Macromolecules **2006,** *39,* 3770−3776

Toward Rapid and Well-Controlled Ambient Temperature RAFT Polymerization under UV−Vis Radiation: Effect of Radiation Wave Range

Lican Lu, Haijia Zhang, Nianfa Yang, and Yuanli Cai*

College of Chemistry, Xiangtan University, Xiangtan, Hunan 411105, P. R. China

Received January 23, 2006; Revised Manuscript Received April 1, 2006

ABSTRACT: The effect of radiation wave range on living behavior of ambient temperature reversible addition fragmentation chain transfer (RAFT) radical polymerization mediated by either trithiocarbonates or dithioesters chain transfer agents (CTAs) was investigated using UV−vis radiation sources with various wave ranges. The results indicate that CTAs are strongly sensitive to the UV radiation with wave range around their characteristic absorption wavelength, leading to significant decomposition of CTA moieties in the duration of RAFT polymerization, undermining the living character of polymerization. Cutting off these CTA-sensitive short-wave radiations significantly improves the living behavior of these polymerizations. Addition of highly efficient photoinitiator and optimizing functional groups of CTA remarkably suppress retardation effect in RAFT process, thus significantly shortening the initialization period and accelerating overall RAFT process. These provide a facile way toward rapid and well-controlled ambient temperature RAFT polymerization.

Introduction

There has been rapid progress in living radical polymerization in the past decade. In addition to the extensively investigated nitroxide-mediated radical polymerization[1,2] and metal-catalyst living radical polymerization,[3−5] a so-called reversible addition fragmentation chain transfer (RAFT) radical polymerization was developed by Moad and co-workers[6] in 1998. This living radical polymerization is carried out in the presence of a thiocarbonylthio compound, which functions by establishing a dynamic equilibrium between propagating radicals and dormant chains via a mechanism of reversible addition fragmentation chain transfer.[6,7] RAFT polymerization has become a powerful technique for the synthesis of well-defined polymers or copolymers with both low polydispersities and functionalized end groups as well as polymers with complex architectures.[8−11]

From both academic and industrial standpoints, it is desirable to develop a rapid and well-controlled RAFT polymerization under mild conditions. Quinn et al.[12] first proposed that “by adjusting the structure of the Z group in the RAFT agent living polymerization at room temperature is possible”. Most recently, McCormick’s group[13,14] reported the controlled ambient temperature RAFT polymerization of acrylamides. However, for RAFT polymerization, particularly for dithioesters-mediated cases, due to the retardation effect caused by either initialization period[15,16] or slow fragmentation of intermediate radicals,[17] solely adjusting the RAFT agent structure is not sufficient to realize rapid and well-controlled ambient temperature RAFT polymerization of the majority of commonly used monomers.

Another strategy for realizing ambient temperature RAFT polymerization is the resort to radiation activation. γ-ray radiation[18,19] and plasma radiation[20] have been successfully applied to activate or initiate RAFT polymerization at ambient temperature. However, either γ-ray or plasma radiation source is not commonly available for the synthesis. In contrast, UV−vis radiation is going to be a facile and effective activation candidate for rapid and well-controlled ambient temperature RAFT polymerization. Recently, Pan’s group[21] reported the controlled radical polymerization of methyl acrylate and styrene mediated by dibenzyl trithiocarbonate under UV radiation at room temperature. However, only low conversions were achieved under radiation for a long time, e.g., 12−52% methyl acrylate monomer conversions under UV radiation for 15−50 h; no further study on the effect of UV radiation on the photolysis of chain transfer agent (CTA) and its growing-chain derivatives was reported in this paper. Quinn et al.[22] reported the RAFT polymerization of styrene and methyl methacrylate under UV radiation at 42 °C. These polymerizations were well controlled at low conversions (below 20%). However, it was significantly less controlled at relatively high conversions (over 30%). Quinn et al.[22] and our studies[23] demonstrate that the decomposition of the CTA moieties under UV radiation in the duration of RAFT polymerization unavoidably leads to permanently premature termination, thus undermining the living character at relatively high conversions or long radiation time. Seeking an effective strategy to suppress this photolysis is essential toward well-controlled ambient temperature RAFT polymerization.

We recently presented an example of rapid and well-controlled ambient temperature RAFT polymerization of methyl acrylate via the addition of highly efficient photoinitiator under UV radiation in a preliminary communication.[23] This paper focuses on the effect of radiation wave range on living behavior of the ambient temperature RAFT polymerization mediated by either trithiocarbonates or dithioesters under UV−vis radiation.

Experimental Section

Materials. *S*-1-Dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (DDMAT),[24] *S*,*S*′-bis(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (BDMAT),[24] cumyl dithiobenzoate (CDB),[25] and 2-cyanoprop-2-yl(4-fluoro) dithiobenzoate (CPFDB)[26] were synthesized as described in the literature. (2,4,6-Trimethylbenzoyl)diphenylphosphine oxide (TPO, ≥97%) was purchased from Runtec Chem. Co., used without further purification. Methyl acrylate (MA, 99%), *n*-butyl acrylate (*n*BA, 98%), and methyl methacrylate (MMA, 99%) were purchased from Shanghai Reagent Co. and washed with sodium hydroxide aqueous solution (5 wt %) for three times and then distilled water until neutralized. After drying with

---

* Corresponding author: e-mail ylcai98@xtu.edu.cn; Tel +86-732-8292229; Fax +86-732-8292477.

10.1021/ma060157x CCC: $33.50

anhydrous magnesium sulfate, the monomers were distilled under reduced pressure. *N*,*N*-Dimethylformamide (DMF, Shanghai Reagent Co., 99.5%) and benzene (Shanghai Reagent Co., 99.5%) were dried in CaH_2 (Acros, 93%) and distilled prior to use. Soda cutoff glass plates and JB400 cutoff glass plates were purchased from Yaguang Sci. Edu. Equip. Fact., China.

UV−Vis Spectroscopy of CTAs and TPO Photoinitiator. DDMAT, BDMAT, CPFDB, CDB, or TPO solution was prepared using either DMF or acetonitrile as a solvent at 25 °C. UV−vis spectra of these solutions were recorded on a Perkin-Elmer lamda-25 UV−vis spectrometer at 25 °C.

UV−Vis Radiation Sources. A high-pressure mercury vapor lamp with peak emissions at $\lambda = 254$, 302, 313, 365, and 405 nm was used as a radiation source. Soda cutoff glass plates were utilized to cut off the short-wave UV radiation below 320 nm, and JB400 cutoff glass plates were employed to cut off the short-wave UV radiation below 380 nm. Thus, three types of radiation sources for the activation of ambient temperature RAFT polymerization were obtained: one is full-wave radiation in the wave range of 254−405 nm; one is long-wave radiation with the wave range above 320 nm, predominantly at 365−405 nm; another is visible radiation with the wave range above 380 nm, predominantly at 405 nm.

Trithiocarbonate-Mediated Ambient Temperature RAFT Polymerization under UV−Vis Radiation. A protocol for trithiocarbonate-mediated ambient temperature RAFT polymerization under full-wave radiation is as follows: MA (11.66 g, 135.6 mmol), BDMAT (0.2551 g, 0.90 mmol), TPO (0.0312 g, 0.09 mmol), and 4.0 mL of DMF were charged into a 50 mL quartz round-bottom flask capped with rubber septa. The solution was deoxygenated by purging with argon for 30 min. The UV−vis spectrum was recorded after deoxygenation to account for concentration variations induced by evaporation during the deoxygenation process. The flask was placed in a thermostatic bath at 30 °C directly under high-pressure mercury vapor lamp radiation with intensity of 100 $\mu W\ cm^{-2}$ at 365 nm and 70 $\mu W\ cm^{-2}$ at 420 nm, measured by a UV-A radiometer being equipped with a 365 nm sensor and a 420 nm sensor. The samples were removed using degassed syringes at predetermined intervals, quenched by exposure to air and addition of small amount of hydroquinone inhibitor, stored in a freezer prior to analysis. One portion of sample was diluted in DMF for UV−vis spectroscopic analysis, one portion was diluted in $CDCl_3$ for ^1H NMR studies on a 400 MHz Bruker AV-400 NMR spectrometer, and another portion was diluted in tetrahydrofuran (THF) for GPC measurements. The conversion was determined by ^1H NMR studies (see Supporting Information Figure S1): conversion $= (I_{3.5-3.8} - I_{5.8-6.4})/I_{3.5-3.8}$, where $I_{3.5-3.8}$ is the integral of the proton resonance at $\delta = 3.5-3.8$ ppm (CH_3OCO of both PMA and MA monomer) and $I_{5.8-6.4}$ is the integral of the proton resonance at $\delta = 5.8-6.4$ ppm ($CH_2{=}CHCOO$ of MA monomer).

Trithiocarbonate-mediated ambient temperature RAFT polymerization under long-wave radiation is the same as described above, except for utilization of soda cutoff glass plates between flask and high-pressure mercury vapor lamp to cut off the short-wave radiation below 320 nm.

Dithioester-Mediated Ambient Temperature RAFT Polymerization under UV−Vis Radiation. A protocol for dithioester-mediated ambient temperature RAFT polymerization under full-wave radiation is as follows: MMA (14.37 g, 143.7 mmol), CPFDB (0.1147 g, 0.48 mmol), TPO (0.0669 g, 0.19 mmol), and 5.0 mL of DMF were charged into a 50 mL quartz round-bottom flask capped with rubber septa. The solution was deoxygenated by purging with argon for 30 min. The UV−vis spectrum was recorded after deoxygenation to account for concentration variations induced by evaporation during the deoxygenation process. The flask was placed in a thermostatic bath at 30 °C directly under high-pressure mercury vapor lamp radiation with intensity of 300 $\mu W\ cm^{-2}$ at 365 nm and 210 $\mu W\ cm^{-2}$ at 420 nm. Samples were removed using degassed syringes at predetermined intervals, quenched by exposure to air and addition of small amount of hydroquinone inhibitor, and stored in a freezer prior to analysis. One portion of sample was diluted in DMF for UV−vis spectroscopic analysis, one portion was diluted in $CDCl_3$ for ^1H NMR studies, and another portion was diluted in THF for GPC measurements. The conversion was determined by ^1H NMR studies (see Supporting Information Figure S2): conversion $= (I_{0.85} + I_{1.02})/(I_{0.85} + I_{1.02} + I_{5.57} + I_{6.11})$, where $I_{0.85}$ and $I_{1.02}$ are the integrals of the proton resonance at $\delta = 0.85$ and 1.02 ppm ($C(CH_3)CH_2COO$ in PMMA backbone) and $I_{5.57}$ and $I_{6.11}$ are the integrals of the proton resonance at $\delta = 5.57$ and 6.11 ppm ($CH_2{=}C(CH_3)COO$ of MMA monomer).

Dithioester-mediated ambient temperature RAFT polymerization under long-wave radiation or visible radiation is the same as described above, except for either placing soda cutoff glass plates between flask and high-pressure mercury vapor lamp to cut off the short-wave radiation below 320 nm or placing JB400 cutoff glass plates between flask and high-pressure mercury vapor lamp to cut off the short-wave radiation below 380 nm.

Ambient Temperature RAFT Block Copolymerization under UV−Vis Radiation. A protocol for ambient temperature RAFT block copolymerization under long-wave radiation is as follows: *n*BA (4.7480 g, 37.1 mmol), PMA macro-CTA (UV−vis spectrophotometry: 4% CTA moieties decomposed; GPC: $M_n = 11\,400$, $M_w/M_n = 1.10$, 2.1144 g, 0.185 mmol), TPO (0.0065 g, 0.019 mmol), and 5.5 mL of benzene were charged into a 50 mL round-bottom flask capped with rubber septa. The solution was deoxygenated by purging with argon for 30 min, followed by placing the flask in a thermostatic bath at 30 °C under long-wave radiation with intensity of 60 $\mu W\ cm^{-2}$ at 365 nm and 49 $\mu W\ cm^{-2}$ at 420 nm. After radiation for 4 h, the polymerization was ceased by exposure to air and addition of small amount of hydroquinone inhibitor. The conversion was determined by ^1H NMR studies (see Supporting Information Figure S3): conversion $= (I_{3.9-4.2} - I_{5.8-6.4})/I_{3.9-4.2}$, where $I_{3.9-4.2}$ is the integral of the proton resonance at $\delta = 3.9-4.2$ ppm ($CH_3(CH_2)_2CH_2OCO$ of both PMA-*b*-P*n*BA-*b*-PMA and *n*BA monomer) and $I_{5.8-6.4}$ is the integral of the proton resonance at $\delta = 5.8-6.4$ ppm ($CH_2{=}CHCOO$ of *n*BA monomer). The resulting copolymer was isolated by precipitation from a large excess of methanol: yield 92%. ^1H NMR: 97% *n*BA monomer conversion. GPC: $M_n = 26\,100$, $M_w/M_n = 1.20$.

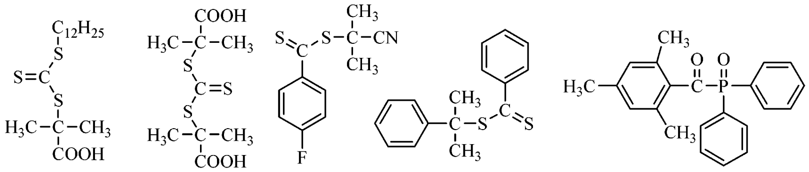
Gel Permeation Chromatography (GPC). GPC measurements were performed on a Waters 1515 GPC setup being equipped with a Waters 2414 differential refractive index detector in THF at 35 °C with a flow rate of 1.0 mL min^{-1}. A column set consisting of a Styragel HR 4 column (7.8 × 300 mm, effective molecular-weight range of 5.0−500.0 kDa), a Styragel HR 3 column (7.8 × 300 mm, effective molecular-weight range of 0.5−30.0 kDa), and a Styragel HR 1 column (7.8 × 300 mm, effective molecular-weight range of 0.1−5.0 kDa) was employed. Narrow distributed polystyrene standards in the range of 0.5−1000.0 kDa (PSS, Mainz, Germany) were used for calibration.

Results and Discussion

Under UV radiation, the chain transfer agent (CTA, thiocarbonylthio compounds) is partially decomposed to generate active radicals that can initiates radical polymerization. This polymerization is mediated via reversible addition fragmentation chain transfer mechanism.[21,22] On the other hand, CTA moieties at the end of growing chains are also sensitive to UV radiation, which may be decomposed in the duration of RAFT polymerization,[22,23] unavoidably undermining their mediation exerting over this radical polymerization.

On the basis of our previous experimental results,[23] CTAs and their growing-chain derivatives are strongly sensitive to the UV radiation with wave range around their characteristic absorption wavelength, leading to significant photolysis of CTA moieties. Thus, a radiation source with CTA-sensitive wave range cut off is expected to suppress this undesired photolysis. Accordingly, the UV−vis spectroscopic characteristics of the thiocarbonylthio compounds (DDMAT, BDMAT, CPFDB, CDB) were intensively investigated (see Chart 1).

Chart 1



DDMAT **BDMAT** **CPFDB** **CDB** **TPO**

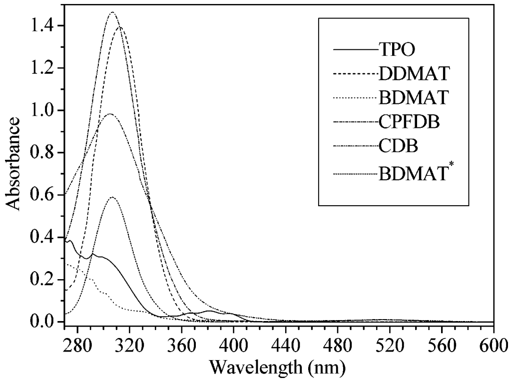


Figure 1. UV–vis spectra of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TPO), *S*-1-dodecyl-*S*′-(α,α′-dimethyl-α′′-acetic acid) trithiocarbonate (DDMAT), *S*,*S*′-bis(α,α′-dimethyl-α′′-acetic acid) trithiocarbonate (BDMAT), cumyl dithiobenzoate (CDB), and 2-cyanoprop-2-yl(4-fluoro) dithiobenzoate (CPFDB) solutions (0.1 mmol L^{-1} in either *N*,*N*-dimethylformamide or (*) acetonitrile).

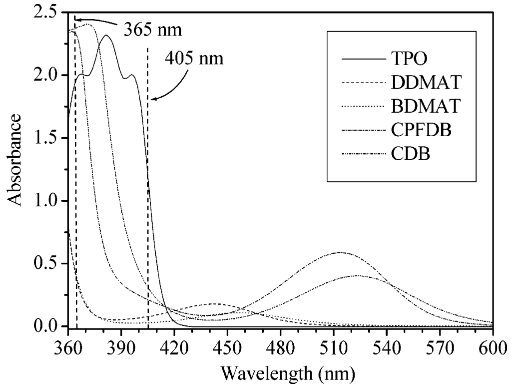


Figure 2. UV–vis spectra of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TPO), *S*-1-dodecyl-*S*′-(α,α′-dimethyl-α′′-acetic acid) trithiocarbonate (DDMAT), *S*,*S*′-bis(α,α′-dimethyl-α′′-acetic acid) trithiocarbonate (BDMAT), cumyl dithiobenzoate (CDB), and 2-cyanoprop-2-yl(4-fluoro) dithiobenzoate (CPFDB) solutions (5.0 mmol L^{-1} in *N*,*N*-dimethylformamide).

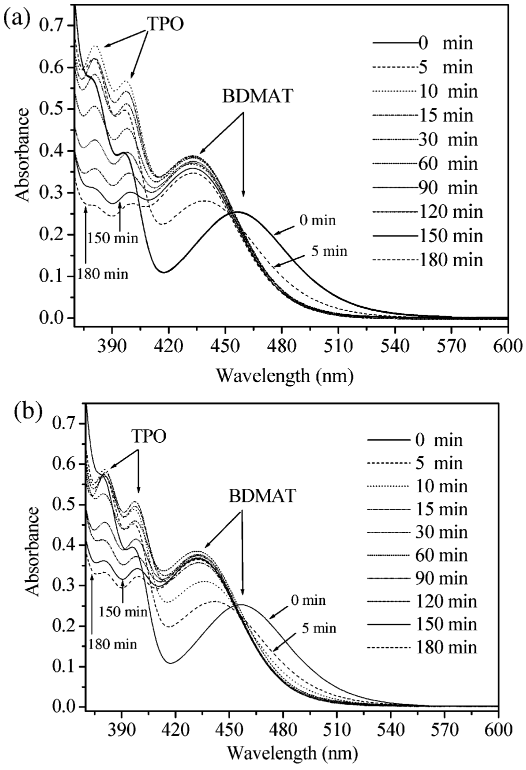


Figure 3. UV–vis spectroscopic evolution of *S*,*S*′-bis(α,α′-dimethyl-α′′-acetic acid) trithiocarbonate (BDMAT) in methyl acrylate (MA) polymerizing solutions under UV–vis radiations: (a) full-wave radiation in the wave range predominantly 254–405 nm with intensity of 100 μW cm^{-2} at 365 nm and 70 μW cm^{-2} at 420 nm; (b) long-wave radiation in the wave range above 320 nm predominantly at 365–405 nm with intensity of 100 μW cm^{-2} at 365 nm and 80 μW cm^{-2} at 420 nm. Conditions: $[\mathrm{BDMAT}]_0 = 56.3$ mmol L^{-1}, $[\mathrm{MA}]_0$:$[\mathrm{BDMAT}]_0$:$[\mathrm{TPO}]_0 = 150{:}1{:}0.1$ in *N*,*N*-dimethylformamide at 30 °C. TPO = (2,4,6-trimethylbenzoyl)diphenylphosphine oxide.

UV–Vis Spectroscopic Studies for CTAs and TPO Photoinitiator. As expected, UV–vis absorption behavior of CTA solutions is strongly dependent on the selected solvent, e.g., quite different UV–vis absorption spectrum of BDMAT solution in DMF and acetonitrile (Figure 1). DMF was selected as a solvent for all below-mentioned studies. As shown in Figure 1, all CTA dilute solutions (0.1 mmol L^{-1} in DMF) have strong absorption in the wave range 280–360 nm because of the $\pi \rightarrow \pi^*$ transition of C=S groups, which are remarkably weakened in the wave range above 360 nm.

As increasing CTA concentration to 5.0 mmol L^{-1} (Figure 2), the absorbance of dithioesters, CDB and CPFDB, is still strong in the wave range 365–405 nm, and a weak peak appears at 450–570 nm. The absorbance of trithiocarbonates, DDMAT and BDMAT, is remarkably lower than that of dithioesters in the range 365–405 nm, and a weak peak appears at 400–480 nm. This indicates that each CTA has its characteristic UV–vis absorption, which provides a possibility to suppress the undesired photolysis of CTA moieties via selection of a radiation with CTA-sensitive-wave or short-wave cutoff.

Our previous experimental results indicate that,[23] under long-wave radiation, polymerization initiated solely by the CTA-derived radicals is quite slow, e.g., only 6% MA monomer conversions under long-wave radiation with intensity of 300 μW cm^{-2} at 365 nm and 240 μW cm^{-2} at 420 nm at 30 °C for 6 h. Thus, a commercially available TPO photoinitiator was employed to initiate polymerization. Its α-cleavable rate constant[27] is above 1.0×10^9 s^{-1}, and the addition rate constant[28] of phosphonyl radical is 1.79×10^7 M^{-1} s^{-1}. Moreover, TPO (maximum absorption wavelength $\lambda_{\max} = 380$ nm in DMF; see Figure 2) is quite sensitive to long-wave radiation selected for trithiocarbonate-mediated ambient temperature RAFT polymerization as to be discussed below.

Effect of Radiation Wave Range on Trithiocarbonate-Mediated Ambient Temperature RAFT Polymerization. As shown in Figure 3a, the original BDMAT in MA polymerizing solution exhibits a characteristic absorption peak at 456 nm

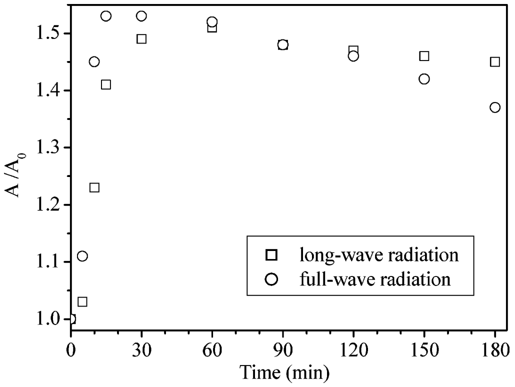


Figure 4. Absorbance evolution of *S*,*S*′-bis(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (BDMAT) moieties characteristic peak at 456−432 nm in methyl acrylate (MA) polymerizing system under UV−vis radiations: (○) full-wave radiation predominantly in the wave range of 254−405 nm with intensity of 100 μW cm^{-2} at 365 nm and 70 μW cm^{-2} at 420 nm; (□) long-wave radiation in the wave range above 320 nm predominantly at 365−405 nm with intensity of 100 μW cm^{-2} at 365 nm and 80 μW cm^{-2} at 420 nm. Conditions: $[\mathrm{BDMAT}]_0 = 56.3$ mmol L^{-1}, $[\mathrm{MA}]_0$:$[\mathrm{BDMAT}]_0$:$[\mathrm{TPO}]_0$ = 150:1:0.1 in *N*,*N*-dimethylformamide at 30 °C. A_0 = the solution absorbance before radiation, A = the solution absorbance in a predetermined radiation interval, and TPO = (2,4,6-trimethylbenzoyl)diphenylphosphine oxide.

because of the n → π* forbidden transition of C═S groups. Under full-wave radiation, this peak rapidly blue shifts to 432 nm in ca. 10 min and keeps at this wavelength thereafter. This period is the so-called initialization period;[15,16] i.e., the original BDMAT was converted to its single monomer adducted derivatives in 10 min. The absorbance of this peak significantly increases, indicating that the extinction coefficient of this single monomer adducted BDMAT derivatives is larger than that of original BDMAT. This leads to the remarkable increase of absorbance at 380−420 nm, contributed by both TPO and BDMAT, despite the absorbance decrease caused by TPO photolysis. Only 3% monomer conversion was detected by ^{1}H NMR studies in this period.

Similar UV−vis spectroscopic evolution was observed in the duration of ambient temperature RAFT polymerization under long-wave radiation (Figure 3b). However, this peak blue shifts to 432 nm in ca. 15 min, indicating that the initialization process performed relatively slowly due to less initiator-derived radicals generated under long-wave radiation (Figure 3b; see TPO characteristic absorption evolution). However, its absorbance reaches the maximum in ca. 60 min, 45 min later after its characteristic wavelength blue shift carried out (Figure 4). This phenomenon was also observed in the BDMAT-mediated RAFT polymerization under full-wave radiation, for which only ca. 5 min delay was observed (Figure 4). No reasonable explanation can be given for this phenomenon at present. Approximately 4% monomer conversion was detected under long-wave radiation for 15 min. The solution changes from initially light yellow to yellow in 15 min due to this spectroscopic blue shift and characteristic absorbance increase. No color variation was observed thereafter.

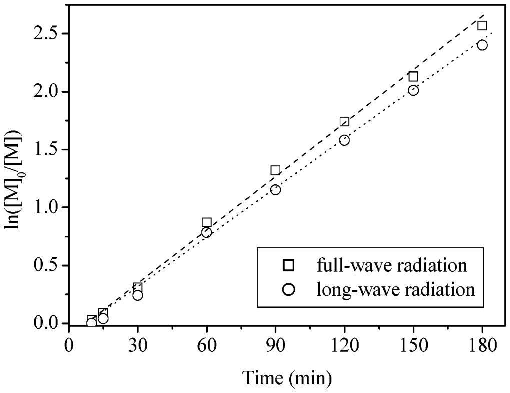


Figure 5. Kinetic curves of the ambient temperature RAFT polymerization of methyl acrylate (MA) under UV−vis radiations: (○) long-wave radiation predominantly at 365−405 nm with intensity of 100 μW cm^{-2} at 365 nm and 80 μW cm^{-2} at 420 nm; (□) full-wave radiation predominantly at 254−405 nm with intensity of 100 μW cm^{-2} at 365 nm and 70 μW cm^{-2} at 420 nm. Conditions: $[\mathrm{BDMAT}]_0 = 56.3$ mmol L^{-1}, $[\mathrm{MA}]_0$:$[\mathrm{BDMAT}]_0$:$[\mathrm{TPO}]_0$ = 150:1:0.1 in *N*,*N*-dimethylformamide at 30 °C. BDMAT = *S*,*S*′-bis(α,α′-dimethyl-α″-acetic acid) trithiocarbonate; TPO = (2,4,6-trimethylbenzoyl)diphenylphosphine oxide.

Figure 4 shows the absorbance evolution of the BDMAT moieties absorption peak at 456−432 nm in the duration of RAFT polymerization, where A_0 is the absorbance of solution before radiation and A is the absorbance of solution in a predetermined radiation interval. Under long-wave radiation, A/A_0 slightly decreases and then levels off after initialization period. Whereas under full-wave radiation, A/A_0 continuously decreases after the initialization period. Assuming that all original BDMAT has been completely consumed in the initialization period, where A/A_0 reaches a maximum, thereafter the decrease of A/A_0 is predominantly attributed to the decomposition of BDMAT moieties. According to the Lambert−Beer law, under radiation for 3 h, only 4% BDMAT moieties has been decomposed under long-wave radiation, whereas 9% BDMAT moieties has been decomposed under full-wave radiation. This indicates cutting off BDMAT-sensitive short-wave radiation can effectively suppress photolysis of BDMAT moieties, thus keep living character of this polymerization.

Typical pseudo-first-order kinetics with respect to MA monomer was observed for the BDMAT-mediated RAFT polymerization under either full-wave or long-wave radiation at 30 °C (Figure 5). This indicates the roughly constant steady-state radical concentration over the duration of polymerization. Moreover, RAFT polymerization of MA under long-wave radiation proceeded at a comparable rate to that under full-wave radiation. RAFT polymerization keeps living character under full-wave radiation, despite BDMAT moieties was partial decomposed (up to ca. 9% in 3 h).

Well-controlled behavior of BDMAT-mediated ambient temperature RAFT polymerization of MA under long-wave radiation was also confirmed by a clear shift of GPC traces (see Supporting Information Figure S4). Moreover, the number-average molecular weight of PMA shows a clearly linear evolution with MA monomer conversions, even up to a high conversion of 90% (Figure 6). The polydispersity index (M_w/M_n) of PMA obtained at 21% monomer conversion is 1.28, indicating that BDMAT exert well control over this radical polymerization at relatively low conversion, which decreases to less than 1.10 at the monomer conversions above 50%.

Figure 7 shows the GPC traces of PMA and its corresponding chain-extended PMA-*b*-P*n*BA-*b*-PMA triblock copolymer. PMA was synthesized under long-wave radiation with 4% BDMAT moieties decomposed. The corresponding chain-extended PMA-*b*-P*n*BA-*b*-PMA triblock copolymer was synthesized via RAFT polymerization of *n*BA monomer under long-wave radiation at 30 °C for 4 h, using this PMA as a macro-CTA. There is a clear shift to higher molecular weight, indicating chain extension of PMA with *n*BA monomer. Only a slight peak tail of either residual PMA precursor or P*n*BA homopolymer impurities was detected, indicating significantly high chain transfer efficiency of this PMA macro-CTA. This demonstrates that, using this PMA macro-CTA, ambient temperature RAFT polymerization

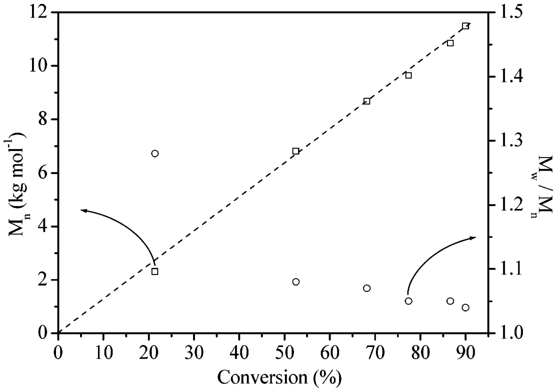


Figure 6. Number-average molecular weight (□) and polydispersity index (○) of poly(methyl acrylate) (PMA) evolution with methyl acrylate (MA) conversions for the RAFT polymerization under long-wave radiation predominantly at 365−405 nm with intensity of 100 μW cm^{-2} at 365 nm and 80 μW cm^{-2} at 420 nm; $[BDMAT]_0 = 56.3$ mmol L^{-1}, $[MA]_0$:$[BDMAT]_0$:$[TPO]_0$ = 150:1:0.1 in *N*,*N*-dimethylformamide at 30 °C. BDMAT = *S*,*S*′-bis(α,α′-dimethyl-α″-acetic acid) trithiocarbonate; TPO = (2,4,6-trimethylbenzoyl)diphenylphosphine oxide.

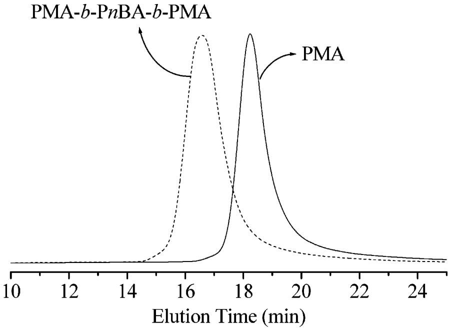


Figure 7. GPC traces of poly(methyl acrylate) (PMA, ^{1}H NMR: 92% conversion; UV−vis spectrophotometry: 5% of photolysis degree; GPC: $M_n = 11\,400$, $M_w/M_n = 1.10$) and its corresponding poly(methyl acrylate)-*block*-poly(*n*-butyl acrylate)-*block*-poly(methyl acrylate) (PMA-*b*-P*n*BA-*b*-PMA) triblock copolymer. Copolymerization conditions: under long-wave radiation predominantly at 365−405 nm with intensity of 60 μW cm^{-2} at 365 nm and 49 μW cm^{-2} at 420 nm; $[n\mathrm{BA}]_0$:$[PMA]_0$:$[TPO]_0$ = 200:1:0.1 in 50 vol % benzene at 30 °C for 4 h. ^{1}H NMR: 97% *n*BA monomer conversion; GPC: $M_n = 26\,100$, $M_w/M_n = 1.20$. TPO = (2,4,6-trimethylbenzoyl)diphenylphosphine oxide.

under long-wave radiation is sufficient to suppress undesirable decomposition side reactions even up to 97% *n*BA monomer conversion.

Similar living behavior of ambient temperature RAFT polymerization of MA was observed as using DDMAT as a CTA under either full-wave radiation or long-wave radiation. The results are partially presented in our previous paper.[23] This demonstrates that trithiocarbonates are excellent CTAs for ambient temperature RAFT polymerization of acrylates under UV−vis radiation.

Effect of Radiation Wave Range on Dithioester-Mediated Ambient Temperature RAFT Polymerization. The dithioester CDB is strongly sensitive to the UV radiation in the wave range around 365 nm, which is readily decomposed to radicals and carbon disulfide in the duration of ambient temperature RAFT polymerization.[22,23] This photolysis can be significantly suppressed by cutting off the CDB-sensitive short-wave radiation, e.g., ca. 84% CDB moieties was decomposed under full-wave radiation at 30 °C for 6 h, whereas only 25% CDB moieties was decomposed under long-wave radiation at 30 °C for 6 h.[23]

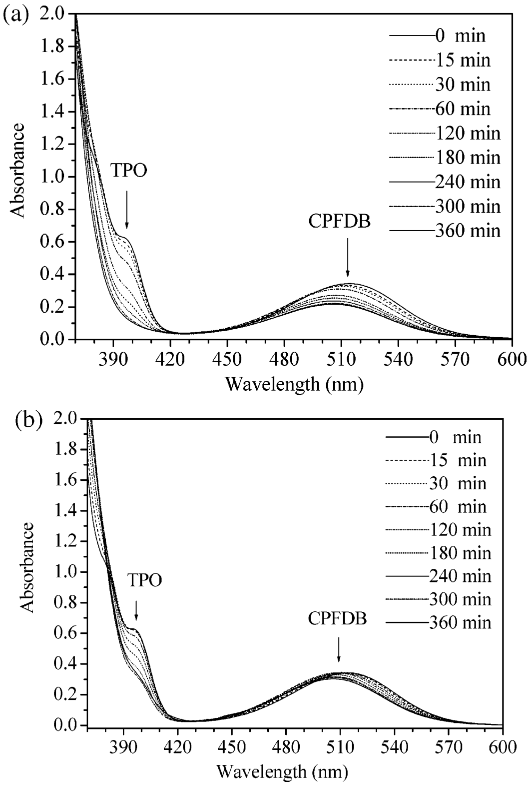


Figure 8. UV−vis spectroscopic evolutions of 2-cyanoprop-2-yl(4-fluoro) dithiobenzoate (CPFDB) in methyl methacrylate (MMA) polymerizing solutions under UV−vis radiations: (a) full-wave radiation predominantly at 254−405 nm with intensity of 300 μW cm^{-2} at 365 nm and 210 μW cm^{-2} at 420 nm; (b) visible radiation in the wave range above 380 nm predominantly at 405 nm with intensity of 0.8 μW cm^{-2} at 365 nm and 420 μW cm^{-2} at 420 nm. Conditions: $[CPFDB]_0 = 24.0$ mmol L^{-1}, $[MMA]_0$:$[CPFDB]_0$: $[TPO]_0$ = 300:1:0.4 in DMF at 30 °C. TPO = (2,4,6-trimethylbenzoyl)diphenylphosphine oxide.

CPFDB exerts well control over thermoinitiating RAFT polymerization of MMA.[26,29] Moreover, CPFDB has significantly weaker absorption in the wave range of 365−405 nm than that of CDB (Figure 2); i.e., CPFDB is much less sensitive to the long-wave or visible radiation, as compared with CDB. As shown in Figure 8a, under full-wave radiation, the absorbance of TPO characteristic peak at ca. 400 nm decreases rapidly and disappears in 5 h, indicating that this photoinitiator completely decomposed. A significant decrease of the absorbance of CPFDB characteristic peak at ca. 510 nm was also detected (Figure 8a), suggesting significant decomposition of CPFDB moieties in the duration of polymerization. In contract, both TPO and CPFDB decomposed much more slowly under visible radiation (Figure 8b).

The absorbance evolutions of the characteristic peak of CPFDB moieties at ca. 520 nm in MMA polymerizing solution, under radiations with various wave ranges, are summarized in Figure 9. A/A_0 is the ratio of this peak absorbance at a predetermined radiation interval to that before radiation. Clearly, A/A_0 tends to decrease under these radiations. At a comparable radiation intensity, CPFDB photolysis rate (R) follows $R_{254-405\ \mathrm{nm}} > R_{365-405\ \mathrm{nm}} > R_{405\ \mathrm{nm}}$. According to the Lambert−Beer law, 11% CPFDB moieties was decomposed at 46% MMA monomer conversion under visible radiation at 30 °C for 6 h and 26% CPFDB moieties was decomposed at 49% monomer conversion under long-wave radiation at 30 °C for 6 h, while 38% CPFDB moieties was decomposed at 51% monomer conversion under full-wave radiation at 30 °C for 6 h.

Overall pseudo-first-order kinetics with respect to MMA monomer was observed for CPFDB-mediated RAFT polymer-

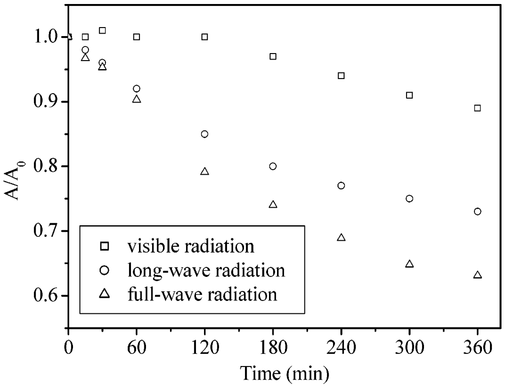


Figure 9. Absorbance evolution of 2-cyanoprop-2-yl(4-fluoro) dithiobenzoate (CPFDB) moieties characteristic absorption peak at 514−505 nm in methyl methacrylate (MMA) polymerizing solutions under UV−vis radiations: (△) full-wave radiation predominantly at 254−405 nm with intensity of 300 μW cm^{-2} at 365 nm and 210 μW cm^{-2} at 420 nm; (○) long-wave radiation in the wave range above 320 nm predominantly at 365−405 nm with intensity of 300 μW cm^{-2} at 365 nm and 240 μW cm^{-2} at 420 nm; (□) visible radiation in the wave range above 380 nm predominantly at 405 nm with intensity of 0.8 μW cm^{-2} at 365 nm and 420 μW cm^{-2} at 420 nm. Conditions: $[\text{CPFDB}]_0 = 24.0$ mmol L^{-1}, $[\text{MMA}]_0{:}[\text{CPFDB}]_0{:}[\text{TPO}]_0 = 300{:}1{:}0.4$ in *N*,*N*-dimethylformamide at 30 °C, where A_0 is the solution absorbance before radiation and A is the solution absorbance in a predetermined radiation interval. TPO = (2,4,6-trimethylbenzoyl)diphenylphosphine oxide.

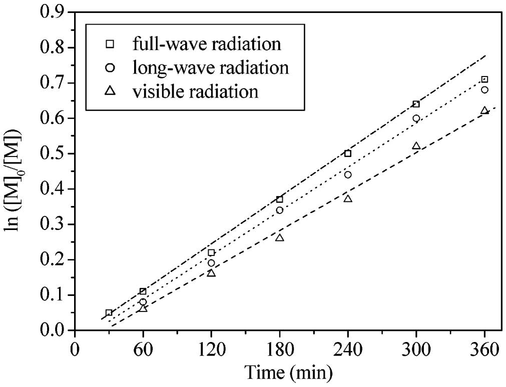


Figure 10. Kinetic curves for the ambient temperature RAFT polymerization of methyl methacrylate (MMA) under UV−vis radiations: (□) full-wave radiation in the wave range of 254−405 nm with intensity of 300 μW cm^{-2} at 365 nm and 210 μW cm^{-2} at 420 nm; (○) long-wave radiation in the wave range above 320 nm predominantly at 365−405 nm with intensity of 300 μW cm^{-2} at 365 nm and 240 μW cm^{-2} at 420 nm; (△) visible radiation in the wave range above 380 nm predominantly at 405 nm with intensity of 0.8 μW cm^{-2} at 365 nm and 420 μW cm^{-2} at 420 nm. Conditions: $[\text{CPFDB}]_0 = 24.0$ mmol L^{-1}, $[\text{MMA}]_0{:}[\text{CPFDB}]_0{:}[\text{TPO}]_0 = 300{:}1{:}0.4$ in *N*,*N*-dimethylformamide at 30 °C. CPFDB = 2-cyanoprop-2-yl(4-fluoro) dithiobenzoate; TPO = (2,4,6-trimethylbenzoyl)diphenylphosphine oxide.

ization of MMA under full-wave, long-wave, or visible radiation at 30 °C for 5 h (Figure 10). This indicates the roughly constant steady-state radical concentration in this time scale. Although 11% CPFDB moieties were decomposed under visible radiation for 6 h, $\ln([\text{M}]_0/[\text{M}])$ evolution with conversion still remains linear tendency up to 46% monomer conversion. However, clearly deviation at 49% monomer conversion was observed for RAFT polymerization under long-wave radiation for 6 h due to the loss of control caused by 26% decomposition of CPFDB moieties. Much more pronounced deviation was observed at 51% monomer conversion under full-wave radiation for 6 h because of significant decomposition of CPFDB moieties (38%). Under visible radiation, the initialization period prolongs to ca. 30 min (Figure 10), despite high radiation intensity up to 420 μW cm^{-2} being employed. This is attributed to less initial TPO-derived radicals generated under visible radiation. Another possibility is the slow fragmentation of dormant CPFDB−PMMA radical intermediates or expelled radicals and propagating radicals tend to add to CTA derivatives rather than to monomer.[25,30] Accordingly, it seems that a more effective photoinitiator under visible radiation is needed for better-controlled dithioester-mediated RAFT polymerization since it can significantly accelerate the overall polymerization, minimizing the possibility of CTA moieties decomposition.

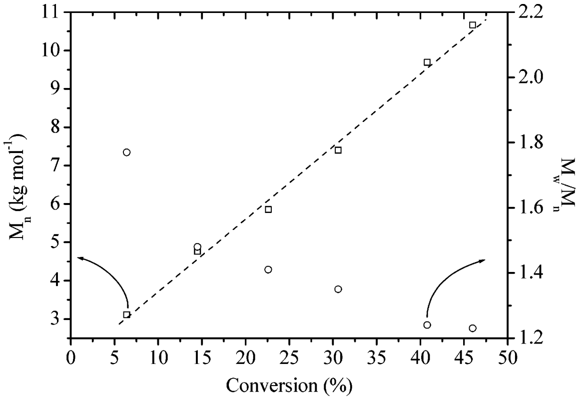


Figure 11. Number-average molecular weight (□) and polydispersity index (○) of poly(methyl methacrylate) (PMMA) evolution with conversions of methyl methacrylate (MMA) for RAFT polymerization under visible radiation in the wave range above 380 nm predominantly at 405 nm with intensity of 0.8 μW cm^{-2} at 365 nm and 420 μW cm^{-2} at 420 nm. $[\text{CPFDB}]_0 = 24.0$ mmol L^{-1}, $[\text{MMA}]_0{:}[\text{CPFDB}]_0{:}[\text{TPO}]_0 = 300{:}1{:}0.4$ in *N*,*N*-dimethylformamide at 30 °C. CPFDB = 2-cyanoprop-2-yl(4-fluoro) dithiobenzoate; TPO = (2,4,6-trimethylbenzoyl)diphenylphosphine oxide.

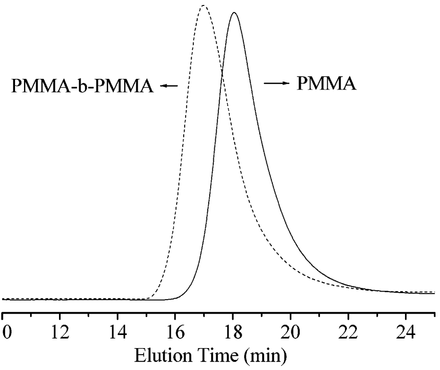


Figure 12. GPC traces of poly(methyl methacrylate) (PMMA, ^{1}H NMR: 46% conversion; UV−vis spectrophotometry: 11% CPFDB moieties decomposed; $M_n = 11\,100$, $M_w/M_n = 1.21$) and its corresponding poly(methyl methacrylate)-*block*-poly(methyl methacrylate) (PMMA-*b*-PMMA) self-block copolymer. Conditions: under visible radiation in the wave range above 380 nm predominantly at 405 nm with intensity of 0.8 μW cm^{-2} at 365 nm and 420 μW cm^{-2} at 420 nm; $[\text{MMA}]_0{:}[\text{PMMA}]_0{:}[\text{TPO}]_0 = 140{:}1{:}0.2$ in 50 vol % *N*,*N*-dimethylformamide at 30 °C for 4 h. ^{1}H NMR: 38.3% conversion; GPC: $M_n = 17\,500$, $M_w/M_n = 1.28$. TPO = (2,4,6-trimethylbenzoyl)diphenylphosphine oxide.

For CPFDB-mediated ambient temperature RAFT polymerization of MMA under visible radiation, the number-average molecular weight of PMMA shows a roughly linear evolution with MMA conversions (Figure 11). The polydispersity index (M_w/M_n) of PMMA obtained at 14% monomer conversion is 1.48, indicating that CPFDB exerts reasonable mediation over this radical polymerization at this conversion. M_w/M_n of PMMA decreases to lower than 1.30 at monomer conversions over 41%.

Figure 12 shows the GPC traces of PMMA and its corresponding self-extended PMMA-*b*-PMMA self-block copolymer.

PMMA (synthesized under visible radiation with 11% CPFDB moieties decomposed) was utilized as a macro-CTA for the polymerization of MMA monomer under visible radiation at 30 °C for 4 h, giving rise to its corresponding PMMA-*b*-PMMA self-block copolymer. There is an overall shift to higher molecular weight from PMMA to its corresponding PMMA-*b*-PMMA self-block copolymer (Figure 12), indicating chain extension of PMMA macro-CTA. The low molecular weight peak tail of its GPC trace indicates that some residual PMMA precursor exists. Optimizing the functional groups of dithioester for better-controlled ambient temperature RAFT polymerization of methacrylates toward well-defined targeted all-methacrylates copolymers is in progress but is beyond the scope of this paper.

Conclusions

Living behavior of ambient temperature RAFT polymerization mediated by either trithiocarbonates or dithioesters is significantly dependent on the UV−vis radiation wave range. Trithiocarbonates, e.g. BDMAT and DDMAT, exert well control over the ambient temperature RAFT polymerization of MA using TPO photoinitiator under UV−vis radiation. Under long-wave radiation, only slight CTA moieties were decomposed (4% decomposition up to 90% monomer conversion), giving rise to narrow distributed PMA ($M_w/M_n < 1.10$) and well-defined all-acrylates block copolymers.

In contrast, dithioesters, e.g., CDB and CPFDB, are strongly sensitive to UV radiation with wave range around their characteristic absorption wavelength, leading to significant decomposition of their moieties in the duration of RAFT polymerization, undermining the control exerting over ambient temperature RAFT polymerization of MMA. Cutting off this dithioester-sensitive short-wave radiation can significantly improve the living behavior of these RAFT polymerizations. It can be envisaged that rapid and better-controlled dithioester-mediated ambient temperature RAFT polymerization of methacrylates can be realized via optimizing the functional groups of dithioester and utilizing highly efficient photoinitiator under visible radiation. This work is in progress and is going to be presented in the next paper.

Acknowledgment. This work was financially supported by the State Education Ministry Scientific Research Foundation for the Returned Overseas Chinese Scholars, the Hunan Provincial Natural Science Foundation of China (05JJ40023), the Start-up Research Foundation of Xiangtan University (04QDZ31), and the Inter-discipline Natural Science Foundation of Xiangtan University (05IND12).

Supporting Information Available: ^{1}H NMR spectra of MA, MMA, and block copolymerizing solution and GPC traces of PMA. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Macromolecules* **1993**, *26*, 2987−2988.

(2) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.* **2001**, *101*, 3661−3688.

(3) Wang, J.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901−7910.

(4) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990.

(5) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689−3746.

(6) Chiefari, J.; Chong, Y. K. B.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559−5562.

(7) Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Kristina, J.; Moad, G.; Postma, A.; Thang, S. H. *Macromolecules* **2000**, *33*, 243−245.

(8) Chong, B. Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 2071−2074.

(9) Mayadunne, R. T. A.; Jeffery, J.; Moad, G.; Rizzardo, E. *Macromolecules* **2003**, *36*, 1505−1513.

(10) Li, Y.; Lokitz, B. S.; McCormick, C. L. *Macromolecules* **2006**, *39*, 81−89.

(11) Liu, B.; Kazlauciunas, A.; Guthrie, J. T.; Perrier, S. *Macromolecules* **2005**, *38*, 2131−2136.

(12) Quinn, J. F.; Rizzardo, E,; Davis, T. P. *Chem. Commun.* **2001**, 1044−1045.

(13) Convertine, A. J.; Ayres, N.; C. Scales, W.; Lowe, A. B.; C. McCormick, L. *Biomacromolecules* **2004**, *5*, 1177−1180.

(14) Convertine, A. J.; Lokitz, B. S.; Lowe, A. B.; Scales, C. W.; Myrick, L. J.; McCormick, C. L. *Macromol. Rapid Commun.* **2005**, *26*, 791−795.

(15) McLeary, J. B.; McKenzie, J. M.; Tonge, M. P.; Sanderson, R. D.; Klumperman, B. *Chem. Commun.* **2004**, 1950−1951.

(16) McLeary, J. B.; Calitz, F. M.; McKenzie, J. M.; Tonge, M. P.; Sanderson, R. D.; Klumperman, B. *Macromolecules* **2004**, *37*, 2383−2394.

(17) Perrier, S.; Barner-Kowollik, C.; Quinn, J. F.; Vana, P.; Davis, T. P. *Macromolecules* **2002**, *35*, 8300−8306.

(18) Bai, R.; You, Y.; Pan, C. *Macromol. Rapid Commun.* **2001**, *22*, 315−319.

(19) Barner, L.; Quinn, J. F.; Barner-Kowollik, C.; Vana, P.; Davis, T. P. *Eur. Polym. J.* **2003**, *39*, 449−459.

(20) Chen, G.; Zhu, X.; Zhu, J.; Cheng, Z. *Macromol. Rapid Commun.* **2004**, *25*, 818−824.

(21) You, Y.; Hong, C.; Bai, R.; Pan, C.; Wang, J. *Macromol. Chem. Phys.* **2002**, *203*, 477−483.

(22) Quinn, J. F.; Barner, L.; Barner-Kowollik, C.; Rizzardo, E.; Davis, T. P. *Macromolecules* **2002**, *35*, 7620−7627.

(23) Lu, L.; Yang, N.; Cai, Y. *Chem. Commun.* **2005**, 5287−5288.

(24) Lai, J. T.; Filla, D.; Shea, R. *Macromolecules* **2002**, *35*, 6754−6756.

(25) Moad, G.; Chiefari, J.; Chong, Y. K.; Kristina, J.; Mayadunne, R. T. A.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polym. Int.* **2000**, *49*, 993−1001.

(26) Benaglia, M.; Rizzardo, E.; Alberti, A.; Guerra, M. *Macromolecules* **2005**, *38*, 3129−3140.

(27) Fouassier, J. P. In *Radiation Curing in Polymer Science and Technology*; Fouassier, J. P., Rabek, J. F., Eds.; Elsevier: London, 1993; Vols. I−IV (II), p 8.

(28) Sluggett, G. W.; McGarry, P. F.; Koptyug, I. V.; Turro, N. J. *J. Am. Chem. Soc.* **1996**, *118*, 7367−7372.

(29) Chong, Y. K.; Kristina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2003**, *36*, 2256−2272.

(30) Monteiro, M. J.; Brouwer, H. *Macromolecules* **2001**, *34*, 349−352.

MA060157X