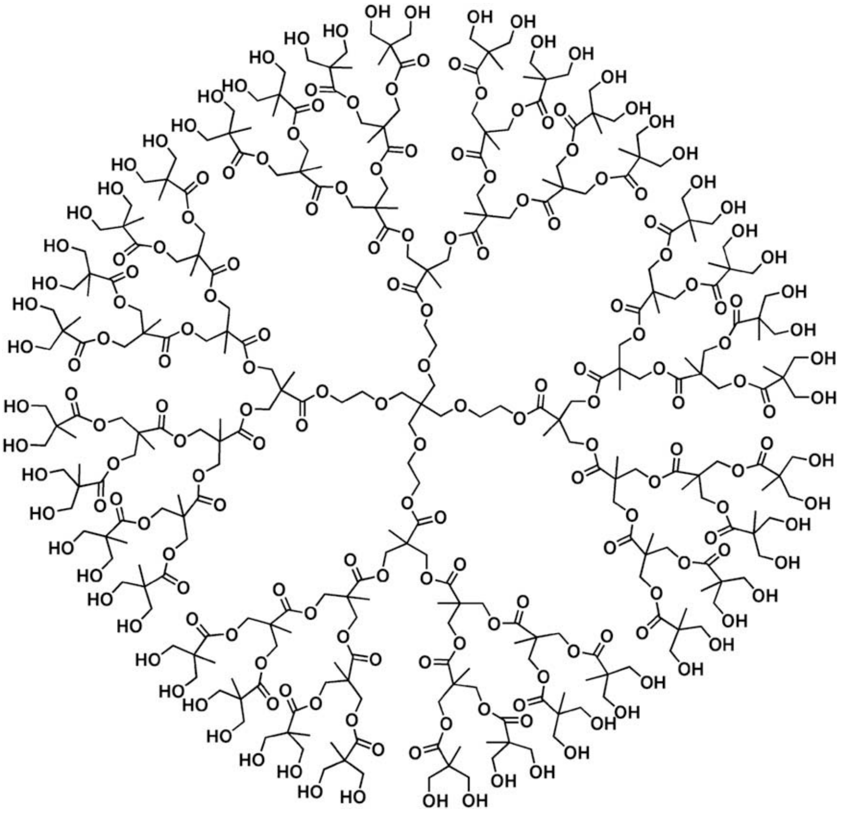
3.1. Characterization

The ideal schematic representation of hyperbranched polyester polyol H40 and the synthetic routes of MCTH40 and PVBMC are shown in Schemes 1–3.

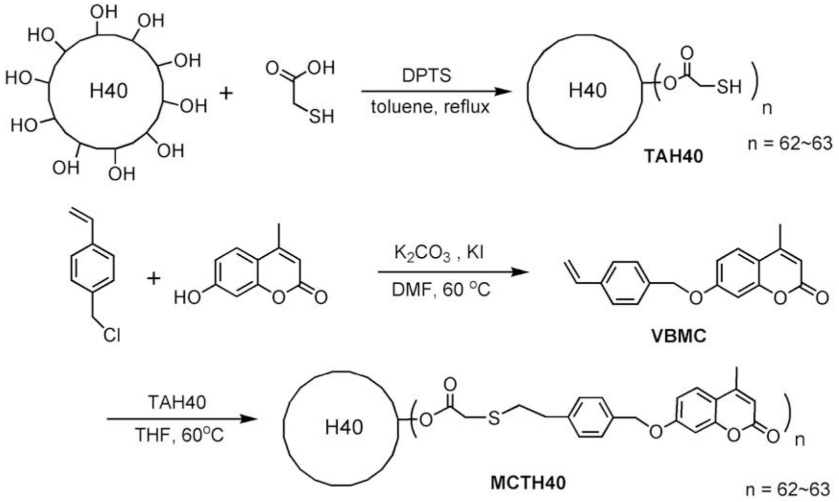
The hyperbranched polyester polyol, Boltorn™ H40 theoretically owns 64 terminal hydroxyl groups. After esterification the solubility of thiol-modified H40 (TAH40) was greatly improved for most of polar organic solvents. From the ^{1}H NMR spectrum of TAH40 in CDCl$_3$ (Fig. 1-a), the thiol proton of thioglycolic group resonates at around 2.03–2.06 ppm. According to the integral results of the peaks at 3.28–3.30 ppm (–CH$_2$–S–) in the ^{1}H NMR spectrum of TAH40, the conversion of –OH group of H40 was calculated to be 97%. Furthermore, the methylene proton of disulfide (–CH$_2$–S–S–CH$_2$–) resonating at the higher δ value of around 3.6 ppm is absent, which proves that most of the thiol groups were kept without oxidation [27].

Compared with the ^{1}H NMR analysis results of TAH40, VBMC and MCTH40, as shown in Fig. 1, it can be seen that after thiol–ene addition the –SH signal is absent, whereas the new signal peaks attributed to thiol–ether proton (–S–CH$_2$–CH$_2$–) are observed at 2.91–3.01 ppm. Moreover, the signal peaks of main backbone of TAH40 are observed (Fig. 1-c), such as for methyl protons at 1.39 ppm, methylene protons at 3.28–3.31 ppm (–CH$_2$–S–) and 4.29–4.39 ppm (–CH$_2$–O–). The signal peaks attributed to the 4-methylcoumarin benzyl ether structure are also observed, such as for protons of benzopyrone ring at 6.16, 6.86, 6.89–6.93 and 7.50 ppm (partially overlapped with the phenyl signals at 7.37–7.50 ppm), methyl protons of VBMC at 2.39 ppm and benzyl methylene protons at 5.05 ppm [28,29]. Based on the integral results the functional group conversion was calculated to be 98%, approximately.

The structural unit of purified linear PVBMC was also characterized with ^{1}H NMR spectrum (Fig. 2). The typical broad peaks representing polystyrene backbone are observed at 1.4, 1.8, 6.5 and 7.1 ppm, respectively [30]. The benzyl methylene proton shows a single peak at 5.12 ppm. The single peaks attributed to 4-methylcoumarin units resonate at 2.35 and 6.13 ppm [17]. Furthermore, the conversion of monomer was calculated to be 87% based on the



Scheme 1. Ideal schematic representation of Boltorn™ H40 based on dendritic model.

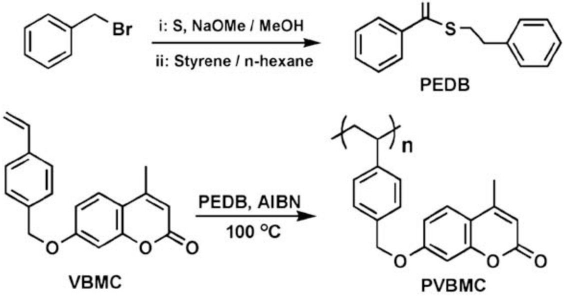


Scheme 2. Synthetic routes of VBMC and MCTH40.

integral NMR results of crude product obtained by RAFT polymerization.

The GPC results listed in Table 1 demonstrated that the PDI of refined H40 decreases to 1.38 ($M_n = 5930$ g/mol) compared with 1.8 of the commercial product ($M_n = 2833$ g/mol) [22]. After esterification the PDI of TAH40 is 1.39, showing a little increase ($M_n = 9583$ g/mol). It is reflected that because of the special molecular shape of the hyperbranched polymer, the retention time of polymer sample is effected by its hydrodynamic volume, and thus the average molecular weight was measured as lower than its practical value [22]. One unavoidable side reaction of thiol–ene system is the homopolymerization of the vinyl monomer. So it is necessary to purify the crude product of MCTH40 by precipitation. The GPC result of MCTH40 shows that the number-average molecular weight of purified MCTH40 was 21 620 g/mol with a PDI of 1.41, indicating that the content of homopolymers becomes minimized. For PVBMC, the number-average molecular weight was measured to be 28 300 g/mol, and the PDI was well controlled as 1.12.

Fig. 3(A) shows the FT-IR spectrum of VBMC. The benzopyrone ring of 4-methylcoumarin structure shows the peaks at 1560, 1613 and 1731 $\mathrm{cm^{-1}}$ [31,32], and the peak at 1387 $\mathrm{cm^{-1}}$ attributed to $-CH_3$ stretching. According to the FT-IR spectroscopic analysis (Fig. 3-B), TAH40 shows a weak peak at 2573 $\mathrm{cm^{-1}}$ (–S–H stretching) and three strong bands at 1147 $\mathrm{cm^{-1}}$ (–C(C=O)–O– symmetric stretching), 1290 $\mathrm{cm^{-1}}$ (–C(C=O)–O– asymmetric stretching) and 1739 $\mathrm{cm^{-1}}$ (–C=O stretching). And the stretching vibration of CH_3– and $-CH_2$– of 2,2-bis(hydroxymethyl) propionate structural unit shows a band at 2882–2950 $\mathrm{cm^{-1}}$.



Scheme 3. RAFT polymerization to prepare PVBMC.

Comparing the FT-IR curve of MCTH40 (Fig. 3-C, D) with that of VBMC and TAH40 (Fig. 3-A, B), it can be seen that after thiol–ene addition reaction the peak attributed to –S–H stretching disappeared from Fig. 3-C, and the typical peaks representing 4-methylcoumarin structure are observed, partially overlapping with the peaks attributed to the hyperbranched polyester backbone. The conversion in the addition reaction of –S–H with C=C was calculated to be 99.2% based on the FT-IR results, indicating that the surface of thiol-modified H40 was fully endcapped with 4-methylcoumarin monomers.

3.2. Reversible photo-crosslinking and photo-cleavage behavior

The photo-crosslinking behavior of MCTH40 through the photodimerization of 4-methylcoumarin units was characterized with UV–vis spectroscopic analysis. The typical UV absorption bands of 4-methylcoumarin structural unit, including the K band absorption ($\lambda_{max} = 289$ nm) attributed to the phenyl group, and the B band absorption ($\lambda_{max} = 319$ nm) attributed to the benzopyrone ring of 4-methylcoumarin moieties, are apparently observed in the UV–vis spectrum (Fig. 4). Under UVA irradiation 4-methylcoumarin dimer was generated via [2 + 2] cycloaddition [33]. As the carbon–carbon double bond of benzopyrone ring of 4-methylcoumarin unit was consumed by UV-induced photodimerization to form a saturated cyclobutane ring, the content of unsaturation in the polymer system decreased correspondingly. Based on the NMR and GPC results the functionality of MCTH40 was calculated as around 62, and the degree of polymerization of PVBMC was calculated as around 95. Thus the concentration of polymer solution was adjusted to make sure that both MCTH40 and PVBMC solutions have the same concentration of 4-methylcoumarin group (0.05 $\mathrm{mmol\,L^{-1}}$ for MCTH40 and 0.03 $\mathrm{mmol\,L^{-1}}$ for PVBMC). As MCTH40 and PVBMC have the same chromophore, 7-benzyloxyl-4-methylcoumarin, it can be assumed that the difference in the extinction coefficient of the chromophore in two polymers is neglectable. From Fig. 4-a and b, it can be seen that the UV absorbance at 289 and 319 nm representing 4-methylcoumarin structure decreases gradually to the minimum of 17% of initial level after irradiated for around 35 min under UVA light ($\lambda_{max} = 365$ nm, 9.2 $\mathrm{mW\,cm^{-2}}$). Because the decrease of UV absorbance at 319 nm is proportional to the extent of photodimerization, the conversion of 4-methylcoumarin moieties of MCTH40 could be evaluated quantitatively according to the relationship: Conversion (%) = $(1 - I/I_0) \times 100\%$. Therefore, the conversion of photo-crosslinking

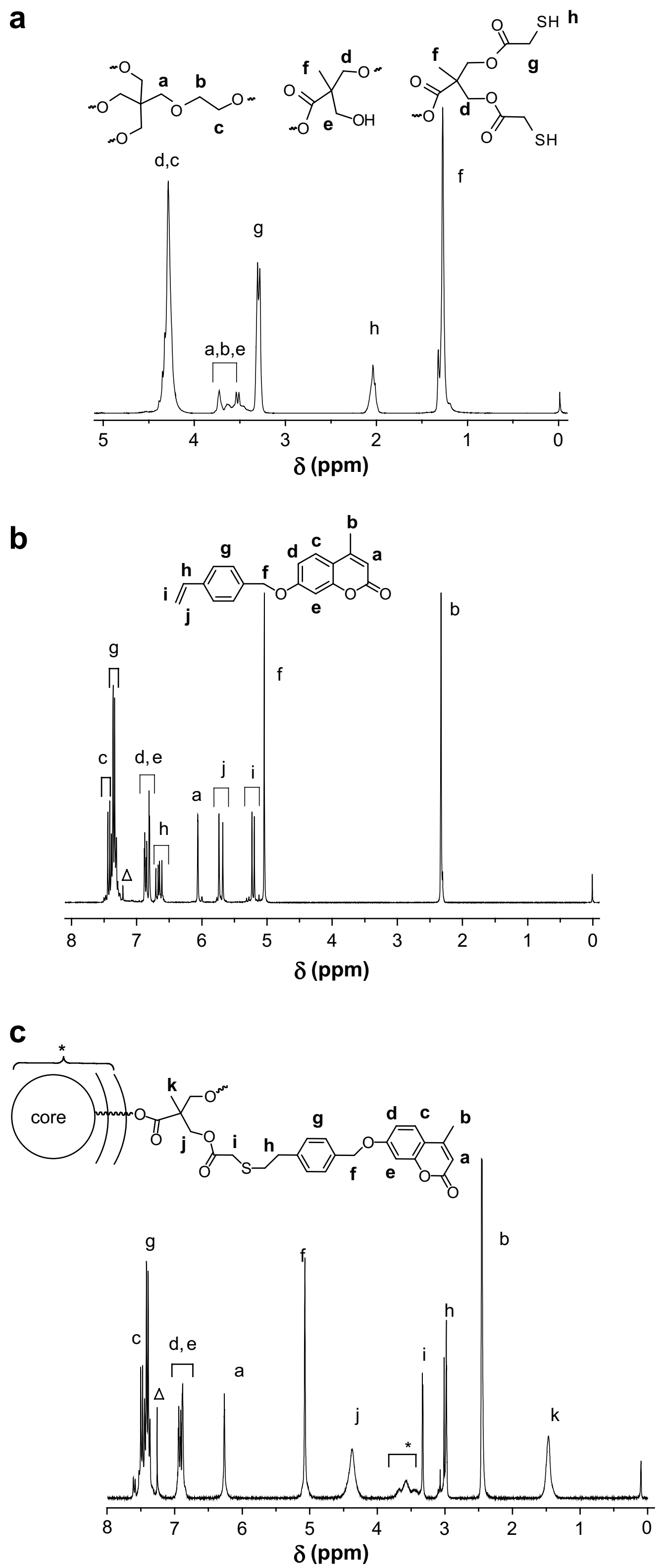


Fig. 1. ^{1}H NMR spectra of TAH40 (a), VBMC (b) and MCTH40 (c) in $CDCl_3$ ($\Delta = CDCl_3$).

increases with increasing the UVA dose and finally reaches a maximum value of 82% with the UVA dose of 19.3 J cm^{-2} (inset in Fig. 4-a). Whereas, the maximal conversion for PVBMC is calculated to be 71% with the UVA dose of 24.8 J cm^{-2} (inset in Fig. 4-c).

The process of photo-cleavage of photodimer of coumarin derivative is much more rapid than photo-crosslinking [34]. According to the determination results of UV absorbance at 319 nm under irradiation of UVC light ($\lambda_{max} = 254$ nm, 8.6 mW cm^{-2}), it is indicated that the content of coumarin moiety of MCTH40 recovered swiftly to 91.4% of original level (Fig. 4-b), and that of PVBMC only recovered to 86.9% of original level (Fig. 4-d). In both cases, the maximum contents of recovered coumarin moieties were lower than the initial values because of the equilibrium between photo-crosslinking and photo-cleavage processes [35].

It was reported in some early literature that the transition of FT-IR spectra also demonstrated the dimerization process [31,32].

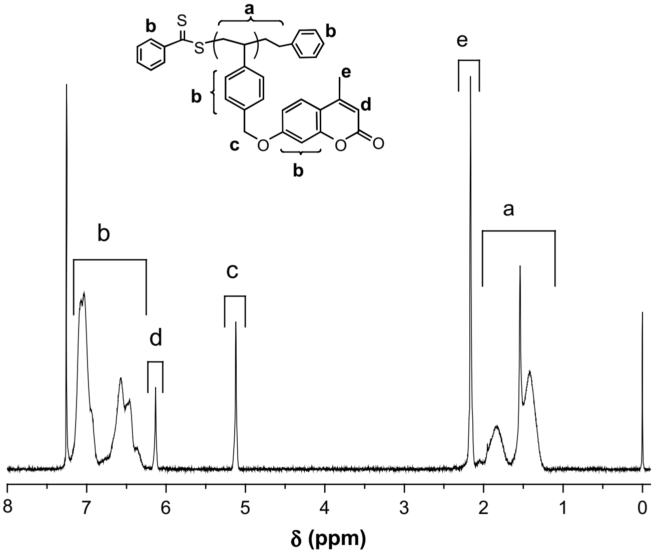


Fig. 2. ^{1}H NMR spectrum of PVBMC in $CDCl_3$.

Table 1
GPC analysis results of H40, TAH40, MCTH40 and PVBMC

Sample	M^a (theoretical)	$M_n{}^b$ (NMR)	$M_n{}^c$ (GPC)	M_w/M_n (PDI)
H40 (fractionalized)	7316	7500	5930	1.38
TAH40	12 059	11 760	9583	1.39
MCTH40	30 830	29 360	21 620	1.41
PVBMC	29 200	25 400	28 300	1.12

[a] Calculated based on dentritic model or on feed ratio ([M]/[I] = 100/1).
[b] Calculated based on ^{1}H NMR data.
[c] Measured by GPC with polystyrene as a standard and THF as an eluent.

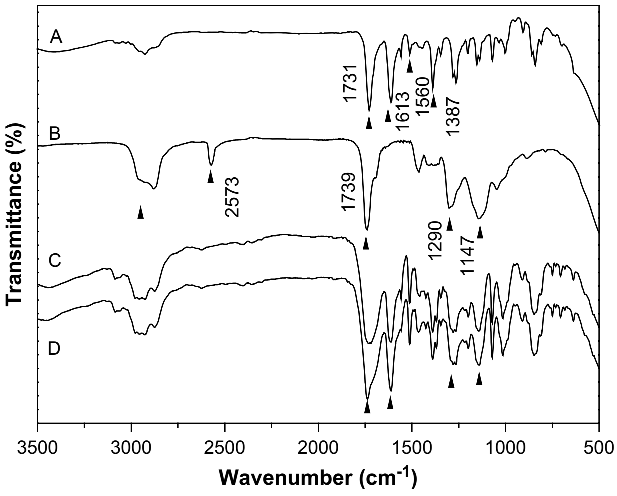


Fig. 3. FT-IR spectra of VBMC (A), TAH40 (B), MCTH40 before UV irradiation (C) and MCTH40 after three photo-reversible cycles (D).

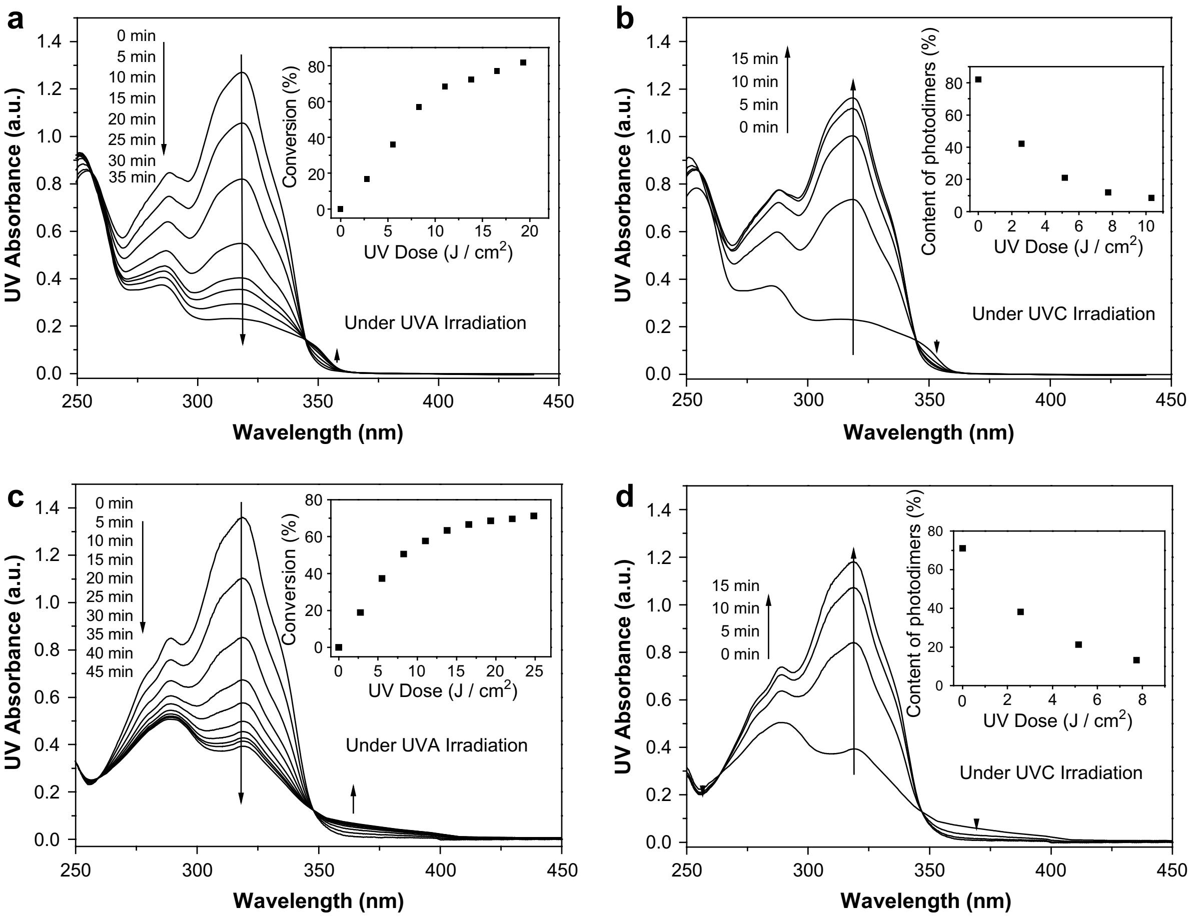


Fig. 4. UV absorbance change of (a and b) MCTH40 (0.05 mmol L^{-1}) and (c and d) PVBMC (0.03 mmol L^{-1}) in chloroform solution irradiated by UVA and UVC light (the arrows indicate trends with increasing irradiation time and inset figure shows the conversion of 4-methylcoumarin moieties or the content of photodimers in the system with increasing UV dose).

However, Fig. 3(C) and (D) shows that the fine structures of FT-IR curves for MCTH40 are badly influenced by the stretching peaks of polyester backbone. It can be also found that only a small increase in the stretching peaks at 1731 and 1613 cm^{-1} attributed to the photodimerization still can be observed by comparing the FT-IR curves of MCTH40 before and after UV irradiation [32]. But other typical transition of FT-IR peaks, which implied the photo-cross-linking and the structures of isomer of photodimer (e.g. head-to-head dimer and head-to-tail dimer) [36], overlapped with the bands of polymer backbone and were difficult to identify.

3.3. Evaluation of photo-reversibility

The photo-reversibility of MCTH40 was compared with linear PVBMC in chloroform solution within three cycles of the photo-crosslinking/photo-cleavage based on the determination of the absorbance at 319 nm of UV–vis spectra (Fig. 5). It has been found that the average reversible period of MCTH40 is much shorter than that of PVBMC under the same concentration of 4-methylcoumarin moiety, indicating that 4-methylcoumarin terminal functionalized H40 performed more rapid response to UV irradiation. The average irradiation dose of UVA light for reaching to the maximum conversion of 4-methylcoumarin moiety through photo-cross-linking was 19.3 J cm^{-2} for MCTH40 and 24.8 J cm^{-2} for PVBMC. The average dose of UVC light for the complete photo-cleavage was 9.44 J cm^{-2} for MCTH40 and 9.58 J cm^{-2} for PVBMC. Moreover, the coumarin-content of MCTH40 averagely changed in the range of 22–87% within three circles, for PVBMC that was 31–84%. Therefore, it was indicated that MCTH40 performed a larger extent of photo-reversibility than that of PVBMC.

Because the 4-methylcoumarin moiety contains the conjugated benzopyrone ring and performs strong fluorescence emission

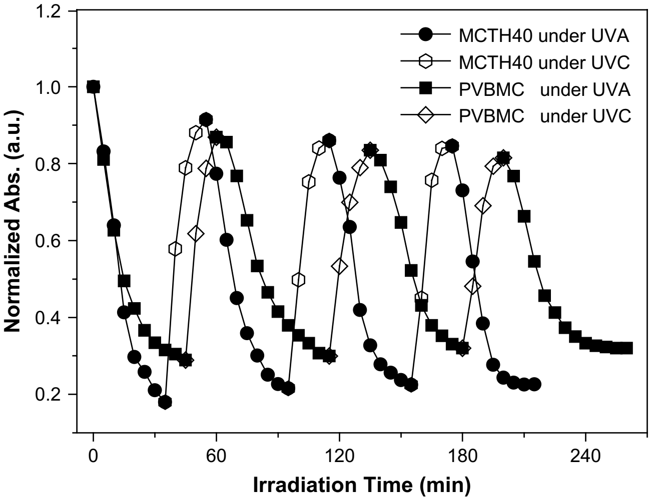


Fig. 5. UV absorbance changes of MCTH40 and PVBMC at 319 nm with irradiation of UVA light ($\lambda_{max} = 365$ nm, decrease in absorbance) and UVC light ($\lambda_{max} = 254$ nm, increase in absorbance) for three cycles.

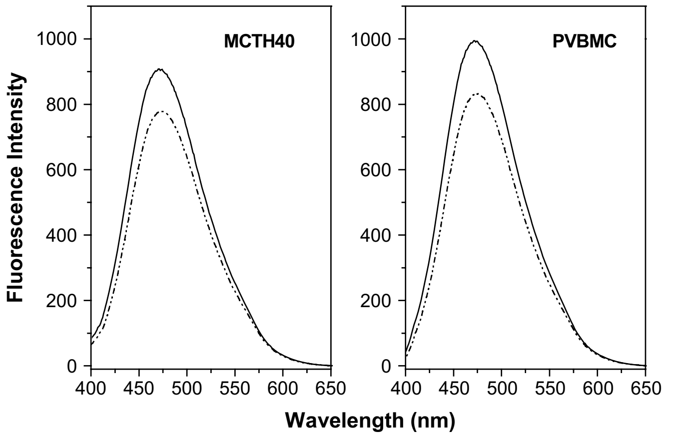


Fig. 6. Fluorescence spectral change of MCTH40 (0.05 mmol L^{-1}) and PVBMC (0.03 mmol L^{-1}) before UV irradiation (solid lines) and after three photo-reversible cycles (dash dot lines).

intensity [11], the 4-methylcoumarin-containing polymers were also characterized with fluorescence analysis (Fig. 6). The MCTH40 shows a broad emission peak at λ_{max} of 469 nm (excitation at 340 nm). However, the fluorescent emission peak of PVBMC was determined at 472 nm (excitation at 340 nm). After three photo-crosslinking/photo-cleavage cycles, the fluorescence intensity of MCTH40 at 469 nm shows a decrease to 85.2% of original level. Whereas, the fluorescence intensity of PVBMC decreases to 83.5%. The results are consistent with the UV–vis analysis, demonstrating that the equilibrium between photo-crosslinking and photo-cleavage leads to a considerable remnant of photodimer in photo-reversible polymer systems and influences the fluorescence intensity of 4-methylcoumarin-containing polymers.

It is necessary to investigate the variation of fractional components of photo-cleaved 4-methylcoumarin-containing polymers by GPC method [17]. The polymer samples photo-cleaved under UVC irradiation were collected after three UVA/UVC irradiation cycles for GPC analysis, and the results were compared with those before photo-crosslinking. As shown in Fig. 7, the average molecular weight and the PDI of MCTH40 and PVBMC are all slightly affected by the equilibrium of photo-crosslinking/photo-cleavage process. Based on the GPC analysis results listed in Table 1, the M_n of MCTH40 increases from 21 620 to 24 300 after three cycles, while the PDI is also broadened from 1.41 to 1.47. It is indicated that a small amount of photodimer of 4-methylcoumarin still remained inter-macromolecules or intramolecules. The GPC analysis results of PVBMC also show that the average molecular weight and PDI of PVBMC both increase after three photo-crosslinking/photo-cleavage cycles. The M_n of PVBMC increases from 28 300 to 29 010, and the PDI is broadened from 1.12 to 1.16, correspondingly. Furthermore, the slightly shortened retention time of the polymer fractions after repeated UV irradiation cycles also indicates that the average hydrodynamic volume of the remained partially crosslinked polymer clusters slightly decreased in the solution. As the concentration of polymer solution was very low (0.05 mmol L^{-1} for MCTH40 and 0.03 mmol L^{-1} for PVBMC), the proportion of large-scale intermolecular crosslinking was greatly reduced. And the considerable content of remaining photodimer in cleaved polymer system did not bring the increase of molecular weight in several times. It is indicated that the increase in the average molecular weight and PDI was mainly attributed to intramolecular photodimerization. It is indicated that after three photo-reversible cycles, the MCTH40 and PVBMC did not completely recover their original components, but contained a small amount of fraction of higher molecular weight attributed to the remnant cyclobutyl linkage in polymer systems.

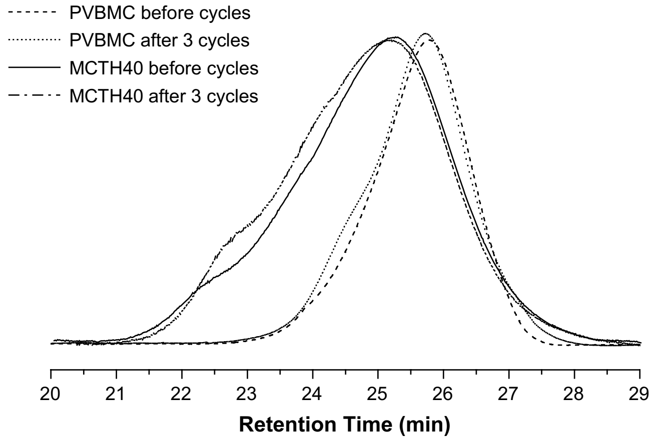


Fig. 7. GPC traces of MCTH40 and PVBMC before UV irradiation and after three photo-reversible cycles.

4. Conclusions

In this work, 4-methylcoumarin terminal functionalized hyperbranched polymer, MCTH40, was prepared via thiol–ene addition reaction of thiol-modified H40 (TAH40) with vinylbenzyl ether of 4-methylcoumarin (VBMC) with high conversion under mild conditions. And a linear polymer, PVBMC was prepared via RAFT polymerization for comparison. The thiol–ene addition reaction was proved as a highly efficient method for modification based on the ^{1}H NMR and FT-IR analyses. The reversible photo-crosslinking/photo-cleavage behavior was investigated based on the UV–vis spectroscopic analysis. It was found that the process of photo-cleavage was much faster than photo-crosslinking. And MCTH40 performed a lager photo-reversible extent than linear PVBMC. Based on the UV–vis analysis, it was concluded that MCTH40 with hyperbranched structure performed a shorter photo-reversible period than linear PVBMC. The GPC analysis indicated that the average molecular weight and the PDI of MCTH40 and PVBMC both showed slight increase after three reversible cycles due to the equilibrium between photo-crosslinking and photo-cleavage.

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