

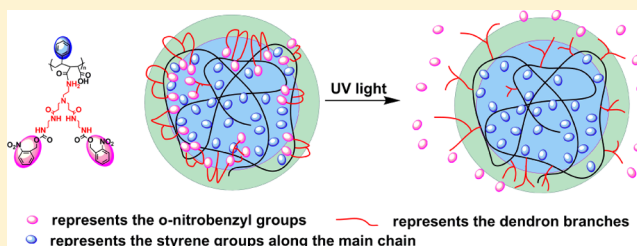
Photoresponsive Dendronized Copolymers of Styrene and Maleic Anhydride Pendant with Poly(amidoamine) Dendrons as Side Groups

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Supporting Information

ABSTRACT: A series of photoresponsive dendronized polymers **PGn-NB** ($n = 1, 2, 3$) were synthesized by attaching *o*-nitrobenzyl alcohol-terminated amidoamine dendrons (**G1–G3**) to the alternating styrene and maleic anhydride copolymer (PSt-*alt*-PMAH). The structures and the molecular weights of the obtained polymers were characterized by ^1H NMR and FTIR measurements. It is found that the coverage degrees of the dendrons are 74%, 42%, and 26%, respectively, indicating that the numbers of the appended dendrons decrease in the order of **G1** > **G2** > **G3** due to the steric hindrance of higher generation dendrons with more branches. The photocleavable behavior of **G1–G3** was detected by UV–vis and ^1H NMR measurements. As a result, **G2** showed a faster cleavage rate compared to **G1** and **G3**. The critical aggregation concentration (CAC) of **PGn-NB** ($n = 1, 2, 3$), measured by using pyrene as a fluorescence probe, were 0.05 mg/mL (**PG1-NB**), 0.01 mg/mL (**PG2-NB**), and 0.03 mg/mL (**PG3-NB**), which displayed that the structure of **PG2-NB** was in favor of forming aggregates at lower concentrations. Light scattering study indicated that both the apparent molecular weight and the chain density of the aggregates formed by **PG2-NB** decreased with the irradiation time. Atomic force microscope (AFM) measurements also showed that the size of the aggregates increased dramatically from 15 to 70 nm before and after UV irradiation, evidencing that the UV light induced structure change. Nile Reds, as the guest molecules, were loaded in the aggregates from **PG2-NB**, and the release profiles upon UV stimulus were monitored by the fluorescence spectroscopy.



INTRODUCTION

In the past decades, considerable efforts have been paid to advance our knowledge on developing stimuli-responsive materials, including the stimulus of pH,^{1–4} temperature,^{5,6} redox,^{7,8} oxidation,⁹ electric field,^{10,11} and light¹² for various applications such as drug delivery,^{13,14} microrobots,¹⁵ sensors,^{16,17} and catalysis.¹⁸ Of particular interest are the photoresponsive materials for their advantages of ease application, good stability, relative biocompatibility, great selectivity under remote control at the spatial and temporal precision, no additives, and environmental friendly.¹⁹ In recent years, more and more photoresponsive systems have been reported to show novel properties; for example, Fréchet et al. reported a PEG-lipid with the 2-diazo-1,2-naphthoquinones (DNQ) as the hydrophobic end groups. The structure of DNQ transformed to hydrophilic by UV irradiation at 350 nm, resulting in the damage of the micelles and release of the payloads.²⁰ Yang et al. synthesized the novel photolabile diblock copolymers bearing truxillic acid derivative junctions that could take a reversible photochemical [2 + 2] cyclo-addition reaction, such leading to the copolymers break or combine together under UV irradiation around 260 nm.²¹ McGrath and co-workers have reported a series of photo-switchable dendrimers based on the azobenzene structure.

Under UV irradiation, the azobenzene derivatives carry the isomerization and show different physical properties.^{22–26}

As is well-known, *o*-nitrobenzyl alcohol derivatives are widely studied photosensitive compounds.²⁷ The *o*-nitrobenzyl groups can be cleaved with UV light (300–365 nm), thus inducing the photoisomerization of *o*-nitrobenzyl alcohol derivatives to *o*-nitrosobenzaldehyde.²⁸ The activated light wavelength of these compounds could be tuned by changing the substituent groups on benzyl rings.²⁹ Various *o*-nitrobenzyl alcohol derivative-based photoresponsive systems were constructed including gels,^{30–32} micelles,^{33,34} nanoparticles,^{35,36} and dendrimers.³⁷ Thayumanavan et al. reported the amphiphilic dendrimers by linking *o*-nitrobenzyl ester moieties with the lipophilic units and the hydrophilic domains. Upon UV irradiation, the cleavage of the *o*-nitrobenzyl bonds broke the hydrophilic–lipophilic balance and disrupted the micelles.³⁸ Recently, Zhao et al. reported a new strategy enabling the use of a near-infrared (NIR) laser to cleave the drug carriers bearing *o*-nitrobenzyl groups and subsequently release the payloads. They encapsulated the NaYF₄:TmYb upconverting nanoparticles inside the micelles and found that the emitted photons in the UV region

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activated the *o*-nitrobenzyl groups and cleaved the polymer chains when the carriers were exposed to the NIR light.³⁹ Their results differed from that the *o*-nitrobenzyl groups were usually used as a junction⁴⁰ to combine the hydrophobic and hydrophilic parts or to decorate them into side chains for increasing the hydrophobicity and showed great potential for the application in drug delivery systems.

Dendronized polymers, a merger of two concepts of dendrimers and polymers, possess the particular structures constructed by a linear polymer chain surrounded with certain structural dendrons at the repeating units. The superiority of such polymers with stimuli-responsiveness refers to easily incorporating the responsive motifs into the polymers for the densely packed modifiable peripheral groups of dendrons; the balance of the molecular structures, for example, the hydrophilicity–hydrophobicity ratios, can be easily adjusted by converting the generation, interior building blocks, and surface groups of the dendrons. Previously, we reported the dendronized polymers synthesized either by attaching butylamide-terminated amidoamine dendrons to PSt-*alt*-PMAh copolymer or by polymerization of dendron-pendent 2-hydroxyethyl methacrylate.^{41,42} It was found that the properties of polymers were dependent on the generation of the dendrons and the molecular weights.

Herein, we report a kind of novel photoresponsive dendronized polymer constructed with PSt-*alt*-PMAh copolymer as the main chain on which jacketed the *o*-nitrobenzyl decorated the amidoamine dendrons. We expect to take the advantages of dendritic side chains with multiple modifiable end groups, by which affords the polymers with multitudinous UV light cleavable groups and balances the hydrophilic/hydrophobic properties of the polymers and further changes such characters with UV light. In this way, we aim to explore the self-assembly behavior, guest molecules encapsulation, and release properties of the obtained dendronized polymers.

EXPERIMENTAL SECTION

Materials. Amidoamine dendrons were synthesized according to the method reported previously.⁴³ PSt-*alt*-MAh copolymer was kindly provided by Professor Zichen Li's group with the number molecular weight of 10 800 and the PDI of 1.32. *N,N*-Dimethylformamide, triethylamine, and tetrahydrofuran were purchased from Chemical Reagent Beijing Co. and purified according to the standard procedures. All the reagents and the common solvents were obtained from the commercial sources and used as received unless stated otherwise.

Synthesis of Compound 1. 1.00 g of *o*-nitrobenzyl (6.54 mmol) alcohol was dissolved in anhydrous THF, and 1.20 mL of triethylamine (TEA) was added dropwise. The mixture was cooled in an ice salt bath for 20 min. Then a solution of *p*-nitrophenyl chloroformate (1.56 g, 7.76 mmol) in THF was added dropwise within 10 min. After the solution was stirred at room temperature for 24 h, the resulting white salt TEA-HCl was filtrated, and the filtrate was collected and evaporated in vacuo. The crude product was purified through a silica column. The structure and molecular weight of the compound **1** were determined by the ¹H NMR and ESI MS.

Compound 1. White solid. Yield: 44%. ¹H NMR (300 MHz, CDCl₃, TMS, *T* = 298 K): 8.34–8.25 (m, 2H, ArH), 8.24–8.17 (br, 1H, ArH), 7.77–7.74 (m, 1H, ArH), 7.74–7.72 (br, 1H, ArH), 7.64–7.53 (m, 1H, ArH), 7.47–7.38 (m, 2H, ArH), 5.77–5.69 (s, 2H, ArCH₂O). ESI MS: calcd for C₁₄H₁₀N₂O₇, [M + Na]⁺: 341; found: 341.

Synthesis of G1. 1.46 g of compound **1** (4.6 mmol) was dissolved in anhydrous DMF, and a DMF solution of 0.71 g (1.8 mmol) of **G1** aminoamine dendron was added to the mixture dropwise. After being stirred at room temperature for 48 h, the solution was evaporated in

vacuo, and the crude product was purified through a silica column with THF as the eluent.

G1. This was obtained as a pale yellow solid. Yield: 75%. ¹H NMR (300 MHz, CDCl₃, TMS, *T* = 298 K): 8.14–8.05 (br, 2H, NHC=O), 8.00–7.89 (t, 2H, ArH), 7.84–7.74 (t, 2H, ArH), 7.70–7.54 (m, 4H, ArH), 7.50–7.41 (t, 1H, NHC=O), 6.2–5.85 (s, 1H, –CH₂NHC=O), 5.55–5.44 (s, 4H, –OCHH₂Ar), 3.43–3.27 (m, 8H, NCH₂CH₂–, O=CNHCH₂–), 3.21–3.08 (m, 2H, O=CNHCH₂CH₂–), 2.75–2.60 (m, 4H, –CH₂NHC=O), 2.53–2.42 (m, 2H, –CH₂CH₂N–(CH₂)–), 2.39–2.24 (m, 4H, –CH₂CH₂C=O), 1.52–1.30 (m, 9H, (CH₃)₃CO–). ESI FTMS calculated for C₃₃H₄₆N₈O₁₂, [M + H]⁺: 747.32, [M + Na]⁺: 769.32, [M + K]⁺: 785.32; found: 747.3, 769.3, 785.3. EA calculated for C, 53.08; H, 6.21; N, 15.01; O, 25.71; measured: C, 52.99; H, 6.25; N, 14.84. FT-IR: 3333, 3079, 2972, 1703, 1645, 1527, 1450, 1342, 1265, 1155, 1032, 860, 789, 730, 673 cm^{–1}.

Synthesis of G2. **G2** was synthesized with the same procedures of **G1**. 2.00 g (6.29 mmol) of compound **1** was dissolved in the anhydrous DMF, and a solution of **G2** aminoamine dendron (0.53 g, 0.63 mmol) in 10 mL of anhydrous DMF was added to the mixture dropwise. After being stirred at room temperature for 48 h, the solution was evaporated in vacuo, and the crude product was purified through a silica column using methanol/chloroform (1:5) as the eluent.

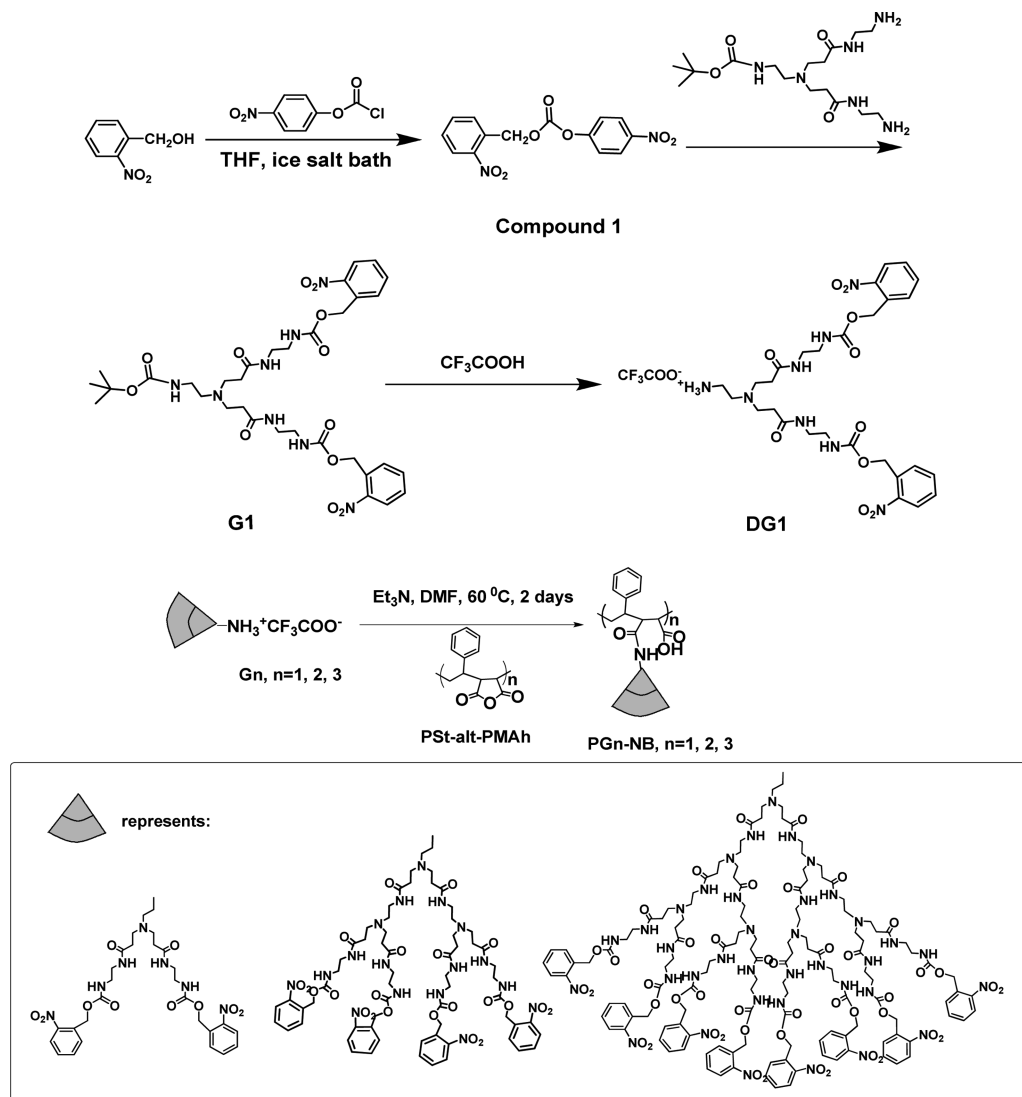
G2. This was obtained as a pale yellow solid. Yield: 46%. ¹H NMR (300 MHz, CDCl₃, TMS, *T* = 298 K): 8.09–8.00 (m, 4H, NHC=O, ArH), 7.64–7.56 (m, 8H, ArH), 7.51–7.39 (m, 6H, ArH), 6.60–6.17 (m, 5H, NHC=O), 5.50–5.39 (m, 8H, OCH₂Ar), 3.45–3.12 (m, 24H, NCH₂CH₂CO–, O=CNHCH₂CH₂N), 2.79–2.62 (m, 12H, O=CNHCH₂CH₂NH–), 2.58–2.47 (m, 6H, NHCH₂CH₂N), 2.42–2.27 (m, 12H, NCH₂CH₂CO), 1.51–1.35 (s, 9H, (CH₃)₃CO–). ESI FTMS calculated for C₆₉H₉₆N₁₈O₂₄, [M + H]⁺: 1561.69; found: 1561.7. FTIR: 3418, 3078, 2939, 2852, 2293, 1711, 1650, 1528, 1443, 1353, 1255, 1150, 1035, 860, 786, 732, 669 cm^{–1}.

Synthesis of G3. **G3** was synthesized by the same procedures of **G1**. 1.60 g of compound **1** (5.03 mmol) was dissolved in the anhydrous DMF, and a solution of **G3** aminoamine dendron (0.55 g, 0.31 mmol) in 10 mL of anhydrous DMF was added into the mixture dropwise. After being stirred at room temperature for 48 h, the solution was evaporated in vacuo, and the crude product was purified through a silica column using methanol/chloroform (1:1) as the eluent.

G3. This was obtained as a pale yellow solid. Yield: 29%. ¹H NMR (300 MHz, CDCl₃, TMS, *T* = 298 K): 8.08–7.98 (m, 8H, NHC=O, ArH), 7.71–7.53 (m, 28H, ArH), 7.47–7.39 (m, 8H, ArH), 6.55–6.39 (m, 8H, NHC=O), 5.49–5.39 (m, 16H, OCH₂Ar), 3.42–3.15 (m, 48H, NCH₂CH₂CO–, O=CNHCH₂CH₂N), 2.80–2.64 (m, 28H, O=CNHCH₂CH₂NH–), 2.58–2.46 (m, 14H, NHCH₂CH₂N), 2.41–2.26 (m, 28H, NCH₂CH₂CO), 1.45–1.35 (s, 9H, (CH₃)₃CO–). ESI FTMS calculated for C₁₄₁H₁₉₆N₃₈O₄₈, [M + H]⁺: 3191.4, [M + 2H]²⁺: 1596.2, [M + 3H]³⁺: 1064.5, [M + 4H]⁴⁺: 798.6, [M + 5H]⁵⁺: 639.1, [M + 6H]⁶⁺: 532.7; found: 3192.5, 1596.2, 1064.5, 798.6, 639.1, 532.3. FTIR: 3309, 3078, 2941, 2840, 1716, 1650, 1527, 1444, 1347, 1256, 1147, 1035, 860, 787, 733, 671 cm^{–1}.

Synthesis of PGr-NB (*n* = 1, 2, 3). All the reactions were carried out with anhydrous DMF as the solvent and the representative procedures were as follows: 0.30 g of **G1** (0.40 mmol) was dissolved in 1 mL of CH₂Cl₂, and then 0.5 mL of trifluoroacetic acid (TFA) was added into the mixture dropwise within 5 min. The reaction was monitored by thin-layer chromatography (TLC). After the solution was being stirred at room temperature for 1 h, the excess TFA was evaporated in vacuo, and the crude product was dissolved in 1 mL of methanol and precipitated in diethyl ether three times. The viscous liquid (**DG1**) was measured by ¹H NMR to confirm the elimination of Boc group. 305.6 mg of **DG1** (0.40 mmol) was dissolved in the anhydrous DMF, and 0.2 mL of TEA was added into the mixture dropwise. A solution of 69.25 mg of PSt-*alt*-PMAh in 4 mL of DMF was added into the mixture. After stirred at 60 °C in an oil bath for 48 h, the solution was evaporated in vacuo, and the crude product was precipitated in THF three times. The obtained precipitate was characterized by ¹H NMR and FTIR measurements.

Scheme 1. Synthesis and Structures of PGn-NB



PG1-NB. This was obtained as a yellow solid. Yield: 51%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, TMS, room temperature): 8.31, 8.08, 7.89, 7.75, 7.64, 7.57, 7.41, 7.09, 5.35, 3.08, 2.09. IR (cm^{-1} , KBr): 3323, 2924, 1701, 1655, 1523, 1453, 1342, 1251, 1141, 1031, 858, 731, 703.

PG2-NB. This was obtained as a yellow solid. Yield: 36%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, TMS, room temperature): 8.08, 7.64, 7.57, 7.43, 7.01, 5.35, 3.07, 2.33, 2.09. IR (cm^{-1} , KBr): 3309, 3081, 2943, 1702, 1663, 1524, 1454, 1343, 1253, 1200, 1032, 858, 792, 731, 704.

PG3-NB. This was obtained as a yellow solid. Yield: 21%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$, TMS, room temperature): 8.08, 8.01, 7.76, 7.64, 7.58, 7.42, 7.00, 5.35, 3.07, 2.79, 2.28, 2.08. IR (cm^{-1} , KBr): 3306, 3081, 2938, 1715, 1653, 1523, 1343, 1254, 1200, 1032, 858, 792, 731, 702.

Measurements. ^1H NMR spectra were recorded on 300 MHz (Varian Mercury) and 400 MHz (Bruker) spectrometers operated at room temperature with CDCl_3 or $\text{DMSO}-d_6$ as the solvents and tetramethylsilane (TMS) as the internal standard. FTIR spectra were recorded on a VECTOR 22 Fourier transform IR spectrometer (Bruker) with KBr as substrates. UV-vis spectra were obtained on a Lambda 35 UV/vis spectrometer (PerkinElmer). The slit width was 1.0 nm. A gel permeation chromatograph (GPC) equipped with a Waters 410 refractive index detector, a Waters 515 HPLC pump, and Ultrastaygel columns (104, 103, and 500 Å) with THF as an eluent at a flow rate of 1.0 mL/min. Monodispersity polystyrene standards were used for calibration. The fluorescence spectra were recorded on a

F4500 spectrometer (Hitachi). The AFM images of the aggregates of PG2-NB were recorded by a Nanoscope Scanning Probe Microscopes System (Digital Instrument). Differential scanning calorimetric (DSC) measurement was performed on TA Instruments DSC Q100. The polymer samples were sealed in the aluminum pans. An empty aluminum pan was used as the reference. A scanning rate of $10.0\text{ }^\circ\text{C}/\text{min}$ was used for both heating and cooling processes between -50 and $120\text{ }^\circ\text{C}$. The glass transition temperature (T_g) was obtained from the second heating run and corresponded to the midpoint of discontinuity in the heat flow.

Light Cleavable Experiments of the Dendrons Gn ($n = 1, 2, 3$). All the light-responsive experiments were carried out under the Blak-Ray B-100AP/R high-intensity UV lamp (100 W, 365 nm). The samples were put in a platform with a distance of 9 cm under the Lamp. UV-vis and ^1H NMR analyses were used to measure the light-cleavable properties of the dendrons Gn ($n = 1, 2, 3$). In the UV-vis spectra experiments, the concentration of the *o*-nitrobenzyl group was fixed at $1.2 \times 10^{-4}\text{ mol/L}$ to monitor the cleavage speed. The solution was added into a quartz pool and put under the UV lamp. For the NMR measurement, the Gn ($n = 1, 2, 3$) samples were put into an NMR glass tube, and the concentration of *o*-nitrobenzyl group in $\text{DMSO}-d_6$ was fixed at the 0.04 mol/L.

Critical Aggregation Concentration (CAC) Measurement. The CACs of the dendronized polymers were determined by the fluorescence method reported previously with pyrene as a probe.^{44,45}

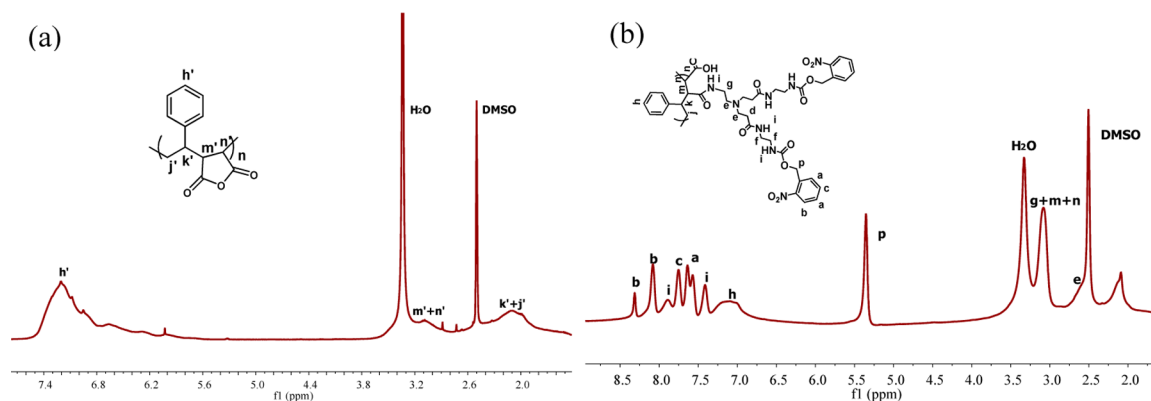


Figure 1. ^1H NMR spectra of (a) PSt-*alt*-PMAh and (b) PG1-NB.

100 μL of THF solution of pyrene (1.0×10^{-3} mol/L) was added to a 100 mL volumetric flask, and the solvent was removed by the nitrogen flow. Then the deionized water was added. The DMSO solutions of PGn-NB ($n = 1, 2, 3$) were added into the aqueous solution of pyrene to prepare the samples with various concentrations. The polymer solutions were equilibrated for 24 h at room temperature. The fluorescence spectra were recorded on a F4500 spectrometer (Hitachi). The excitation and emission slit width of the fluorometer were set at 5.0 and 2.5 nm, respectively. The excitation wavelength was set up at 339 nm, and the emission spectra were recorded from 360 to 580 nm at a scanning rate of 240 nm/min. The I_1 value was defined as the emission intensity at 374 nm and the I_3 value at 384 nm.

Light-Responsive Behavior of the Dendronized Polymers PGn-NB ($n = 1, 2, 3$). Both dynamic light scattering (DLS) and static light scattering (SLS) measurement of PG2-NB (0.05 mg/mL in deionized water) were performed on a Brookhaven goniometer (BI-200SM) equipped with a BI-TurboCorr digital correlator and a thermostatic bath with temperature accuracy of 0.01 $^\circ\text{C}$. A vertically polarized solid-state laser operating at 532 nm was used as the light source (100 mW, CNI Changchun GXC-III, China). For a dilute solution, the root-mean-square radius of gyration (R_g) can be obtained from SLS data on the basis of

$$HC/R_{90}(\theta) = (1/M_w)[1 + (1/3)R_g^2q^2] + 2A_2C$$

where $H = 4\pi^2 n^2 (dn/dc)^2 / (N_A \lambda^4)$ and $q = 4\pi n / \lambda \sin(\theta/2)$; N_A , n , dn/dc , and λ are Avogadro's number, the solvent refractive index, the specific refractive index increment, and the wavelength of light in a vacuum, respectively. In DLS, by using a Laplace inversion program, CONTIN, the normalized distribution function of the characteristic line width was obtained which could be further converted into the hydrodynamic radius R_h by using the Stokes–Einstein equation $D = k_B T / 6\pi\eta R_h$, where D , k_B , T , and η are the translational diffusive coefficient, the Boltzmann constant, the absolute temperature, and the viscosity of the solvent, respectively. The morphologies of the aggregates before and after UV irradiation were recorded on the Nanoscope Scanning Probe Microscopes System (Digital Instrument). All the samples were prepared as follows: 5 μL solution of PG2-NB was dropped onto a mica platform before irradiation and water was evaporated in the atmosphere.

Encapsulation and Release of Nile Red. The Nile Red was chosen as a hydrophobic guest for its stability under UV irradiation.^{34,36} 0.47 mg (1.5 μmol) of Nile Red and 5.01 mg of PG2-NB were dissolved in 100 μL of DMSO. 5 μL of the above solution was added into 5 mL of deionized water to adjust the final concentration of PG2-NB to be 0.05 mg/mL. The solution was equilibrated for 24 h at room temperature. The release of the model guest molecules was measured by the fluorescence spectrometer. The F4500 fluorescence spectrometer was used to measure the fluorescence spectra. The excitation and emission slit width were 5.0 and 5.0 nm, respectively. The excitation wavelength was set up at 540 nm, and the emission spectra were recorded from 560 to 750 nm at a scanning speed of 240 nm/min.

RESULTS AND DISCUSSION

Synthesis of the Dendronized Polymers. PSt-*alt*-PMAh copolymer was synthesized by the reversible addition–fragmentation transfer (RAFT) polymerization with the number-average molecular weight of 10 800 and the PDI of 1.32 characterized by GPC. Gn ($n = 1, 2, 3$) were obtained by the reaction of compound 1 with amino-terminated amido-amine dendrons. The dendronized polymers PGn-NB ($n = 1, 2, 3$) were prepared through removing the focal Boc group of the dendrons with trifluoroacetic acid and then attached them to the PSt-*alt*-PMAh copolymer chains via a ring-opening reaction of exposed NH_2 on the periphery of dendrons with maleic anhydride groups of the copolymer in the excess triethylamine.

The structures and molecular weights of the resulting dendronized polymers were characterized by ^1H NMR and FTIR measurements. Figure 1 shows the ^1H NMR spectra of PSt-*alt*-PMAh and PG1-NB. The following changes were observed: the signal at 5.35 ppm corresponding to the methylene protons of the *o*-nitrobenzyl rings appeared, the peaks around 7.35 ppm emerged, and the peaks at high field attributed to the backbones of aminoamine dendrons arose as the broad peaks. These results indicated that the dendrons were attached to the backbone of the polymer chains. From the integral ratio of the phenyl protons of the styrene units and the methylene protons of the *o*-nitrobenzyl ring at 5.35 ppm, the coverage degrees of PGn-NB ($n = 1, 2, 3$) were calculated to be 74%, 42%, and 26%, respectively. Accordingly, the molecular weights of the dendronized polymers were 2.6×10^4 , 3.3×10^4 , and 4.3×10^4 calculated by the equation

$$M_w = 10800 + 53 \times (M_{\text{DGn}} - 114) \times g$$

where the M_{DGn} are the molecular weight of DGn, 114 is the molecular weight of CF_3COOH , g is the degree of coverage, and 10 800 and 53 are the molecular weight and the degree of polymerization of PSt-*alt*-PMAh, respectively. Obviously, the average attaching number of dendrons decreased in the order of PG1-NB > PG2-NB > PG3-NB. Similar phenomena were also observed by Schlüter et al.^{46,47} and our group in the previous studies.⁴¹ This could be well understood from the architectural effect. The higher generation dendrons with more branches prevented the reaction due to the steric hindrance.

The structures of the resulting dendronized polymers were further confirmed by FTIR measurement. Comparing the FTIR spectra of PGn-NB ($n = 1, 2, 3$) to that of PSt-*alt*-PMAh (Figure 2), we found that (1) the stretching vibration of N–H (the amide groups of aminoamine dendrons) and O–H (the

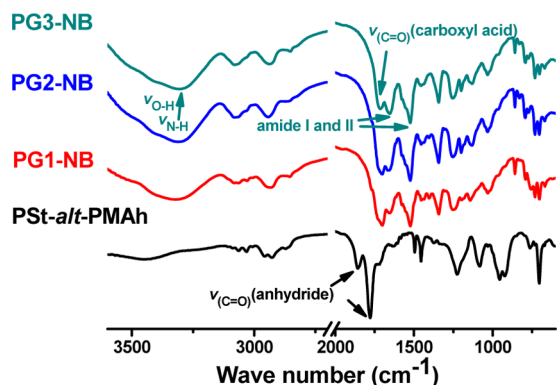


Figure 2. FTIR spectra of PS-*alt*-PMAh and PG n -NB ($n = 1, 2, 3$).

carboxylic acid) were observed as a broad peak at 3315 cm^{-1} ; (2) the peaks at 1859 and 1776 cm^{-1} attributed to the stretching vibration of C=O of maleic anhydride disappeared, while the peak at 1715 cm^{-1} corresponding to the stretching vibration of C=O of carboxylic acid arose; and (3) the peaks at 1653 and 1524 cm^{-1} related to the character of amide I ($\nu_{\text{C=O}}$) and amide II ($\delta_{\text{N-H}}$) bands were clearly visible. These results were in good agreement with the proposed structures. The detailed materials including ^1H NMR results of the dendronized polymers are described in the Supporting Information.

Differential scanning calorimetric (DSC) measurement was performed to understand the thermal properties of the obtained dendronized polymers. During the second heating run, the polymers showed glass transition temperature (T_g) of 90.6 , 79.6 , and $71.1\text{ }^\circ\text{C}$ for PG1-NB, PG2-NB, and PG3-NB, respectively (Figure S3). The glass transitions were also observed during the first cooling run with the cooling rate of $10.0\text{ }^\circ\text{C/min}$ (Figure S3). Compared to PS-*alt*-PMAh (T_g $180\text{ }^\circ\text{C}$), the T_g of the dendronized polymers decreases as the attaching dendrons with higher generations. This result is in agreement with our previous report^{41,42} that the T_g has a significant decrease as a result of increasing the generation of dendritic side chains. The generation of dendrons may dominate the change of T_g despite the less number of higher generation dendrons appended on the polymer main chains. Such results might be mainly due to the dendritic architecture. The higher generation dendrons attached along the polymer chain would occupy more room and enclose the polymer chain inside. This would weaken the stiffness of the polymers and

afford the dendronized polymers with softer nature, leading to a decrease in T_g .

Light-Cleavable Behavior of Gn ($n = 1, 2, 3$). UV-vis measurement was performed to gain insight into the light-cleavable behavior of Gn ($n = 1, 2, 3$). Figure 3a shows the absorption change of Gn ($n = 1, 2, 3$) in methanol upon UV irradiation. The absorption wavelength of the samples shifted from 259 to 280 nm with the increase of irradiation time, indicating the gradual cleavage of *o*-nitrobenzyl groups.^{29–34} However, the isosbestic point could not be observed because of the simultaneous formation of byproducts. The amino end groups of attached dendrons might react with *o*-nitrosobenzaldehyde generated from the dendronized polymers by UV irradiation, which would form imines, dimeric azobenzene, azoxybenzene compounds, and so on.^{28,48,49} A similar phenomenon was also observed by Landfester et al.,³² who synthesized a novel photolabile divinyl cross-linkers based on *o*-nitrobenzyl derivatives to build up photodegradable PMMA microgels. Figure 3b shows the absorbance change of Gn ($n = 1, 2, 3$) at 280 nm upon UV irradiation, which evidenced that G2 degraded faster than G1 and G3. Besides UV-vis spectroscopy, mass spectroscopy also provided the useful information about the cleavage products (G2 sample). The signals of 861 , 1222 , and 1382 referred to four, two and one *o*-nitrobenzyl groups cleaved from G2 dendrons appeared, and the byproducts of imine at 980 , 1515 were also observed (Figure S6).

Such a result is also supported by ^1H NMR measurement. The dendrons were dissolved in DMSO- d_6 at the concentration of 13.33 mg/mL , and then the sample was put under a UV lamp. Obviously, the signal at 5.35 ppm has a significant decrease after UV irradiation for 10 h (Figure 4a). Figure 4b shows the change of integral values of the peaks at 5.35 ppm (methylene protons of *o*-nitrobenzyl ring). It decreases as the UV irradiation time increases. The second-generation dendron G2 also shows a faster degradable rate than the others. This order is independent of the solvent. As reported by Cameron and Fréchet, the photolysis of the *o*-nitrobenzyl groups was “a complex combination of both steric and electronic effects, as well as the statistics of the hydrogen atom abstraction”.^{28,48} Under UV irradiation, the *o*-nitrobenzyl groups will undergo a hydrogen abstraction process to form a five-ring intermediate, which then affords the *o*-nitrosobenzyl aldehyde. In our case, the detailed reasons for the degradation time order of $\text{G2} > \text{G1}$, G3 are not clear now, but we think the steric effect may dominate the photolysis of the *o*-nitrobenzyl moieties for the

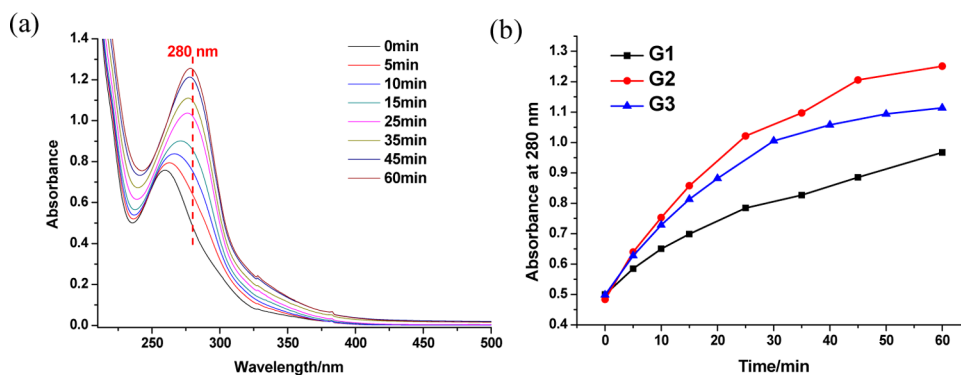


Figure 3. (a) Absorption of methanol solution of G2 with different irradiation time and (b) the absorbance of Gn ($n = 1, 2, 3$) at 280 nm upon UV irradiation with times.

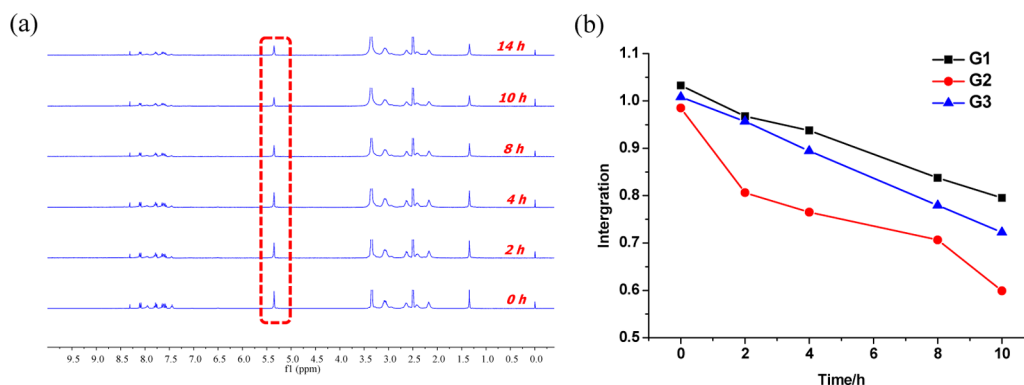


Figure 4. ^1H NMR spectrum of (a) G2 upon UV irradiation with time and (b) the change of the integral values of the peaks at 5.35 ppm toward times with UV irradiation.

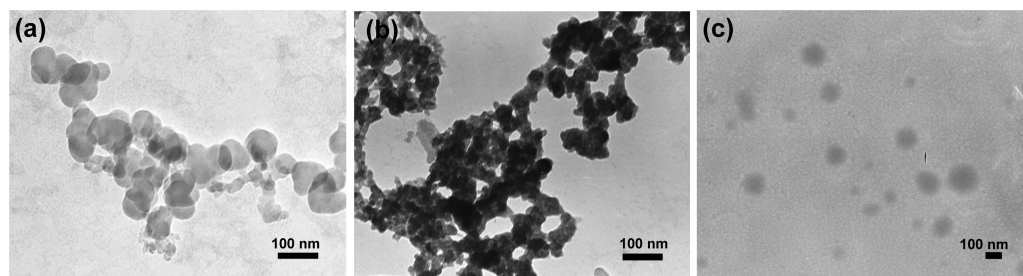
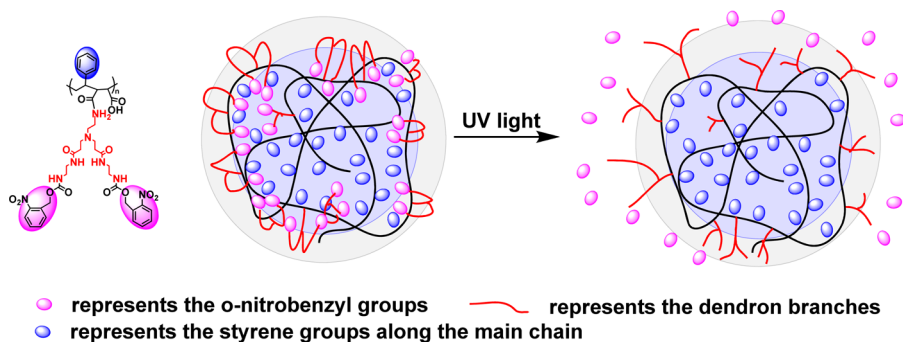


Figure 5. TEM images of the aggregates in water (a) PG1-NB, (b) PG2-NB, and (c) PG3-NB Concentration: 0.05 mg/mL.

Scheme 2. Schematic Mechanism of the Aggregation and Cleavage of PG n -NB ($n = 1, 2, 3$) in the Solution under UV Irradiation



multiple groups on the periphery of the dendritic side chains. Such structures have steric effect apparently and may be in favor of the hydrogen atom abstraction. The degradation of the dendronized polymers was characterized by the GPC experiments. Figure S7 shows the GPC traces of the PG1-NB dendronized polymers before (black) and after (red) UV irradiation for 10 h in DMF. It was found that the elution time increased from 9.00 to 9.65 min after irradiation, indicating the decrease of the molecular weight of PG1-NB dendronized polymers and the degradation of the *o*-nitrobenzyl groups on the periphery.

Aggregation Behavior of PG n -NB ($n = 1, 2, 3$). The dendronized polymers PG n -NB ($n = 1, 2, 3$) are expected to display an amphiphilic property. Therefore, the self-assembly of these amphiphilic dendronized polymers was studied by using pyrene (Py) as a probe. The critical aggregation concentration (CAC) of these polymers was determined by following the change of I_1/I_3 ratio of pyrene with increasing polymer concentration because the I_1/I_3 ratio would decrease as pyrene transferred from a hydrophilic to a hydrophobic environment.⁴⁵

The original plots are shown in Figure S9. The CAC values are in the order of PG1-NB (0.05 mg/mL) > PG3-NB (0.03 mg/mL) > PG2-NB (0.01 mg/mL), suggesting that PG2-NB self-organizes to ordered aggregates more readily than PG1-NB and PG3-NB. The higher CAC value of PG3-NB may be due to the low grafting rate of G3 dendrons with relatively large size, which cannot afford the polymers with better hydrophobic and hydrophilic balance. PG1-NB has higher dendron coverage, but G1 dendron is less hydrophobic than G2, such leading to PG2-NB showing the lowest CAC value. However, compared to other types of the amphiphilic polymers, the resulting dendronized polymers showed very low CACs. Such a result is consistent with our previous report that all the CAC values of poly(aminoamine) dendrimers with a shell of aromatic chromophores are very low in the range of 10^{-5} – 10^{-7} M.⁵⁰

Figure 5a–c shows the TEM images of the aggregates from PG n -NB ($n = 1, 2, 3$). The spherical aggregates with ca. 80 nm (PG1-NB), 50 nm (PG2-NB), and 130 nm (PG3-NB) in diameter are observed. The formation of spherical aggregates can be attributed to the amphiphilic structure of PG n -NB ($n =$

1, 2, 3), i.e., hydrophilic dendritic branches; hydrophobic styrene unites in the main chain and *o*-nitrobenzene at the periphery of the dendrons. The hydrophilic branches of dendrons and the carboxyl groups in the polymer main chains tumble out to occupy more room in water. To minimize the energy in water, the hydrophobic aromatic moieties in the polymers tend to pack together with the aid of π - π interaction to form the hydrophobic domain as illustrated in Scheme 2. When the *o*-nitrobenzyl groups were changed into the dimethoxy-substituted derivatives, the first-generation dendronized polymers (PG1-2MeONB) shows a lower CAC value as 0.01 mg/mL, compared with the same generation PG1-NB, indicating that the dimethoxy groups in the phenyl ring provided the periphery of dendrons with the enhanced hydrophobic property, and expedited them bending into the PS-enriched core (Figure S12).

Photodegradation of the Aggregates of PGn-NB ($n = 1, 2, 3$). The light scattering was employed to monitor the photodegradation behavior of the dendronized polymers by taking PG2-NB as an example. Figure 6A shows the change of

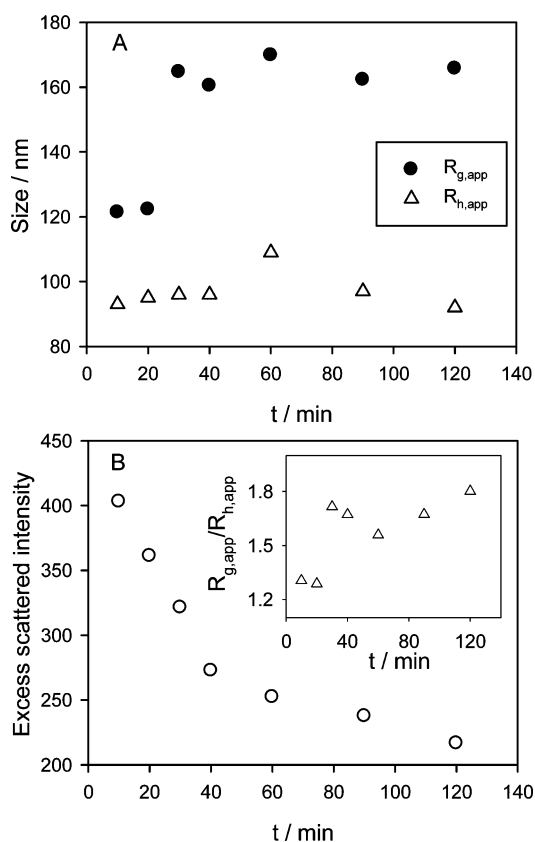


Figure 6. (A) $R_{h,app}$ (hollow triangles) and $R_{g,app}$ (black dots) of the PG2-NB in water. (B) Time evolution of the excess scattered intensity at 30° and the $R_{g,app}/R_{h,app}$ ratio (the inset) of PG2-NB in water (0.05 mg/mL).

$R_{h,app}$ (subscript app represents “apparent”) (hollow triangles) and $R_{g,app}$ (black dots) of the sample (0.05 mg/mL) with the UV irradiation time. Before UV irradiation, only one mode corresponding to the aggregates is observed at every scattered angle (data not shown); the $R_{h,app}$ is 95 nm after extrapolating to zero angle. After UV irradiation, the excess scattered intensity decreases greatly (Figure 6B) while the $R_{h,app}$ of the aggregates remains almost constant (Figure 6A) during the

studied time period. However, the $R_{g,app}$ increases significantly at the same time (Figure 6A). The R_g/R_h ratio is a practical parameter to describe the particle conformation in dilute solution.⁵¹ As shown in the inset in Figure 6B, the $R_{g,app}/R_{h,app}$ ratio increases from 1.2 to 1.6 in 30 min. Combining the decrease of scattered intensity and the increase of $R_{g,app}/R_{h,app}$ ratio, it demonstrates that the tightly combined aggregates become loose and the $M_{w,app}$ of the aggregates decreases due to the cleavage of *o*-nitrobenzyl groups by UV light. A proposed mechanism of the aggregation is shown in Scheme 2. As mentioned previously, the hydrophobic *o*-nitrobenzyl groups on the periphery of the dendrons tended to enter the inter core composed of styrene groups on the polymer main chain upon folding the flexible dendritic branches, with which formed the outer hydrophilic shell. Upon UV irradiation, the periphery of dendrons became more hydrophilic because the *o*-nitrobenzyl groups were cleaved from the exterior of them, thus the branches of the dendrons would extend into the outer hydrophilic environment rather than folding into the inner hydrophobic domains. Therefore, the aggregates became loose and the $M_{w,app}$ was reduced, as demonstrated by the decrease of the scattered intensity (Figure 6B).

The photodegradation behavior of the dendronized polymers was also confirmed by the morphology change of the aggregates from PG2-NB before and after UV irradiation monitored by AFM (Figure 7). The height of the aggregates was about 15 nm (the height curves is shown in Figure 7a, inset) without UV stimulus; however, the height of assemblies obviously increased to about 70 nm with UV irradiation (the height curves is shown in Figure 7b, inset). The size increasing of the aggregates may be due to the degradation of the light-sensitive groups under UV irradiation, such leading to break the intrinsic balance of the amphiphilic properties of the polymers and inducing the reorganization of the assemblies. The result is consistent with that reported for the degradation of an amphiphilic block copolymer containing nitrobenzyl groups in the main chain by Zhao et al.³⁴

Encapsulation and Release of the Guest Molecules.

To explore the encapsulation and release behavior of the aggregates from the dendronized polymers, Nile Red (NR), a commonly used fluorescence probe showing fluorescence with strong dependence on the effective polarity of the environment^{52–54} and good stability under UV irradiation, was entrapped into the aggregates of PG2-NB at a concentration of 0.05 mg/mL. Figure 8a shows the fluorescence emission spectra of NRs loaded in the aggregates before and after UV irradiation in 120 min. Figure 8b displays the plots of normalized fluorescence vs time for the sample without and with UV irradiation in different times of irradiation. It is found that the fluorescence intensity of NRs has no obvious change in the absence of UV light (Figure 8b, black dots), indicating the stable encapsulation of NRs in a hydrophobic environment. However, when the sample was irradiated by UV light, the fluorescent intensity dropped gradually (Figure 8b, red dots) and achieved 60% in 3 h. This is indicative of disintegration of the aggregates and the release of NRs molecules that contacted with water consequently, such quenched the fluorescence of them.

CONCLUSIONS

In conclusion, we synthesized a series of photolabile dendronized polymers PGn-NB ($n = 1, 2, 3$) through a graft-to route by combination of PST-*alt*-PMAH copolymer and *o*-

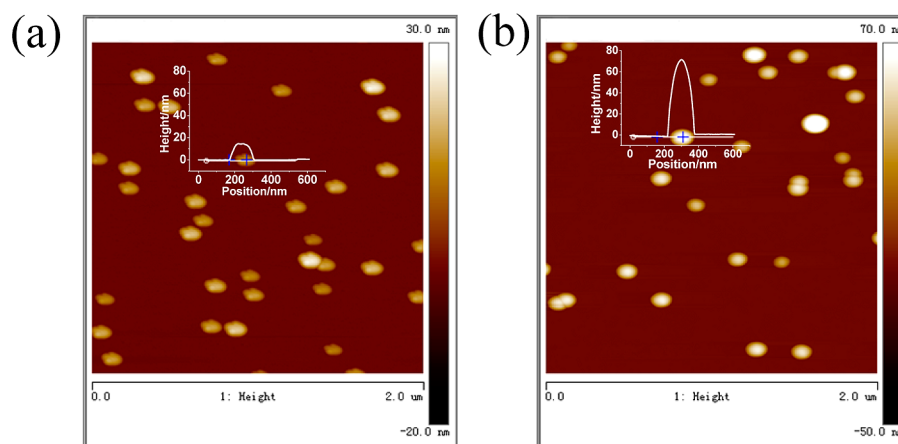


Figure 7. AFM images of the aggregates of PG2-NB in water (a) before and (b) after UV irradiation.

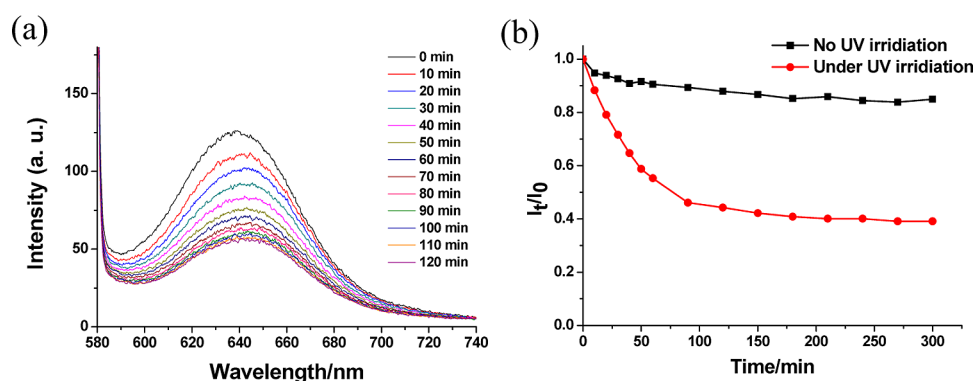


Figure 8. (a) Fluorescence changes of Nile Red encapsulated in the aggregates of PG2-NB (0.05 mg/mL) in water with UV irradiation for different times. (b) Plots of the fluorescence intensity of NRs at 630 nm vs irradiation time.

nitrobenzyl-terminated amidoamine dendrons with amino groups at the focal point. The coverage degree of aminoamine dendrons decreased as the generation increasing due to the steric hindrance of the higher generation dendrons. All the dendrons and the dendronized polymers showed photolabile properties. Specially, G2 showed a faster degradation rate than G1 and G3. The CAC values of the dendronized polymers decreased in the order of PG1-NB > PG3-NB > PG2-NB, which demonstrated that the structure of PG2-NB achieved better hydrophobic and hydrophilic balance, leading to easily form aggregates. The original aggregates were destroyed and became loose under UV irradiation evidenced by laser light scattering and AFM measurements. The guest encapsulation and release properties of the resulting dendronized polymers were explored by using NR as a model compound. The fluorescence intensity of NRs dropped upon UV irradiation, indicating the degradation of the polymers and the release of the payloads. The photoresponsive dendronized polymers with the concrete arrangement of hydrophilic and hydrophobic units differ from conventional ones. Such a system may be potential candidates for drug delivery systems.

■ ASSOCIATED CONTENT

Supporting Information

Details of the dendrons and dendronized polymer synthesis and more characterization results using ^1H NMR, DSC, UV-vis, fluorescence, and GPC. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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