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Effect of Mild Visible Light on Rapid Aqueous RAFT Polymerization of Water-Soluble Acrylic Monomers at Ambient Temperature: Initiation and Activation

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ABSTRACT: Upon irradiation with mild visible light using a *S*-1-ethyl-*S*′-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (EDMAT) and a (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TPO) photoinitiator, water-soluble acrylic monomers undergo a rapid and well-controlled RAFT polymerization directly in acidic aqueous solution at 25 °C. The effect of visible light on this aqueous RAFT polymerization was investigated by employing a periodic light-on−off process. The results demonstrated that EDMAT was stable in acidic aqueous solution but liable to hydrolysis in alkali solution; its absorption covers a wide visible light wave range of 388−520 nm. This led to a rapid and well-controlled RAFT polymerization of acrylic monomers in acidic aqueous solution at 25 °C simply upon irradiation with mild visible light. The kinetic character of RAFT polymerization at 7 °C was quite similar to that at 25 °C, which proceeded rapidly and kept living behavior, implying the negligible thermoactivating effect of this aqueous RAFT polymerization. The trithiocarbonate moieties and monomer units did not hydrolyze in such an acidic aqueous solution over the short duration of RAFT polymerization. A periodic light-on−off process leads to a corresponding repeatable periodic polymerization-on−off process. The essentially polymerization-standstill state in the light-off period indicates the negligible concentration of active radicals and the significant slow intermediate fragmentation reaction. Further turning on this visible light leads to another rapid polymerization process with the same kinetic character as that observed in the former light-on process, suggesting that the fragmentation of intermediate radicals in this aqueous RAFT polymerization was significantly activated by this visible light.

Introduction

The reversible addition−fragmentation chain transfer radical polymerization, or RAFT polymerization,[1−4] is a powerful technique for the facile synthesis of well-defined polymers, particularly water-soluble polymers,[5−15] polymeric bioconjugates,[16−22] and surface modification of nanoparticles.[23−28] In comparison with the well-known atom transfer radical polymerization (ATRP),[29] RAFT polymerization does not need any metallic catalyst, and the thiocarbonylthio functionalities are readily removed from their corresponding polymers by hydrolysis,[30] aminolysis,[31] or reduction with $NaBH_4$[32] to generate thiol end groups. These thiol end groups facilitate the anchoring of the corresponding polymers to biomolecules[20,33] or gold nanoparticles.[34−36] For these particular bio- and nanorelevant applications, RAFT polymerization of water-soluble monomers directly under mild aqueous conditions is certainly desirable.

However, several challenges to successful control of aqueous RAFT polymerization are encountered, including the fact that the polymerization needs to be sufficiently rapid to suppress the hydrolysis of thiocarbonylthio moieties of chain transfer agent (CTA).[37,38] It seems to put us into a dilemma. On one hand, mild aqueous conditions are necessary to suppress these side reactions. On the other hand, mild aqueous conditions inevitably lead to a slow RAFT process, particularly in aqueous media,[39] because of the intrinsic retardation effect caused by either initialization period[40,41] or slow fragmentation of intermediate radicals.[42]

Quinn et al.[43] first proposed that "by adjusting the structure of the Z group in the RAFT agent, living polymerization at room temperature is possible". Recently, McCormick and Sumerlin groups separately reported the synthesis of water-soluble polymers or polymer−protein bioconjugates via aqueous RAFT polymerization of acrylamide monomers at room temperature.[18,44,45] Bai et al.[46] reported an aqueous RAFT polymerization of acrylamide monomers at room temperature using a redox initiator. However, except for acrylamide monomers, rapid aqueous RAFT polymerization of other commonly used monomers at ambient temperature could only be possible with the aid of an additional activation source to suppress the intrinsic retardation effect.[47] For instance, γ-ray[48] and UV radiation[49] were employed to initiate aqueous RAFT polymerization at room temperature. However, γ-ray sources are not commonly available, and UV radiation, particularly in the CTA-sensitive short-wave range, inevitably leads to the photolysis of CTA functionalities.[50,51] Therefore, RAFT polymerization suffers from an actual loss of control because of this permanently premature termination.

Enlightened by the pioneer studies of UV-initiating RAFT polymerization separately reported by Quinn et al.[50] and Pan and coworkers,[52] our group recently developed a rapid and well-controlled ambient-temperature RAFT polymerization in

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organic solution under mild long-wave UV radiation.[53] Our studies demonstrated that the living character of this RAFT polymerization strongly depended on the light wave range.[51] Mild long-wave UV or visible light was sufficient to accelerate RAFT polymerization of acrylic, methacrylic, and even styrenic monomers in organic solution.[54] This versatile technique was recently employed for the synthesis of well-defined pyrrolidone-based thermoresponsive polymers[55] and photoresponsive polymers whose chromophores were bound with pH-labile cyclic acetal linkages.[56] Our results also demonstrated that mild sun light in the visible light wave range is excellent at accelerating ambient temperature RAFT polymerization in organic solution.[57]

In a most recent communication,[58] we reported a rapid and well-controlled RAFT polymerization of poly(ethylene glycol) methyl ether acrylate (PEGA) in 50 wt % water at 25 °C simply under mild visible light radiation. Clearly, this polymerization was initiated by the photolysis of (2,4,6-trimethylbenzoyl) diphenylphosphine oxide (TPO). However, it is still incredible that despite the significant retardation effect in aqueous media,[39] such a rapid RAFT process could be motivated simply by photoinitiation. It seems that this rapid process is attributable to the highly reactive PEGA monomer because it was well-documented that this monomer polymerized rapidly via either ATRP[59,60] or RAFT polymerization.[21] Are other water-soluble acrylic monomers also able to polymerize so rapidly and to keep living character under such mild aqueous conditions? In addition to the photoinitiation effect, what else did the visible light influence on this rapid aqueous RAFT polymerization?

For in-depth understanding of this particular rapid aqueous RAFT polymerization, we investigated the polymerizing conditions; the water-soluble *N*-(2-acryloyloxyethyl) pyrrolidone (NAP) and 2-hydroxyethyl acrylate (HEA) monomers were polymerized under such mild aqueous conditions. Aqueous RAFT polymerization of NAP monomer at 7 °C was also conducted to investigate the thermoactivating effect of this rapid aqueous RAFT polymerization. More importantly, we investigated the effect of visible light on this particular aqueous RAFT polymerization by employing a periodic light-on−off process in this article.

Experimental Section

Materials. *S*-1-Ethyl-*S*′-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (EDMAT) was synthesized according to a literature procedure.[45] (2,4,6-Trimethylbenzoyl)diphenylphosphine oxide (TPO, 97%), purchased from Runtec Chem. Co., was used as received. Poly(ethylene glycol) methyl ether acrylate (PEGA, Aldrich, M_n = 454 g mol^{-1}, M_w/M_n = 1.03) was passed through a basic alumina column to remove inhibitor and stored at −20 °C. HEA (96%, Aldrich) was carefully purified according to a literature procedure.[61] *N*-Hydroxyethyl pyrrolidone (95%) was purchased from Jianhua Co. Ltd. and distilled under reduced pressure. Acryloyl chloride (98%, Acros) was used as received. Triethylamine was distilled over calcium hydride prior to use. Chloroform was washed with distilled water, dried over anhydrous calcium chloride overnight, and distilled prior to use. Methanol (99.99%, Tianjin Ruichengweiye Co. Ltd.) and anhydrous ethyl ether (99.9%, Tianjin Kermel Chem. Reagent Co. Ltd.) were used as received. Water utilized is the highly pure deionized water with resistivity over 18 MΩ cm^{-1}. JB400 filters were purchased from Yaguang Sci. Edu. Equip. Co.

Visible Light Radiation Source. A visible light radiation source was achieved by filtering the shorter-wave UV radiation below 400 nm from a mercury vapor lamp light emitting separately at 254, 302, 313, 365, 405, 436, 545, and 577 nm using JB400 filters. Therefore, a visible light source emitting separately at 405, 436, 545, and 577 nm at intensity of 150 μW cm^{-2} at 420 nm was obtained for RAFT polymerization.

Synthesis of *N*-(2-Acryloyloxyethyl) Pyrrolidone Monomer. NAP (64.50 g, 0.50 mol), triethylamine (60.60 g, 0.60 mol), and 180 mL of chloroform were charged in a 500 mL dried round-bottomed flask. This flask was immersed in a thermostatic ice bath at 0 °C. A solution of acryloyl chloride (47.51 g, 0.525 mol) in 120 mL of chloroform was added dropwise to this flask over 4 h. The mixture was stirred at 10 °C for 12 h. The white ammonium salt was removed by filtration. The solution was concentrated by rotary evaporation and subsequently extracted using 5% Na_2CO_3 solution, saturated NaCl solution, and distilled water until the solution was neutralized. The solution was dried over anhydrous $MgSO_4$ and distilled under vacuum to give a colorless transparent liquid of targeted monomer. Weight: 55 g. Yield: 60%. ^{1}H NMR (in D_2O, δ): 6.42, 6.20, and 6.01 (3H, $CH_2{=}CH$), 4.38 (2H, $COOCH_2CH_2$), 3.46−3.71 (4H, $COOCH_2CH_2$, and $NCOCH_2CH_2CH_2$ in pyrrolidone ring), 2.42 (2H, $NCOCH_2CH_2CH_2$ in pyrrolidone ring), 2.05 (2H, $NCOCH_2CH_2CH_2$ in pyrrolidone ring).

pH-Dependent Stability of EDMAT against Hydrolysis under Visible Light Radiation at 30 °C. EDMAT (134 mg, 0.60 mmol) was dissolved in NAP monomer (5.49 g, 30 mmol) in a 25 mL round-bottomed flask. Water (5.49 g) was added to this flask under stirring. This solution was separated into three parts. One portion of solution at pH 2.6 was directly utilized for stability studies. The other two parts of solution were separately adjusted to pH 7.0 or 10.2 using a 6.0 M NaOH solution. After they were bubbled with highly pure argon gas for 60 min, these aqueous solutions were irradiated with visible light at intensity of 200 μW cm^{-2} at 420 nm at 30 °C. Samples were collected using deoxygenated syringes at each predetermined interval, diluted by methanol for UV−vis spectroscopic measurements.

Aqueous RAFT Polymerization of NAP Monomer under Visible Light Radiation at 25 °C. A protocol for this aqueous RAFT polymerization is as follows: EDMAT (134.4 mg, 0.6 mmol) and TPO (20.9 mg, 0.06 mmol) were dissolved in NAP (5.49 g, 30.0 mmol) in a 25 mL round-bottomed flask. Water (5.49 g) was charged in this flask under stirring. This flask was capped with rubber septa and immersed in a thermostatic water bath at 25 °C. After it was bubbled with highly pure argon gas for 60 min, the solution was irradiated with visible light. Samples were collected using deoxygenated syringes at each predetermined interval and were quenched by exposure to air and the addition of a trace of hydroquinone. One portion was diluted by *N*,*N*-dimethylformamide (DMF) for GPC measurement. Another portion was diluted by D_2O for the assessment of monomer conversion by ^{1}H NMR studies according to the eq 1, where $I_{4.05-4.38}$ is the integral of proton resonance signal at 4.05 to 4.38 ppm ($COOCH_2CH_2$ of both NAP monomer and PNAP polymer) and $I_{6.35}$ is the integral of proton resonance signal at 6.35 ppm (one of $CH_2{=}CHCOO$ of NAP monomer).

$$\text{Conversion} = \frac{I_{4.05-4.38} - 2I_{6.35}}{I_{4.05-4.38}} \qquad (1)$$

After it was irradiated for 58 min, the residual solution was diluted in 20 mL of methanol. PNAP polymer was precipitated from a large excess of diethyl ether and was dried under vacuum at room temperature overnight. ^{1}H NMR: 76% monomer conversion. Weight: 3.2 g. Yield: 90%. GPC: M_n = 13.4 kg mol^{-1}, M_w/M_n = 1.10. ^{1}H NMR: $M_{n,NMR}$ = 6.45 kg mol^{-1}, where $M_{n,NMR}$ was assessed according to eq 2 and $I_{4.28}$ is the integral ratio of proton resonance signal at δ 4.28 ($COOCH_2CH_2$ in PNAP units), $I_{1.17}$ is that at δ 1.17 ($C(CH_3)_2COOH$ and CH_3CH_2S of EDMAT residues), and M_{NAP} and M_{EDMAT}

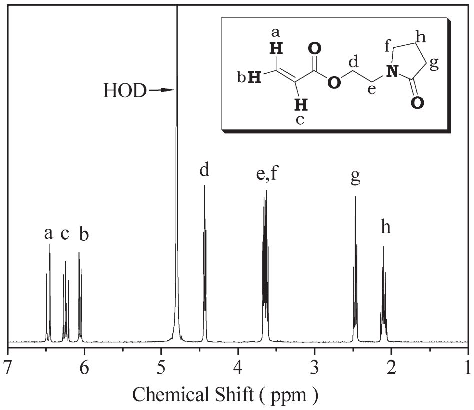

Figure 1. ^{1}H NMR spectrum of *N*-(2-acryloyloxyethyl) pyrrolidone in D_2O.

are molecular weights of NAP monomer and EDMAT compound, respectively.

$$M_{\mathrm{n,NMR}} = \frac{9I_{4.28}}{2I_{1.17}} \cdot M_{\mathrm{NAP}} + M_{\mathrm{EDMAT}} \qquad (2)$$

The thermoactivating effect of this aqueous RAFT polymerization of NAP monomer was investigated according to the same procedure as that described above except for polymerizing at 7 °C. The procedure for aqueous RAFT polymerization of HEA monomer at 25 °C was similar to that described above except for using HEA monomer.

Effect of Visible Light on Aqueous RAFT Polymerization of NAP Monomer. We studied the effect of visible light on the aqueous RAFT Polymerization of NAP monomer by employing a periodic light-on−off process at 7 °C. EDMAT (44.8 mg, 0.2 mmol) and TPO (6.96 mg, 0.02 mmol) were dissolved in NAP (3.66 g, 20.0 mmol) in a 25 mL round-bottomed flask. Water (3.66 g) was charged in this flask under stirring. This flask was capped with rubber septa and immersed in a thermostatic water bath at 7 °C. After being bubbled with highly pure argon gas for 60 min, this solution was irradiated with visible light. This visible light was turned off over the duration of 15−25, 36−46, and 55−65 min. Samples were collected using deoxygenated syringes at each predetermined interval and quenched by exposure to air and the addition of a trace of hydroquinone. One portion of sample was diluted by D_2O for ^{1}H NMR analysis. Another portion was diluted by DMF for GPC measurement.

Aqueous RAFT Copolymerization of PEGA Monomer Using a PNAP Macromolecular Chain Transfer Agent (Macro-CTA) under Visible Light Radiation at 25 °C. The aqueous RAFT copolymerization of PEGA monomer was conducted as follows: PNAP macro-CTA ($M_{\mathrm{n,NMR}}$ = 6.45 kg mol^{-1}, M_w/M_n = 1.10, 0.645 g, 0.1 mmol) and TPO (1.74 mg, 0.005 mmol) were dissolved in PEGA monomer (2.27 g, 5.0 mmol) in a 25 mL round-bottomed flask. Water (6.80 g) was charged in this flask under stirring. This flask was capped with rubber septa and immersed in a thermostatic water bath at 25 °C. After being bubbled with highly pure argon gas for 60 min, this solution was irradiated with visible light. Samples were collected using deoxygenated syringes at each predetermined interval and quenched by exposure to air and the addition of a trace of hydroquinone.

The procedure for aqueous RAFT copolymerization of HEA using a PNAP macro-CTA was similar to that described above, except for using HEA monomer.

Analytical Techniques. *Gel Permeation Chromatography (GPC)*. The molecular weights and polydispersity indices of polymers were determined by a PL-GPC120 setup equipped with a PL HTRI RI detector, and a column set consisting of two PL gel 5 μm mixed-D columns (7.5 × 300 mm, effective molecular weight range of 0.2−400.0 kg mol^{-1}) using DMF that contained 1.0 g L^{-1} LiBr as an eluent at 80 °C at a flow rate of 1.0 mL min^{-1}. Narrowly distributed polystyrene standards over the molecular weight range of 0.5−7500.0 kg mol^{-1} (PSS, Mainz, Germany) were utilized for calibration.

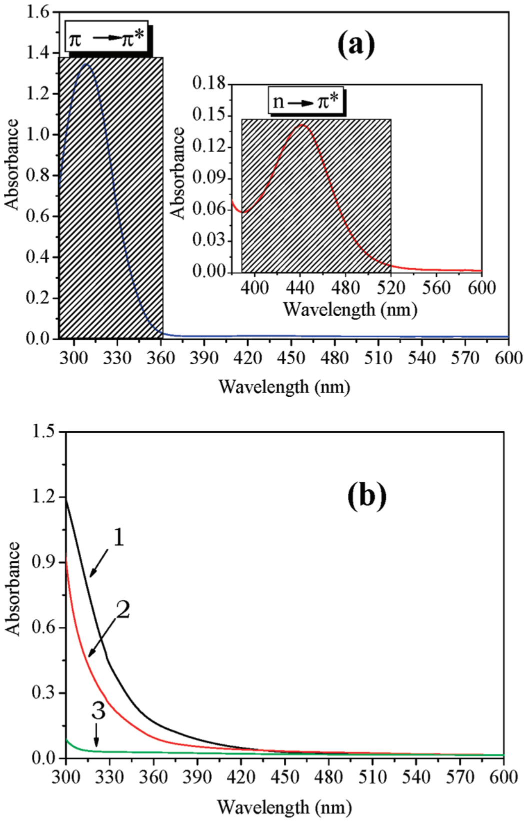

Figure 2. (a) UV−vis spectrum of a solution of 0.1 mmol L^{-1} *S*-1-ethyl-*S*′-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (EDMAT) in methanol (Insert: UV−vis spectrum of a solution of 5.0 mmol L^{-1} EDMAT in methanol) and (b) UV−vis spectra of (1) 0.25 mol L^{-1} *N*-hydroxyethyl pyrrolidone in water, (2) 0.25 mol L^{-1} *N*-(2-acryloyloxyethyl) pyrrolidone in water, and (3) 0.25 mol L^{-1} 2-hydroxyethyl acrylate in water.

Other Measurements. The light intensity was measured by a UV-A radiometer equipped with a 420 nm sensor. ^{1}H NMR spectra were recorded in D_2O with a Bruker AV-400 NMR spectrometer. UV−vis spectra were recorded in methanol or water with a Perkin-Elmer lamda-25 UV−vis spectrometer at 25 °C. The aqueous solution pH was measured on a PHS-3C digital pH-meter.

Results and Discussion

We synthesized NAP, a water-soluble acrylic monomer by esterifying *N*-hydroxyethyl pyrrolidone with acryloyl chloride. As shown in Figure 1, the integral ratio of proton resonance signals of $I_{6.42}/I_{6.20}/I_{6.01}/I_{4.38}/I_{3.46-3.71}/I_{2.42}/I_{2.05}$ was equal to 1:1:1:2:4:2:2, suggesting that the targeted monomer was achieved. Moreover, except for the proton resonance signal of HOD, no other impurities could be detected.

UV−Visible Spectroscopic Studies. The UV−vis absorption of an organic compound solution strongly depends on the solvent. The ideal solvent in this study is pure water. However, EDMAT and TPO compounds do not dissolve well in water. Therefore, a highly polar solvent, methanol,

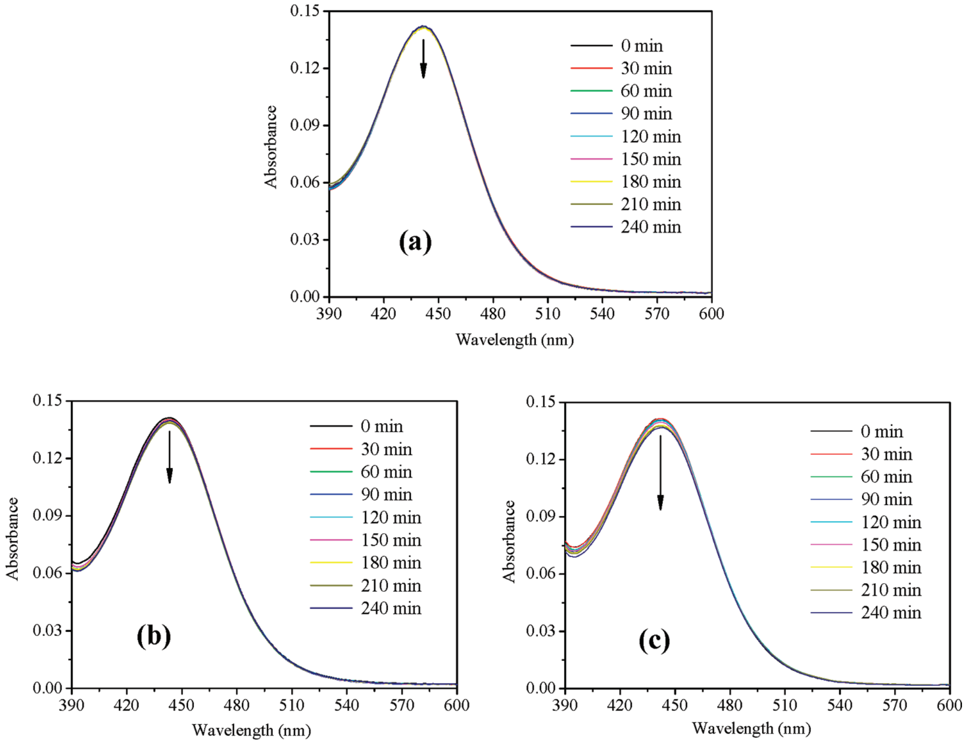

Figure 3. UV−vis spectra of *S*-1-ethyl-*S*′-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (EDMAT) at $\lambda_{max,EDMAT}$ = 442 nm in *N*-(2-acryloyloxyethyl) pyrrolidone (NAP) aqueous solutions at (a) pH 2.6, (b) pH 7.0, and (c) pH 10.2 at each predetermined interval. Conditions: [EDMAT] = 54.7 mmol L^{-1} and [NAP]/[EDMAT] = 50:1 in 50 wt % water under visible light radiation with a mild intensity of 200 μW cm^{-2} at 420 nm at 30 °C. The solutions were diluted by methanol to [EDMAT] = 5.0 mmol L^{-1} prior to measurements.

was selected as an alternative for all of the UV−vis spectroscopic studies discussed below.

As shown in Figure 2a, a dilute solution of EDMAT (0.1 mmol L^{-1}) exhibits a strong absorption at λ_{max} = 308 nm, which covers a UV wave range of 280−362 nm (shaded region). This absorption is attributed to the $\pi \rightarrow \pi^*$ transition of C═S bonds of trithiocarbonate functionalities. This is the highly EDMAT-sensitive wave range that most likely causes the photolysis of trithiocarbonate functionalities. Therefore, UV light emitting in this short-wave range needs to be carefully filtered.

As shown in the insert of Figure 2a, a relatively weak absorption peak at λ_{max} = 441 nm is detectable in a concentrated EDMAT solution (5.0 mmol L^{-1}). This absorption covers a wide visible light wave range of 388−520 nm (shaded region). This absorption is attributable to the $n \rightarrow \pi^*$ transition of C═S bonds of trithiocarbonate functionalities. This particular absorption character makes it possible for visible light to activate these trithiocarbonate functionalities. Moreover, employing a mild visible light source in this wave range possibly avoids the undesired photolysis of trithiocarbonate functionalities. Therefore, a visible light emitting separately at 405, 436, 545, and 577 nm was utilized for this purpose.

A commercially available TPO photoinitiator was selected for this polymerization to initiate this RAFT polymerization rapidly because of its high α-cleavable rate constant[62] ($>10^9$ s^{-1}) and the addition rate constant of phosphonyl radical[63] (1.79×10^7 M^{-1} s^{-1}). Its absorption stretches to a visible light wave range up to 420 nm.[51] The visible light mentioned above covers this wave range and is sufficient to cleave this photoinitiator homogeneously.

pH-Dependent Stability of EDMAT against Hydrolysis under Visible Light Radiation at 30 °C. The hydrolysis of trithiocarbonate functionalities is an important side reaction that needs to be carefully suppressed in aqueous RAFT polymerization. Therefore, the stability of the EDMAT compound against the hydrolysis of trithiocarbonate functionalities in aqueous solution was investigated under visible light radiation at intensity of 200 μW cm^{-2} at 420 nm at 30 °C. NAP monomer was added to improve the solubility of EDMAT in aqueous solution, and it also make this solution similar to the polymerizing state. As shown in Figure 2b, both 0.25 mol L^{-1} *N*-hydroxyethyl pyrrolidone and 0.25 mol L^{-1} NAP aqueous solutions exhibit absorption below 420 nm, whereas the absorption of 0.25 mol L^{-1} HEA aqueous solution is negligible above 330 nm. This indicates that the absorption in the wave range of 330−420 nm is attributed to the absorption of pyrrolidone moieties rather than acrylic functionalities of monomers. This absorption did not affect the absorption variation tendency of trithiocarbonate functionalities of EDMAT because the pyrrolidone moieties are stable under such mild aqueous conditions on the basis of our experimental results.

As shown in Figure 3, in an acidic solution at pH 2.6 (Figure 3a), essentially the same absorption spectra at $\lambda_{max,EDMAT}$ = 442 nm were detected over the whole duration of radiation. However, in a neutral solution at pH 7.0 (Figure 3b), the absorbance at $\lambda_{max,EDMAT}$ declined slightly, suggesting slight hydrolysis of trithiocarbonate functionalities of EDMAT. This hydrolysis tendency was more pronounced in an alkali solution at pH 10.2 (Figure 3c), indicating that trithiocarbonate was unstable in an alkali solution.

This absorbance variation as a function of radiation time was summarized in Figure 4. Essentially the same absorbance of the acidic aqueous solution over the whole duration of radiation demonstrated the excellent stability of trithiocarbonate functionalities. EDMAT compound (1.7%) was hydrolyzed in the neutral solution. Up to 3.3% EDMAT was

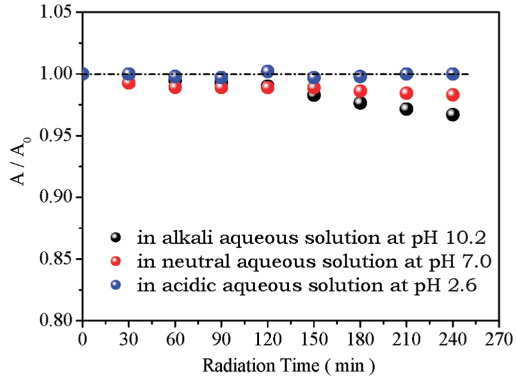

Figure 4. Absorbance variation of *S*-1-ethyl-*S'*-(α,α'-dimethyl-α''-acetic acid) trithiocarbonate (EDMAT) at $\lambda_{\max,\mathrm{EDMAT}}$ = 442 nm in *N*-(2-acryloyloxyethyl) pyrrolidone (NAP) aqueous solution at each predetermined interval. Conditions: [EDMAT] = 54.7 mmol L^{-1} and [NAP]/[EDMAT] = 50:1 in 50 wt % water under visible light radiation at mild intensity of 200 μW cm^{-2} at 420 nm at 30 °C. The solutions were diluted by methanol to [EDMAT] = 5.0 mmol L^{-1} prior to measurements. A_0 is the solution absorbance before radiation; A is the solution absorbance at a predetermined interval.

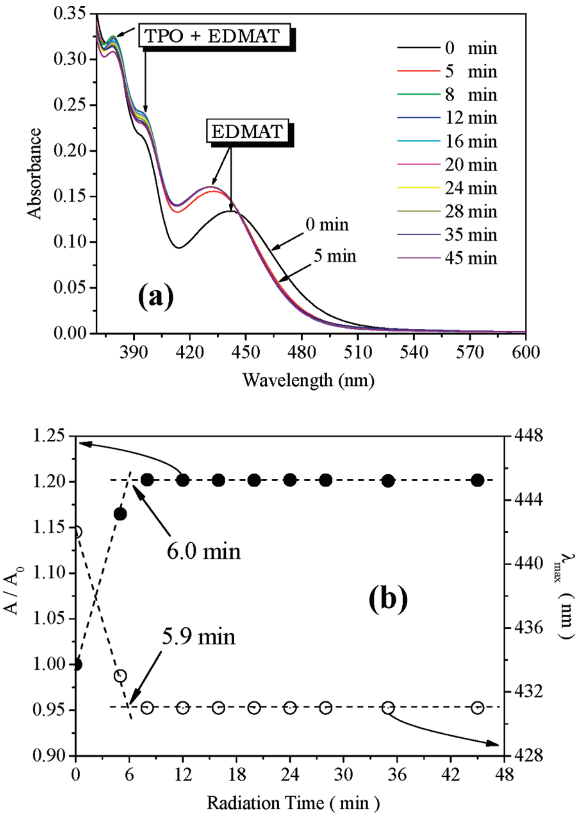

Figure 5. (a) UV–vis spectra of *N*-(2-acryloyloxyethyl) pyrrolidone (NAP) polymerizing solution at a feed molar ratio of $[\mathrm{NAP}]_0/[\mathrm{EDMAT}]_0/[\mathrm{TPO}]_0$ = 100:1:0.1 in 50 wt % water at pH 3.1 under visible light radiation at intensity of 150 μW cm^{-2} at 420 nm at 25 °C at each predetermined interval. The solutions were diluted by methanol to [EDMAT] = 5.0 mmol L^{-1} prior to measurements. (b) Absorbance variation and $\lambda_{\max,\mathrm{EDMAT}}$ shift of this polymerizing solution as a function of radiation time.

hydrolyzed in the alkali solution. This pH-dependent stability against hydrolysis is similar to that of dithioesters,[37,64] but is less significant under such mild conditions. Therefore, all RAFT polymerizations discussed below were conducted in acidic aqueous solutions to avoid this hydrolysis side reaction.

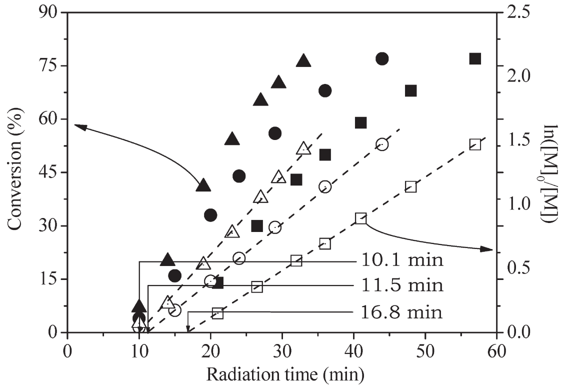

Figure 6. Kinetic curves of RAFT polymerization of *N*-(2-acryloyloxyethyl) pyrrolidone (NAP) using a *S*-1-ethyl-*S'*-(α,α'-dimethyl-α''-acetic acid) trithiocarbonate (EDMAT) chain transfer agent and a (2,4,6- trimethylbenzoyl)diphenylphosphine oxide (TPO) photoinitiator at feed molar ratios of $[\mathrm{NAP}]_0/[\mathrm{EDMAT}]_0/[\mathrm{TPO}]_0$ = 50:1:0.1 in 50 wt % water at pH 2.6 (■), $[\mathrm{NAP}]_0/[\mathrm{EDMAT}]_0/[\mathrm{TPO}]_0$ = 100:1:0.1 in 50 wt % water at pH 3.1 (●), and $[\mathrm{NAP}]_0/[\mathrm{EDMAT}]_0/[\mathrm{TPO}]_0$ = 150:1:0.1 in 50 wt % water at pH 3.4 (▲) under visible light radiation at intensity of 150 μW cm^{-2} at 420 nm at 25 °C.

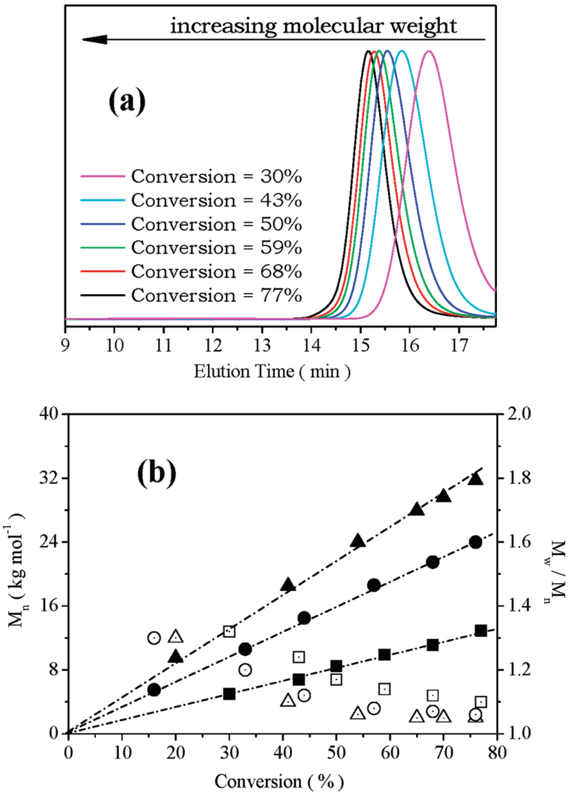

Figure 7. (a) GPC traces of poly[*N*-(2-acryloyloxyethyl) pyrrolidone] (PNAP) synthesized via RAFT polymerization of NAP monomer using an *S*-1-ethyl-*S'*-(α,α'-dimethyl-α''-acetic acid) trithiocarbonate (EDMAT) chain transfer agent and a (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TPO) photoinitiator at a feed molar ratio of $[\mathrm{NAP}]_0/[\mathrm{EDMAT}]_0/[\mathrm{TPO}]_0$ = 50:1:0.1 in 50 wt % water at pH 2.6 under visible light radiation at intensity of 150 μW cm^{-2} at 420 nm at 25 °C. (b) Number-average molecular weights (M_n, solid) and polydispersity indices (M_w/M_n, hollow) of PNAP polymers as a function of monomer conversions; Conditions: $[\mathrm{NAP}]_0/[\mathrm{EDMAT}]_0/[\mathrm{TPO}]_0$ = 50:1:0.1 in 50 wt % water at pH 2.6 (■), $[\mathrm{NAP}]_0/[\mathrm{EDMAT}]_0/[\mathrm{TPO}]_0$ = 100:1:0.1 in 50 wt % water at pH 3.1 (●), and $[\mathrm{NAP}]_0/[\mathrm{EDMAT}]_0/[\mathrm{TPO}]_0$ = 150:1:0.1 in 50 wt % water at pH 3.4 (▲).

To further avoid this hydrolysis, the conditions for RAFT polymerization were milder than those conditions mentioned above, for example, decreased visible light intensity

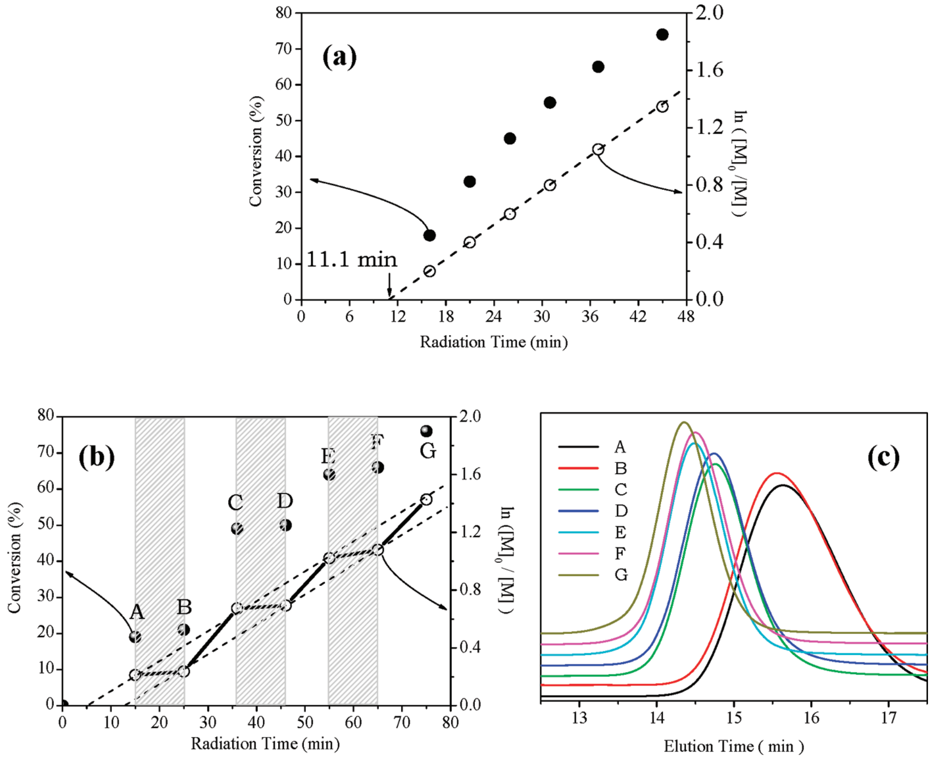

Figure 8. (a) Kinetic curve of RAFT polymerization of *N*-(2-acryloyloxyethyl) pyrrolidone (NAP) using an *S*-1-ethyl-*S*′-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (EDMAT) chain transfer agent and a (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TPO) photoinitiator at a feed molar ratio of $[NAP]_0/[EDMAT]_0/[TPO]_0$ = 100:1:0.1 in 50 wt % water at pH 3.2 under visible light radiation at intensity of 150 μW cm^{-1} at 420 nm at 7 °C. (b) Kinetic curve of RAFT polymerization of NAP monomer under the same conditions, except the light was turned off for a duration of 15−25, 36−46, and 55−65 min, as indicated by the shaded region.(c) GPC trace evolution of RAFT polymerization of NAP monomer under the same conditions as those of b.

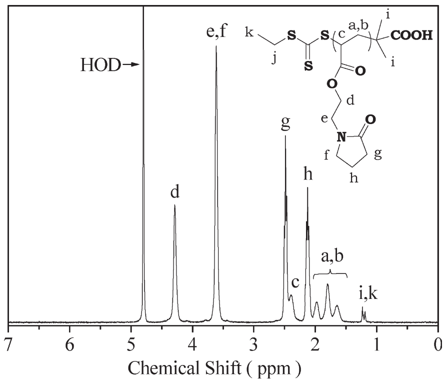

Figure 9. ^{1}H NMR spectrum of poly[*N*-(2-acryloyloxyethyl) pyrrolidone] in D_2O.

to 150 μW cm^{-2} at 420 nm and lowered solution temperature to 25 °C.

UV−vis Spectroscopic Studies on Aqueous RAFT Polymerization of NAP under Visible Light Radiation at 25 °C. As shown in Figure 5a, similar to what was observed in aqueous RAFT polymerization of PEGA monomer,[58] $\lambda_{max,EDMAT}$, which was initially at 442 nm, rapidly blue-shifted to 431 nm in the early stage. Its absorbance significantly increased under this visible light radiation. This indicated a rapid process of the monomer radical insertion to trithiocarbonate groups.[40,41] This significant absorbance increase also suggested the larger extinction coefficient of the monomer-adducted EDMAT derivatives than that of initial EDMAT compound.

Both $\lambda_{max,EDMAT}$ and its absorbance remained constant after this period. On the basis of ^{1}H NMR assessment, roughly 3% monomer has polymerized in this period. Interestingly, this absorbance increase led to the significant increase in absorbance of the peaks at both 395 and 379 nm, which are contributed by the absorption of both trithiocarbonates and TPO functionalities despite the absorption decrease due to the photolysis of TPO.

Both the $\lambda_{max,EDMAT}$ shift and its absorbance variation as a function of radiation time are summarized in Figure 5b. These evolution trends indicated a roughly 6 min initialization period of this RAFT polymerization. After this period, both curves leveled off until this polymerization was ceased in 45 min, implying the constant concentration of trithiocarbonate functionalities over the whole duration of this RAFT polymerization, which implied that this RAFT polymerization probably kept living character.

Kinetic Studies of Aqueous RAFT Polymerization of NAP under Visible Light Radiation at 25 °C. As shown in Figure 6, at feed molar ratios of $[NAP]_0/[EDMAT]_0/[TPO]_0$ ranging from 50:1:0.1 to 150:1:0.1, a linear tendency of the semilogarithmic kinetic curves was observed, suggesting the first-order kinetic character of these RAFT polymerizations. This indicated the constant and steady concentration of active radicals.

Increasing the feed molar ratio of $[NAP]_0/[EDMAT]_0/[TPO]_0$ from 50:1:0.1 to 150:1:0.1 led to a clear slope increase in the semilogarithmic kinetic curves, suggesting that the overall polymerization rate was accelerated. Increasing this feed molar ratio could also significantly shorten the initialization period, for example, from 16.8 min to 11.5 min and finally to 10.1 min, indicating that the retardation effect of RAFT process was suppressed.

As shown in Figure 7a, increasing monomer conversion leads to a clear shift of GPC trace of PNAP polymer to the

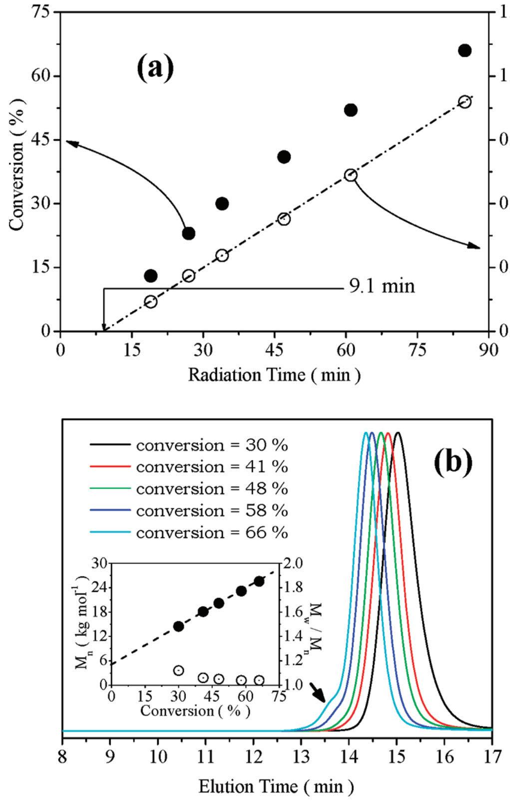

Figure 10. (a) Kinetic curves of RAFT polymerization of 2-hydroxyethyl acrylate (HEA) using an *S*-1-ethyl-*S*′-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (EDMAT) chain transfer agent and a (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TPO) photoinitiator at a feed molar ratio of $[\mathrm{HEA}]_0/[\mathrm{EDMAT}]_0/[\mathrm{TPO}]_0$ = 100:1:0.1 in 50 wt % water at pH 3.0 under visible light radiation at intensity of 150 μW cm^{-1} at 420 nm at 25 °C. (b) GPC trace evolution of this RAFT polymerizing solution at each predetermined interval (Insert: number-average molecular weights (M_n, solid) and polydispersity indices (M_w/M_n, hollow) of PHEA polymers as a function of monomer conversions).

high-molecular-weight side. Moreover, these GPC traces are significantly monomodal and reasonably symmetrical, indicating a well-controlled behavior of this RAFT polymerization. As shown in Figure 7b, the number-average molecular weights (M_n) of PNAP polymer linearly increase with monomer conversion. Moreover, their polydispersity indices (M_w/M_n) are reasonably narrow in the early stage of RAFT polymerization, which decreases to around 1.10 over 75% monomer conversions. This further confirms the well-controlled behavior of this aqueous RAFT polymerization.

The rapid overall polymerization rate and well-controlled behavior of this aqueous RAFT polymerization are comparable to what was observed in aqueous RAFT polymerization of PEGA monomer under the same aqueous conditions.[58] This suggests that this kinetic character is not simply attributable to the highly reactive nature of PEGA monomer.

Thermoactivating Effect of Aqueous RAFT Polymerization at Room Temperature under Visible Light Radiation. To investigate the thermoactivating effect of this rapid aqueous RAFT polymerization, we conducted a control experiment of aqueous RAFT polymerization of NAP monomer under this mild visible light radiation at 7 °C. As shown in Figure 8a, this aqueous RAFT polymerization exhibits essentially the same initialization period and quite similar polymerization rate as that observed in aqueous RAFT polymerization at 25 °C. (See Figure 6.) This suggests that the thermoactivating effect of aqueous RAFT polymerization at 25 °C is negligible.

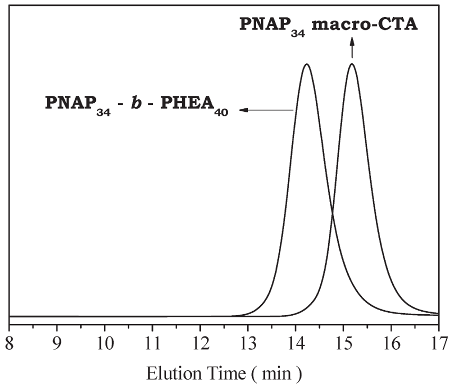

Figure 11. GPC traces of PNAP$_{34}$ macro-CTA (^{1}H NMR: M_n = 6.45 kg mol^{-1}; GPC: M_n = 13.4 kg mol^{-1}, M_w/M_n = 1.10) and its corresponding chain-extending block copolymer with poly(2-hydroxyethyl acrylate) (PHEA). Copolymerization conditions: using a TPO photoinitiator at a feed molar ratio of $[\mathrm{HEA}]_0/[\mathrm{PNAP\ macro\text{-}CTA}]_0/[\mathrm{TPO}]_0$ = 200:1:0.05 in 60 wt % water under visible light radiation at intensity of 150 μW cm^{-1} at 420 nm at 25 °C for 30 min. ^{1}H NMR: 21% monomer conversion. ^{1}H NMR: PNAP$_{34}$-*b*-PHEA$_{40}$. GPC: M_n = 25.5 kg mol^{-1}. M_w/M_n = 1.05.

Effect of Visible Light on Aqueous RAFT Polymerization. The effect of visible light on aqueous RAFT polymerization of NAP monomer was further studied, employing a periodic light-on−off process at 7 °C. First, the visible light was turned on until 19% NAP monomer was polymerized. At such conversion, the initialization period was completed, and sufficient primary radicals were generated. Thereafter, this light was periodically turned off over the duration of 15−25, 36−46, and 55−65 min.

As shown in Figure 8b, this polymerization was essentially standstill in the light-off period, indicating the negligible concentration of active radicals and the significant slow intermediate fragmentation reaction. Further turning on this visible light leads to another rapid polymerization process with the same kinetic character as that observed in the former light-on process. This repeatable periodic polymerization-on−off process demonstrates that this visible light exerts good control over this aqueous RAFT polymerization not only through photoinitiation, but also by significantly activating the fragmentation of intermediate radicals.

As shown in Figure 8c, after each light-on period, the GPC traces of PNAP polymer clearly shifted to the high-molecular-weight side. These GPC traces are quite narrow and monomodal up to relatively high conversions. Whereas, after each light-off period, the GPC traces only slightly shifted. This behavior further confirmed that this visible light significantly activated the fragmentation of intermediate radicals and thus motivated a rapid process of this aqueous RAFT polymerization.

As shown in Figure 9, no signal at δ 6.35, 6.12, and 5.92 (CH_2=CH of NAP monomer) is detectable from the ^{1}H NMR spectrum, indicating that the monomer was completely removed. The integral ratio of proton resonance signals of $I_{4.28}/I_{3.61}/I_{2.60-2.26}/I_{2.24-1.51}$ is equal to 2:4:3:4 within the analysis errors, suggesting the intact structure of this targeted PNAP polymer. This indicates that the hydrolysis of ester linkages of monomer units did not occurr under such mild aqueous conditions. Except for the proton resonance signal of HOD, no other proton resonance signal of impurities is detectable from this ^{1}H NMR spectrum.

Aqueous RAFT Polymerization of HEA under Visible Light Radiation at 25 °C. As shown in Figure 10a, at a feed molar ratio of $[\mathrm{HEA}]_0/[\mathrm{EDMAT}]_0/[\mathrm{TPO}]_0$ = 100:1:0.1 in 50 wt % water at pH 3.0, a linear semilogarithmic kinetic curve up to

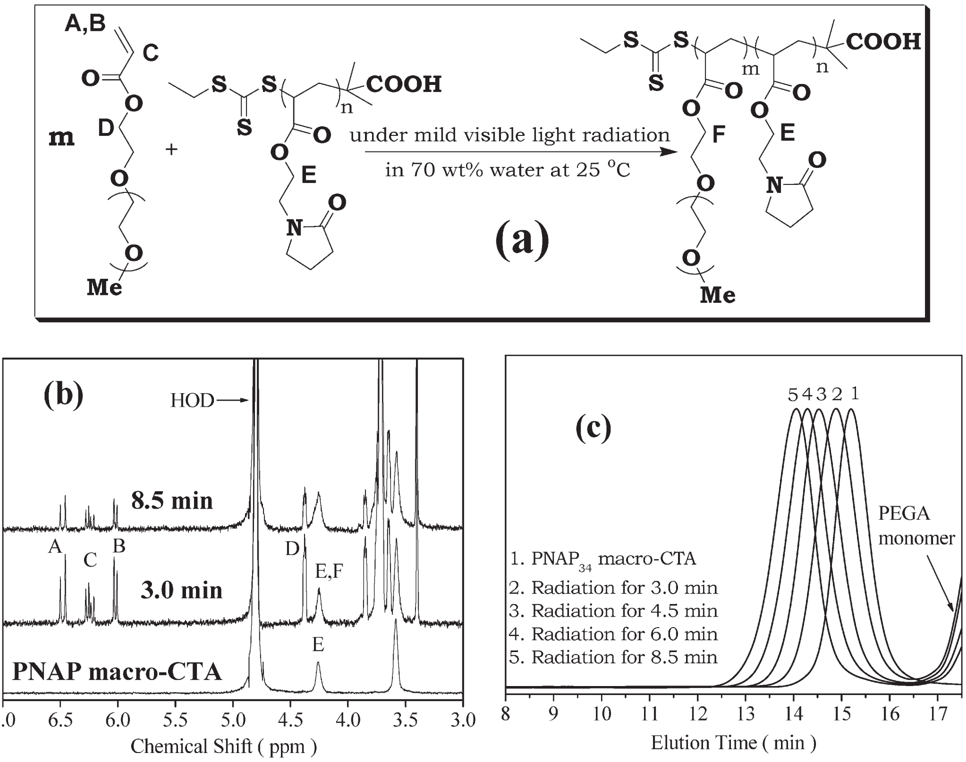

Figure 12. (a) Schematic illustration of the chain-extending RAFT copolymerization of poly(ethylene glycol) methyl ether acrylate (PEGA) monomer using an above-synthesized PNAP macro-CTA, a (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TPO) photoinitiator at a feed molar ratio of $[PEGA]_0/[PNAP\ macro\text{-}CTA]_0/[TPO]_0 = 50:1:0.05$ in 70 wt % water under visible light radiation at intensity of 150 μW cm^{-1} at 420 nm at 25 °C. (b) ^{1}H NMR spectroscopic evolution of this chain-extending RAFT copolymerization. (c) GPC trace evolution of this chain-extending RAFT copolymerization.

66% HEA monomer conversion was observed with a initialization period of 9.1 min. This is a typical first-order kinetic character of RAFT polymerization, indicating the constant and steady concentration of active radicals.

As shown in Figure 10b, increasing monomer conversion leads to a clear shift of GPC traces of PHEA polymer to the high-molecular-weight side. Moreover, these GPC traces are significantly monomodal and reasonably symmetrical. This indicates a well-controlled behavior of this RAFT polymerization. As shown in the insert of Figure 10b, M_n of PHEA polymer linearly increased with monomer conversion. The polydispersity indices (M_w/M_n) are reasonably narrow in the early stage, which decreases to 1.12 at 30% monomer conversion. A shoulder at the high-molecular-weight side was detected at 66% monomer conversion. This was presumably caused by traces of diacrylate or acrylic acid impurities.[61,65] This causes well-defined PHEA to be synthesized at only low monomer conversions.

Aqueous RAFT polymerization of HEA monomer was also conducted using a PNAP synthesized above as a macromolecular chain transfer agent (macro-CTA). As shown in Figure 11, in 60 wt % water at 25 °C upon radiation with visible light for 30 min, 21% HEA monomer has been polymerized, leading to a clear shift of GPC trace to the high-molecular-weight side. The GPC trace of this copolymer was monomodal and symmetrical, indicating the living character of this RAFT polymerization.

Aqueous RAFT Copolymerization of PEGA Using a PNAP Macro-CTA under Visible Light Radiation at 25 °C. As shown in Figure 12a, this RAFT copolymerization was conducted in 70 wt % water under mild visible light radiation at 25 °C. On the basis of ^{1}H NMR assessment (Figure 12b), under such mild aqueous conditions, 7% PEGA monomer was polymerized in 3 min. After irradiation with visible light for 8.5 min, 57% PEGA monomer was polymerized, leading to a narrow-distributed PNAP-*b*-polyPEGA copolymer (Figure 12c). The GPC traces of the block copolymers at each interval were significantly monomodal and symmetrical, indicating the living character of this aqueous RAFT polymerization.

The doubly water-soluble PNAP-*b*-polyPEGA and PNAP-*b*-PHEA copolymers are water-soluble. More importantly, the PEG-derived comb-shaped polymer is excellently biocompatible[66] and nonadhesive to proteins.[67,68] It is reasonable to expect that these block copolymers are of interest in biomedical and pharmaceutical fields.

Conclusions

The UV−vis absorption character of EDMAT and its pH-dependent stability against hydrolysis under visible light radiation at 30 °C was investigated. RAFT polymerization of acrylic monomers, including NAP and HEA, was conducted in 50−70 wt % acidic aqueous solution under mild visible light radiation at 25 °C. The thermoactivating effect of this aqueous RAFT polymerization was investigated. The effect of visible light on this aqueous RAFT polymerization was investigated by employing a periodic light-on−off process.

The results demonstrated that EDMAT exhibits an absorption covering a wide visible light wave range of 388−520 nm. It was stable in acidic aqueous solution but liable to hydrolysis in alkali solution. This leads to a rapid and well-controlled RAFT polymerization of water-soluble acrylic monomers in acidic aqueous solution at 25 °C simply upon radiation with visible light. The kinetic character of this RAFT polymerization at 7 °C is quite similar to that observed at 25 °C, which proceeded rapidly and kept living character, suggesting the negligible thermoactivating effect of this aqueous RAFT polymerization.

The trithiocarbonate moieties and monomer units did not hydrolyze in this acidic aqueous solution over the short duration of this aqueous RAFT polymerization.

A periodic light-on−off process led to a corresponding repeatable periodic polymerization-on−off process. The essentially polymerization-standstill state in the light-off period indicates the negligible concentration of active radicals and the significantly slow intermediate fragmentation reaction. Further turning on this visible light leads to another rapid polymerization process with the same kinetic character as that observed in the former light-on process, suggesting that the fragmentation of intermediate radicals in this aqueous RAFT polymerization was significantly activated upon radiation with this visible light.

This versatile approach opened an avenue toward facile and rapid synthesis of bio- and nanorelevant water-soluble polymers, for example, protein−polymer or other water-soluble polymeric bioconjugates, in situ surface modification of nanoparticles by water-soluble polymers under such environmentally friendly mild aqueous conditions.

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