Ambient-Temperature RAFT Polymerization of Styrene and Its Functional Derivatives under Mild Long-Wave UV−vis Radiation

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ABSTRACT: Well-defined polystyrene and its functional derivatives, poly(vinylbenzyl chloride) (PVBC), poly(*N*,*N*-diethyl vinylbenzylamine) (PDEVBA), and poly(vinylbenzyl alcohol) (PVBA) were synthesized via (*S*)-1-dodecyl-(*S*′)-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate-mediated ambient-temperature reversible addition−fragmentation chain transfer radical (RAFT) polymerization of the corresponding styrenic-based monomers under mild *long-wave radiation*, using a (2,4,6-trimethylbenzoyl) diphenylphosphine oxide photoinitiator. The effect of chloromethyl, hydroxymethyl, and *tert*-amino functionalities on reactivity and controlled behavior of ambient-temperature RAFT polymerization of styrenic-based monomers under mild conditions was studied in this paper. The results indicated that the photolysis of trithiocarbonate groups and the irreversible termination reactions of their intermediate radicals were significantly suppressed for the duration of the RAFT polymerization under mild long-wave radiation, thus keeping the characteristic living behavior. Kinetic studies confirmed the well-controlled behavior of these RAFT polymerizations. Moreover, the chloromethyl, *tert*-amino, or hydroxymethyl functionalities significantly improved reactivity of styrenic-based monomers, thus remarkably accelerating the process of ambient-temperature RAFT polymerization. Although RAFT polymerization of DEVBA and VBC monomers proceeded at a comparable rate, the initialization period in RAFT polymerization of DEVBA monomer was clearly longer than that of the VBC monomer. VBA was the most reactive monomer among these styrenic-based monomers. Ambient-temperature RAFT polymerization of VBA under mild long-wave radiation was well controlled up to 31% monomer conversion in 1.5 h. The living behavior of these ambient-temperature RAFT polymerizations facilitated the direct synthesis of well-defined all-styrenic-based block copolymers under mild conditions.

Introduction

Reversible addition−fragmentation chain transfer radical polymerization or RAFT polymerization is a highly versatile technique for the synthesis of well-defined polymers.[1−7] This radical polymerization is well-controlled in the presence of thiocarbonylthio compound chain transfer agent (CTA), which functions by establishing a dynamic equilibrium between active propagating radicals and dormant intermediate radicals via a RAFT mechanism, leading to a proportional propagating chain growth with monomer conversions.[1,2] This novel technique was successfully employed for the synthesis of a wide variety of polymers with controlled molecular weights and distributions and targeted architectures and functionalities[3−7] from many monomers.

RAFT polymerization under mild conditions is of considerable interest from both academic and industrial standpoints. Ambient-temperature RAFT polymerization favors the synthesis of well-defined thermo-unstable polymers or polymers from thermodegradable monomers, e.g., the thermodenaturalized biomolecular derivative monomers, without using protecting chemistry. This methodological exploration was pioneered by Davis and co-workers.[8] They 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 co-workers[9−11] reported a series of novel examples for the well-controlled ambient-temperature RAFT polymerization of acrylamide monomers. However, due to the intrinsic retardation effect caused by the initialization period,[12,13] irreversible termination reactions of intermediate radicals,[14−18] or slow fragmentation of intermediate radicals[19] solely optimizing the structure of CTA is not sufficient for a highly efficient and well-controlled ambient-temperature RAFT polymerization of the majority of commonly used monomers.

Many studies were focused on the radiation-activated ambient-temperature RAFT polymerization in recent years. Several radiation sources employed for this purpose, e.g., γ-ray[20−22] and plasma radiation,[23] were utilized to initiate or activate the ambient-temperature RAFT polymerization. Clearly, there are certain practical limitations of employing either γ-ray or plasma radiation source for the synthesis. As comparison, handling and setting up UV lamps are more facile, safer, and cheaper than using either γ-ray or plasma radiation. Pan and co-workers[24] and Quinn et al.[25] separately investigated the UV-radiation-initiated ambient-temperature RAFT polymerization. Most recently, Barner and co-workers[26] reported the UV-radiated ambient-temperature RAFT polymerization of acrylic acid in aqueous solution. Their experimental results demonstrated that the RAFT polymerization was well controlled at relatively low conversions. However, these polymerizations exhibited a significantly long initialization period or proceeded quite slow.[24−26] Moreover, the living behavior of these RAFT polymerizations was significantly deteriorated at relatively high conversions due to the significant photolysis of CTA moieties under UV radiation for prolonged time.[25]

Our experimental results[27,28] demonstrated that CTA compounds and their corresponding growing chain derivatives were strongly sensitive to the UV radiation covering the characteristic maximum absorption wavelength of CTA functionalities, which caused significant photolysis of CTA moieties during RAFT polymerization. Thus, when the the CTA-sensitive shorter wave radiation was cut off, it significantly suppressed the above

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photolysis and remarkably improved the living behavior of these polymerizations. Moreover, the addition of the highly efficient (2,4,6-trimethylbenzoyl) diphenylphosphine oxide (TPO) photoinitiator remarkably shortened the initialization period and significantly accelerated the RAFT process.[29] These quite favored the ambient-temperature RAFT polymerization of acrylic monomers and methacrylic monomers, e.g., glycidyl methacrylate.[29] Most recently, our group[30] successfully extended the activation source from the man-made separated-spectral-emission UV−vis radiation to the natural continuous-spectral-emission solar radiation for the highly efficient and well-controlled ambient-temperature RAFT polymerization.

As one of the types of important polymeric materials, polystyrene and its functional derivatives are extensively utilized in a wide variety of applications. Exploring a method for the facile synthesis of well-defined styrenic-based polymers under mild conditions is undoubtedly desirable. However, to the best of our knowledge, there is no report related to the ambient-temperature RAFT polymerization of styrene and its functional derivatives to date, presumably due to the challenge caused by the strong retardation effect in RAFT process of styrene monomer. This paper describes our recent progress on the ambient-temperature RAFT polymerization of styrene and its functional derivatives, e.g., 4-vinylbenzyl chloride, *N*,*N*-diethyl vinylbenzylamine, and 4-vinylbenzyl alcohol, under mild long-wave UV−vis radiation or long-wave radiation. The effect of chloromethyl, hydroxymethyl, and *tert*-amino functionalization on the reactivity and controlled behavior of ambient-temperature RAFT polymerization of these styrenic-based monomers was studied in this paper.

Experimental Section

Materials. (*S*)-1-Dodecyl-(*S*′)-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (DDMAT) was synthesized according to the literature procedure.[31] TPO (97%) was purchased from Runtec Chemical Co. and used without further purification. Styrene (St, 97%) was purchased from Shanghai Reagent Co. and washed with 5 wt % NaOH aqueous solution and then with distilled water until neutralized. After being dried over anhydrous $MgSO_4$, the monomer was distilled under reduced pressure. 4-Vinylbenzyl chloride (VBC) was purchased from Zhejiang Shangda Co. Ltd. and distilled under reduced pressure. *N*,*N*-Diethyl vinylbenzylamine (DEVBA)[32] and 4-vinylbenzyl alcohol (VBA)[33] were synthesized according to literature procedures. *N*,*N*-Dimethylformamide (DMF, Shanghai Reagent Co., 99.5%) was dried over CaH_2 (Acros, 93%) and was distilled prior to use. Soda filters were purchased from Yaguang Sci. Edu. Equip. Co. The other reagents were used as received.

Long-Wave Radiation Source. A mercury vapor lamp emitting separately at 254, 302, 313, 365, 405, 436, 545, and 577 nm was employed as the radiation source. Soda filters were utilized to cut off shorter wave radiation below 320 nm and to adjust the intensity. Thus, a mild long-wave radiation emitting separately at 365, 405, 436, 545, and 577 nm was achieved.

Kinetic Studies for Ambient-Temperature RAFT Polymerization of Styrene under Mild Long-Wave Radiation. A protocol for DDMAT-mediated ambient-temperature RAFT polymerization of styrene under mild long-wave radiation is as follows: St (14.49 g, 139.4 mmol), DDMAT (113 mg, 0.3 mmol), and TPO (43 mg, 0.1 mmol) were charged in a 50 mL round-bottom flask capped with rubber septa. The solution was deoxygenated by purging with highly pure nitrogen gas for 40 min. UV−vis spectrum was recorded after deoxygenating to account for concentration variation induced by evaporation during the deoxygenating process. The flask was immersed in a thermostatic water bath at 30 °C, and soda filters were placed between the flask and mercury vapor lamp to cut off the shorter wave radiation below 320 nm and adjust the intensity to 100 μW cm^{-2} at 365 nm and 80 μW cm^{-2} at 420 nm, on the basis of the measurement of a UV-A radiometer equipped with 365 and 420 nm sensors. Samples were removed using deoxygenated syringes at predetermined intervals and the reaction quenched by exposure to air and addition of trace amounts of hydroquinone inhibitor prior to measurements. One portion of the sample was diluted in tetrahydrofuran for UV−vis spectroscopic analysis on a Perkin-Elmer lamda-25 UV−vis spectrometer, one portion was diluted in $CDCl_3$ for ^{1}H NMR studies on a 400 MHz Bruker AV-400 NMR spectrometer, and another portion of the sample was diluted in $CHCl_3$ for gel permeation chromatography (GPC) measurements. The monomer conversions were assessed by ^{1}H NMR studies according to eq 1, where $I_{6.3-7.6}$ is the integral of proton resonance signals at $\delta = 6.3-7.6$ ppm (CH_2CH of styrene monomer and C_6H_5 of both the polymer and styrene monomer), $I_{5.6-5.8}$ is the integral of proton resonance signal at $\delta = 5.6-5.8$ ppm (one of $PhCH{=}CH_2$ in styrene monomer), I_0 is the integral of proton resonance signal of tetramethylsilane (TMS) at $\delta = 0$ ppm, and $I_{7.26}$ is the integral of proton resonance signal of $CDCl_3$ solvent at $\delta = 7.26$ ppm.

$$\text{Conversion} = \frac{I_{6.3-7.6} - I_{5.6-5.8} - 5I_{5.6-5.8} - I_0\left[\dfrac{I_0}{I_{7.26}}\right]}{I_{6.3-7.6} - I_{5.6-5.8} - I_0\left[\dfrac{I_0}{I_{7.26}}\right]} \qquad (1)$$

The procedures for the ambient-temperature RAFT polymerizations of VBC, DEVBA, and VBA monomers under long-wave radiation were the same as that described above. The monomer conversion for the ambient-temperature RAFT polymerization of VBC monomer was calculated according to eq 2, where $I_{4.4-4.8}$ is the integral of proton resonance signals at $\delta = 4.4-4.8$ ppm ($PhCH_2Cl$ of both VBC monomer and VBC polymer) and $I_{5.7-5.9}$ is the integral of proton resonance signal at $\delta = 5.7-5.9$ ppm (one of $PhCH{=}C\boldsymbol{H}_2$ in VBC monomer).

$$\text{Conversion} = \frac{I_{4.4-4.8} - 2I_{5.7-5.9}}{I_{4.4-4.8}} \qquad (2)$$

For ambient-temperature RAFT polymerization of DEVBA monomer, the monomer conversion was calculated according to eq 3, where $I_{3.2-3.6}$ is the integral of proton resonance signals at $\delta = 3.2-3.6$ ppm ($PhCH_2N(CH_2CH_3)_2$ of both DEVBA monomer and DEVBA polymer) and $I_{5.7-5.8}$ is the integral of proton resonance signal at $\delta = 5.6-5.8$ ppm (one of $PhCH{=}CH_2$ in DEVBA monomer).

$$\text{Conversion} = \frac{I_{3.2-3.6} - 2I_{5.6-5.8}}{I_{3.2-3.6}} \qquad (3)$$

For ambient-temperature RAFT polymerization of VBA monomer, the monomer conversion was calculated according to eq 4, where $I_{4.2-4.6}$ is the integral of proton resonance signals at $\delta = 4.2-4.6$ ppm ($PhCH_2OH$ of both VBA monomer and VBA polymer) and $I_{5.7-5.9}$ is the integral of the proton resonance signal at $\delta = 5.7-5.9$ ppm (one of $PhCH{=}CH_2$ in VBA monomer).

$$\text{Conversion} = \frac{I_{4.2-4.6} - 2I_{5.7-5.9}}{I_{4.2-4.6}} \qquad (4)$$

Synthesis of All-Styrenic-Based Diblock Copolymers via Ambient-Temperature RAFT Polymerization under Mild Long-Wave Radiation. A protocol for the synthesis of PS-*b*-PVBC diblock copolymer is as follows: PS macromolecular chain transfer agent (PS macro-CTA, synthesized via RAFT polymerization of styrene as described above; UV−vis spectrophotometry, 7% of S=C groups lost; GPC, number-average molecular weight (M_n) of 4.6 kg mol^{-1}, molecular weight distribution (M_w/M_n) of 1.24; 0.552 g, 0.12 mmol), VBC (4.733 g, 31.0 mmol), TPO (7.2 mg, 0.02 mmol), and DMF (1.17 g) were charged in a 25 mL round-bottom flask

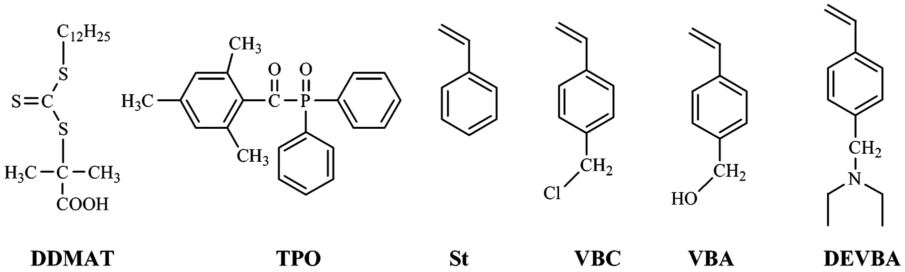

Figure 1. Chemical structures of (*S*)-1-dodecyl-(*S*′)-(α,α′-dimethyl-α′′-acetic acid) trithiocarbonate (DDMAT), (2,4,6-trimethylbenzoyl)-diphenylphosphine oxide (TPO), styrene (St), 4-vinylbenzyl chloride (VBC), 4-vinylbenzyl alcohol,(VBA) and *N*,*N*-diethyl vinylbenzylamine (DEVBA).

capped with rubber septa. The solution was deoxygenated by purging with nitrogen gas for 40 min. The flask was immersed in a thermostatic water bath at 30 °C under long-wave radiation with a mild intensity of 100 μW cm^{-2} at 365 nm and 80 μW cm^{-2} at 420 nm for 7.5 h. The polymerization was ceased by exposure to air and by addition of traces of hydroquinone. The resultant diblock copolymer was precipitated from large excess of methanol and dried in vacuum for 24 h: yield, 92%; ^{1}H NMR, 21% VBC monomer conversion; GPC, $M_n = 13.7$ kg mol^{-1} and $M_w/M_n = 1.35$.

The procedures for the synthesis of PS-*b*-VBA and PVBC-*b*-PVBA diblock copolymers were the same as described above except that a different monomer or macro-CTA was used. In order to minimize the calibration errors of the GPC analysis caused by the strong polarity of PVBA blocks, the hydroxyl groups of the VBA units in these diblock copolymers were capped by acetic anhydride (see Supporting Information Figure S1) prior to GPC measurements.

GPC Measurements were performed on a Waters 1515 GPC setup equipped with a Waters 2414 differential refractive index detector. The polymers were measured under the following conditions: (1) GPC traces of polystyrene and all-styrenic-based copolymers shown in Figures 6, 7, and 10−12 were measured on the GPC setup equipped with a column set consisting of two PLgel 5 μm MIXED-D columns (7.5 mm × 300 mm, effective molecular weight range of 0.2−400.0 kDa) using $CHCl_3$ as an eluent at 30 °C with a flow rate of 1.0 mL min^{-1}, (2) GPC traces of PDEVBA in Figure 8 were measured on the GPC setup equipped with a column set consisting of a Styragel HR4 column (7.8 mm × 300 mm, effective molecular weight range of 5.0−500.0 kDa), a Styragel HR3 column (7.8 mm × 300 mm, effective molecular weight range of 0.5−30.0 kDa), and a Styragel HR1 column (7.8 mm × 300 mm, effective molecular weight range of 0.1−5.0 kDa) using tetrahydrofuran as an eluent at 35 °C with a flow rate of 1.0 mL min^{-1}, (3) GPC traces of PVBA in Figure 9 were measured on the GPC setup equipped with a column set consisting of two PLgel 5 μm MIXED-D columns (7.5 mm × 300 mm, effective molecular weight range of 0.2−400.0 kDa) using *N*,*N*-dimethylformamide as an eluent at 50 °C with a flow rate of 1.0 mL min^{-1}. Narrowly distributed polystyrene standards in the molecular weight range of 0.5−1000.0 kDa (PSS, Mainz, Germany) were utilized for calibration.

Results and Discussion

Thermo-activating RAFT polymerization of styrene has been extensively studied in the recent years.[34−60] Fukuda et al.[34] demonstrated that the only important mechanism for the bulk polymerization of styrene in the presence of polymer−dithiocarbonate adducts was the reversible addition fragmentation chain transfer. With the help of electron spin resonance spectroscopy, the intermediates involved in the process were identified as the species derived from the addition of propagating radicals to CTA, in agreement with the RAFT mechanism.[35−37] PREDICI simulation results demonstrated the “normal” living behavior of RAFT polymerization of styrene; the effective propagating radical sink in the RAFT process ensured the living character of this polymerization.[38,39]

Several types of CTA were employed for the RAFT polymerization of styrene, e.g., phosphoryl- and (thiophosphoryl) dithioformates,[40] macromolecular design via interchange of xanthate (MADIX) agents,[41] phenylethyl phenyldithioacetate and phenyldithioacetic acid,[42] dithiocarbamates with different N groups,[43] and pyridinyl dithioesters and their *N*-oxides.[44] These studies demonstrated that the RAFT polymerization of styrene depended strongly on the structure of the CTA compounds, thus determining the effectiveness and the applicability of a specific CTA. Emulsion polymerization,[45−48] miniemulsion polymerization,[49,50] and dispersion polymerization[51] were employed for the thermoactivating RAFT polymerization of styrene. Köllisch and co-workers[52] accomplished the well-controlled RAFT polymerization of cyclodextrin host−guest complexes of styrene in aqueous solution. In addition, RAFT polymerization has been widely employed for the synthesis of polymers with targeted structures, e.g., block copolymers,[53,54] “gradient” copolymers,[55] alternating copolymers,[56] and graft copolymers.[57] McCormick and co-workers[58] employed RAFT polymerization for the synthesis of hydrophilic styrenic-based polymers and block copolymers in aqueous solution. Quinn et al.[59] reported the facile synthesis of comb, star, and graft polymers via RAFT polymerization from RAFT-prepared PVBC and poly(St-*co*-VBC) random copolymer at 60 °C.

RAFT polymerization of styrene seriously suffers from the drawback of retardation effect. To improve both the rate and the controlled behavior of this polymerization, Vana and co-workers[60] employed high pressure, up to 2500 bar, for RAFT polymerization of styrene. They also accomplished the self-initiated RAFT polymerization of styrene at 120, 150, and 180 °C and 1000 bar.[61] Their results revealed significantly reduced retardation effect under these conditions. Zhu and co-workers[62] observed a asignificant rate enhancement of the RAFT polymerization of styrene under microwave irradiation. However, to the best of our knowledge, there is no report related to the ambient-temperature RAFT polymerization of styrene and its functional derivatives to date, presumably because of the challenge caused by this strong retardation effect.

This paper describes our recent results on the ambient-temperature RAFT polymerization of styrene and its functional derivatives, e.g., VBC, DEVBA, and VBA under long-wave radiation, separately emitting at 365, 405, 436, 545, and 577 nm, with a mild intensity of 100 μW cm^{-2} at 365 nm and 80 μW cm^{-2} at 420 nm. A highly efficient and commercially available (2,4,6-trimethylbenzoyl) diphenylphosphine oxide (Figure 1) photoinitiator was also employed for this purpose. Its α-cleavable rate constant[63] is above 1.0×10^9 s^{-1}, and the addition rate constant of phosphonyl radical[64] is 1.79×10^7 M^{-1} s^{-1}. More importantly, its characteristic absorption is at $\lambda_{max} = 380$ nm,[28] which is quite sensitive to long-wave radiation selected for activating the DDMAT-mediated ambient-temper-

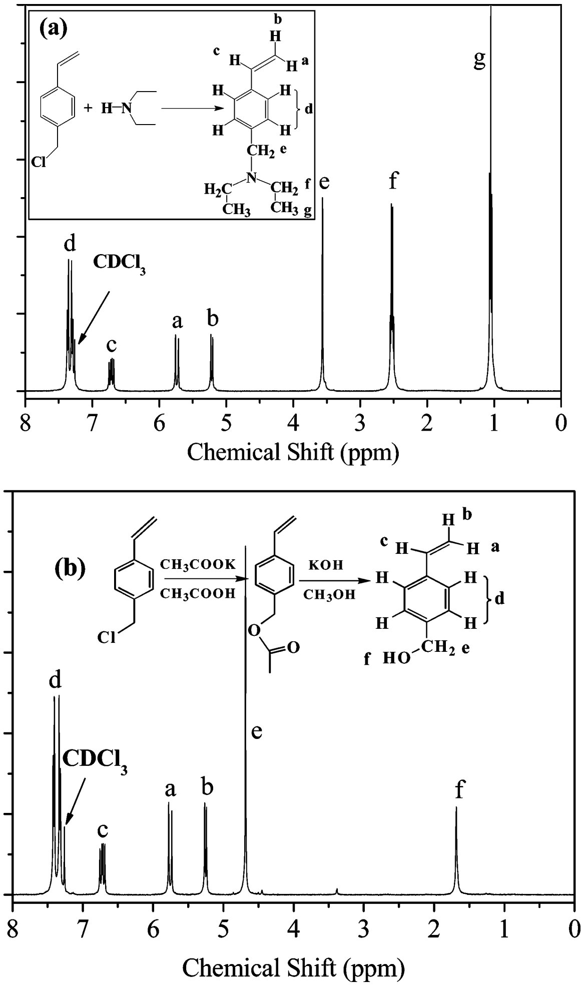

Figure 2. ^{1}H NMR spectra and synthetic routes (schemes in insets) of (a) *N*,*N*-diethyl vinylbenzylamine and (b) 4-vinylbenzyl alcohol.

ature RAFT polymerization of styrenic-based monomers. In addition, DEVBA and VBA monomers with high purity were synthesized to avoid undesirable side reactions (Figure 2).

UV−vis Spectroscopic Studies on Styrenic-Based Monomer Polymerizing Solutions under Mild Long-Wave Radiation. As shown in Figure 3, the initial DDMAT compound in these styrenic-based monomers polymerizing solution exhibited a characteristic absorption peak at 443 nm because of the $n \rightarrow \pi^*$ forbidden transition of C═S groups. Under mild long-wave radiation, this peak rapidly blue-shifted to 434 nm in 10−15 min and remained at this wavelength thereafter. This period was the so-called initialization period,[12,13] i.e., DDMAT compound was converted to its monomer-adducted derivatives[12,13] in 10−15 min. On the basis of ^{1}H NMR assessment a ca. 3% monomer conversion was detected in this period.

As shown in Figure 3b−d, particularly for the DEVBA polymerizing solution (Figure 3c), under long-wave radiation for 10−15 min, the DDMAT characteristic absorption blue-shifted from 443 to 434 nm. Its absorbance also increased significantly, suggesting that the molar extinction coefficient of the monomer-adducted DDMAT derivatives was significantly larger than that of the initial DDMAT compound. Accordingly, this molar extinction coefficient increase led to the remarkable increase in absorbance of the peak at 375−420 nm, which was contributed by the absorption of TPO, DDMAT, and monomers, despite the decrease of absorbance caused by the photolysis of TPO. In addition, among these styrenic-based monomers, the molar extinction coefficient of DEVBA is the largest, up to an absorbance of 0.15 at 375 nm in THF solution (2.0 mol L^{-1}, see Supporting Information Figure S2). Thus, the insertion of DEVBA into the DDMAT compound led to the remarkably rapid increase of absorption at 420−375 nm (Figure 3c).

It was noted that for the deoxygenated DDMAT solution in tetrahydrofuran, under mild long-wave radiation up to 6 h, essentially the same ^{1}H NMR spectrum was detected (Supporting Information Figure S3), which suggested negligible photolysis of the DDMAT moieties. The negligible photolysis of DDMAT under this mild long-wave radiation was also confirmed by high performance liquid chromatography (HPLC), i. e., after long-wave radiation for 6 h, no fragments of DDMAT could be detected from this solution on the basis of HPLC measurements. In addition, essentially the same ^{1}H NMR spectra obtained for the deoxygenated bulk styrene before and after radiation for 6 h (Supporting Information Figure S4) indicated negligible radical formation from the styrene monomer. These results suggested the negligible contribution of radicals from either DDMAT compound or styrenic monomers.

The absorbance evolutions of the DDMAT moieties at 443−434 nm (Figure 3) are summarized in Figure 4, where A_0 is the absorbance of solution before radiation, A_t is the absorbance of solution in a predetermined radiation interval. Under long-wave radiation for 15 min, A_t/A_0 of St, VBC, DEVBA, and VBA polymerizing solutions rapidly increased up to a maximum of 1.38, 1.53, 1.27, and 1.34, respectively, followed by a very slow decrease.

It was assumed that the DDMAT compound was completely converted to the monomer-adducted derivatives in the initialization period,[12,13] where A/A_0 reached a maximum. After the initialization period, the slow decrease of A_t/A_0 was attributed to the loss of S═C groups in DDMAT moieties, or the partial deactivation of DDMAT moieties, predominantly due to the photolysis of trithiocarbonate groups and the irreversible termination reactions of their intermediate radicals during the RAFT process.[14−18] Although trithiocarbonate groups were partially converted to their intermediate radicals, in which the double bonds of S═C groups were converted to the single bond of S−C radicals, its concentration was roughly constant after the initialization period.[12,13] Thus, after initialization period, the influence of intermediate radicals formation on the decrease of A_t/A_0 should be negligible.

According to Lambert−Beer law, under long-wave radiation for 6 h, ~7% of the S═C groups was lost in the styrene polymerizing solution whereas only ~4% of the S═C groups was lost in the VBC polymerizing solution and ~5% of the S═C groups was lost in the DEVBA polymerizing solution. For VBA polymerizing solution, because of the high reactivity of VBA monomers under these conditions, 40% monomer conversion was detected under mild long-wave radiation at 30 °C for 2 h, where a ca. 3% of the S═C groups of the DDMAT moieties was lost.

Kinetic Studies on DDMAT-Mediated Ambient-Temperature RAFT Polymerization of Styrenic-Based Monomers under Mild Long-Wave Radiation. Kinetic curves of the bulk RAFT polymerization of styrene, DEVBA, VBC, and VBA monomers, under mild long-wave radiation at 30 °C, are summarized in Figure 5. Under mild long-wave radiation, the semilogarithmic kinetic curves for the polymerization of styrene, DEVBA, and VBC monomers evolved linearly, indicating a constant steady-state radical concentration, i.e., DDMAT moieties exerted good control over these RAFT polymerizations. Under the same conditions, the polymerizations of DEVBA and VBC monomers proceeded more rapidly than that of styrene,

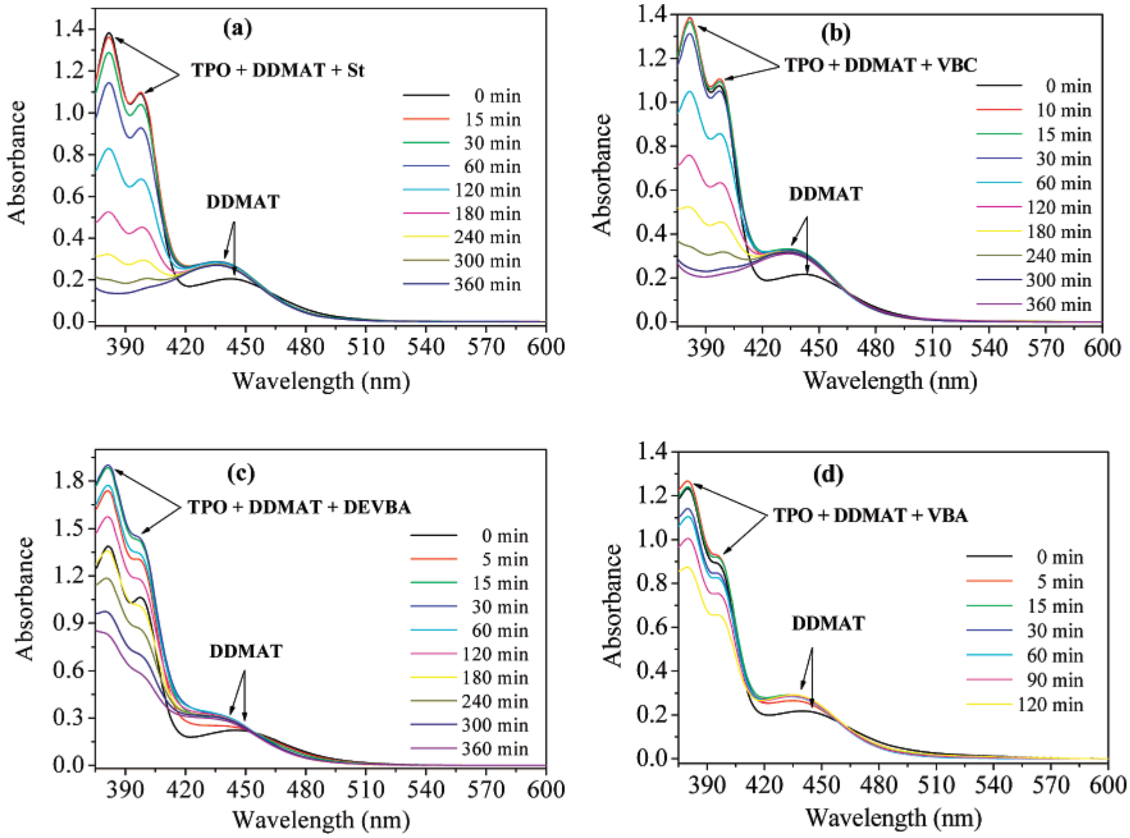

Figure 3. UV−vis spectroscopic evolution of (a) styrene, (b) 4-vinylbenzyl chloride, (c) *N*,*N*-diethyl vinylbenzylamine, and (d) 4-vinylbenzyl alcohol bulk polymerizing solutions at $[\text{monomer}]_0$:$[\text{DDMAT}]_0$:$[\text{TPO}]_0$ = 450:1:0.4 under long-wave radiation with 100 μW cm^{-2} at 365 nm and 80 μW cm^{-2} at 420 nm at 30 °C. VBA polymerizing solutions were diluted with *N*,*N*-dimethylformamide and all the others were diluted with tetrahydrofuran to [DDMAT] = 6.0 mmol L^{-1} prior to UV−vis spectroscopic measurements.

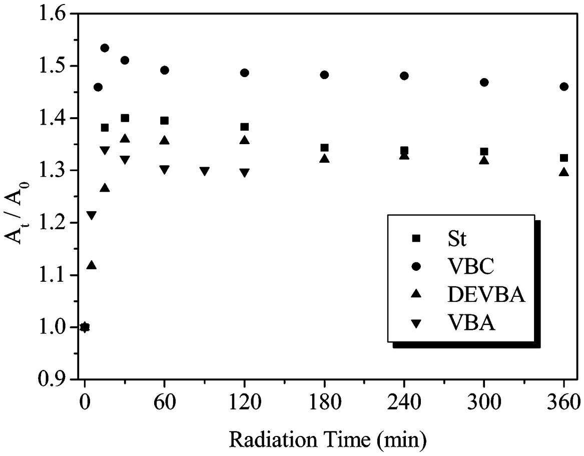

Figure 4. Absorbance evolution trends of (*S*)-1-dodecyl-(*S*′)-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (DDMAT) moieties characteristic peak at 442−435 nm in (■) styrene (St), (●) 4-vinylbenzyl chloride (VBC), (▲) *N*,*N*-diethyl vinylbenzylamine (DEVBA), and (▼) 4-vinylbenzyl alcohol (VBA) bulk polymerizing solutions at $[\text{monomer}]_0$:$[\text{DDMAT}]_0$:$[\text{TPO}]_0$ = 450:1:0.4 under long-wave radiation with 100 μW cm^{-2} at 365 nm and 80 μW cm^{-2} at 420 nm at 30 °C. VBA polymerizing solutions were diluted with *N*,*N*-dimethylformamide and all the others were diluted with tetrahydrofuran to [DDMAT] = 6.0 mmol L^{-1} prior to UV−vis spectroscopic measurements.

e.g., at $[\text{monomer}]_0$:$[\text{DDMAT}]_0$:$[\text{TPO}]_0$ = 450:1:0.4 under mild long-wave radiation at 30 °C for 6 h, 15% styrene monomer conversion, 35% DEVBA monomer conversion, and 39% VBC monomer conversion were detected. This suggested that the 4-chloromethyl or 4-*tert*-amino functionalities significantly improved the reactivity of styrenic-based monomers, which facilitated the ambient-temperature RAFT polymerization.

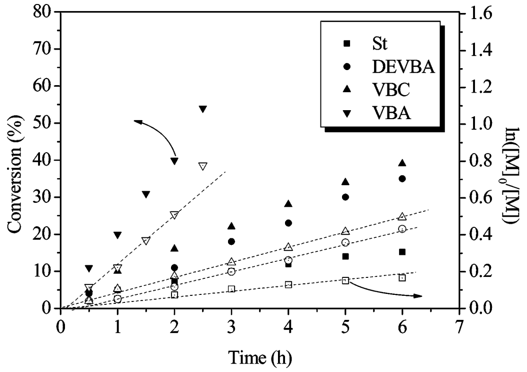

Figure 5. Kinetic curves of the bulk RAFT polymerizations of (■) styrene (St), (●) *N*,*N*-diethyl vinylbenzylamine, (DEVBA), (▲) 4-vinylbenzyl chloride (VBC), and (▼) 4-vinylbenzyl alcohol (VBA) at $[\text{monomer}]_0$:$[\text{DDMAT}]_0$:$[\text{TPO}]_0$ = 450:1:0.4 under long-wave radiation with 100 μW cm^{-2} at 365 nm and 80 μW cm^{-2} at 420 nm at 30 °C.

It was also noted that in these cases the initialization period, assessed by the extrapolation of semilogarithmic kinetic curve to $\ln([M]_0/[M]) \rightarrow 0$, i.e., the duration from the beginning of radiation to the start of polymerization, was less than 20 min. Although the RAFT polymerization of DEVBA and VBC monomers proceeded at a comparable rate, the initialization period in the RAFT polymerization of DEVBA monomer was clearly longer than that of VBC monomer. We cannot give a reasonable explanation at present for this observation.

Strikingly, as shown in Figure 5, the RAFT polymerization of VBA monomer proceeded significantly more rapidly than that of styrene, DEVBA, or VBC monomer. On the basis of ^{1}H NMR assessment, at $[\text{VBA}]_0$:$[\text{DDMAT}]_0$:$[\text{TPO}]_0$ = 450:1:0.4 under mild long-wave radiation at 30 °C for 2.5 h, 54%

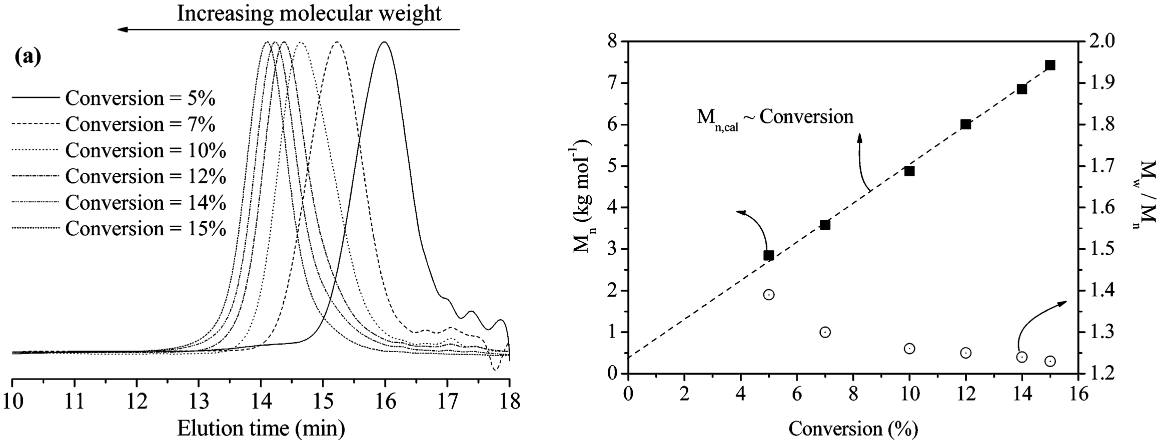

Figure 6. (a) GPC trace evolution trends of polystyrene synthesized via bulk RAFT polymerization of styrene at $[St]_0$:$[DDMAT]_0$:$[TPO]_0$ = 450:1:0.4 under long-wave radiation with 100 μW cm^{-2} at 365 nm and 80 μW cm^{-2} at 420 nm at 30 °C. (b) Number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of PS as a function of monomer conversion at predetermined intervals. $M_{n,cal}$ was calculated according to the following equation: $M_{n,cal} = M_{St} \times \text{Conversion} \times [St]_0/[DDMAT]_0 + M_{DDMAT}$.

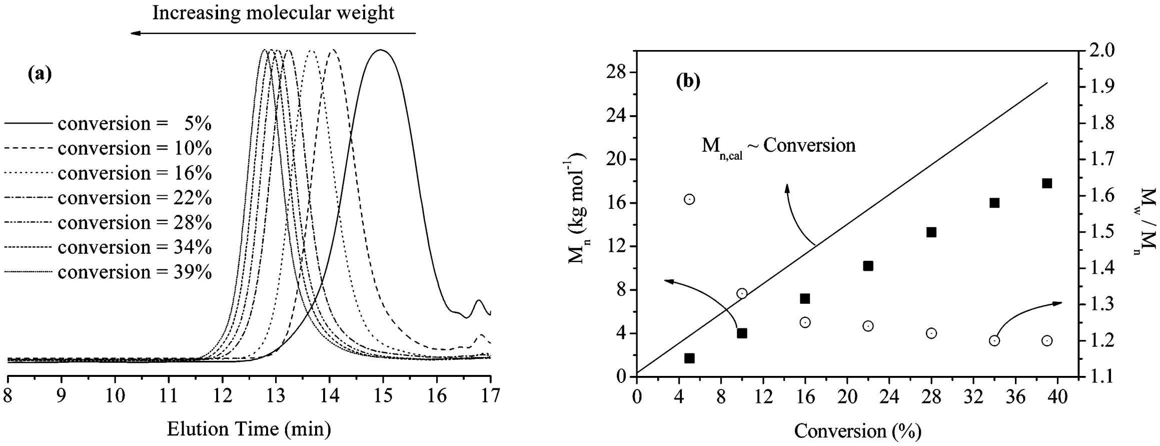

Figure 7. (a) GPC trace evolution trends of poly(4-vinylbenzyl chloride) synthesized via RAFT polymerization of VBC monomer at $[VBC]_0$:$[DDMAT]_0$:$[TPO]_0$ = 450:1:0.4 under long-wave radiation with 100 μW cm^{-2} at 365 nm and 80 μW cm^{-2} at 420 nm at 30 °C. (b) Number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of PVBC as a function of VBC monomer conversion. $M_{n,cal}$ was calculated according to the following equation: $M_{n,cal} = M_{VBC} \times \text{Conversion} \times [VBC]_0/[DDMAT]_0 + M_{DDMAT}$.

monomer conversion was detected, which was remarkably more rapid than that of the above mentioned styrenic-based monomers. A similar phenomenon was also observed in the ambient-temperature RAFT polymerization of methacrylate monomers under long-wave radiation in our previous studies, e.g., hydroxyethyl methacrylate polymerized significantly more rapidly than either 2-(dimethylamino)ethyl methacrylate or ethyl methacrylate. Further investigation to clarify this phenomenon is in progress. The linear evolution tendency of its semilogarithmic kinetic curve remained up to 40% monomer conversion for 2 h. However, clearly, this linear tendency was positively deviated at 54% monomer conversion. This positive deviation was presumably caused by the pronounced exothermal process of the polymerization due to the high reactivity of this 4-hydroxymethyl functionalized monomer, which led to the increase of the reacting solution temperature. A thermostatic water bath was not sufficiently enough to keep the reaction solution constantly at 30 °C, and thus this polymerization was significantly accelerated.

Ambient-Temperature RAFT Polymerization of Styrene under Mild Long-Wave Radiation. As shown in Figure 6a, the well-controlled behavior of the DDMAT-mediated ambient-temperature RAFT polymerization of styrene under mild long-wave radiation was confirmed by a clear shift of the GPC traces of styrene polymers with radiation time. Moreover, as shown in Figure 6b, the number-average molecular weight (M_n) of PS exhibited a clearly linear evolution with the monomer conversion throughout the RAFT polymerization. The polydispersity index (M_w/M_n) of PS was 1.30 at 7% monomer conversion, indicating that DDMAT exerted significant control over this radical polymerization at relatively low conversions, which gradually decreased to 1.23 at 15% monomer conversion.

Ambient-Temperature RAFT Polymerizations of VBC, DEVBA, and VBA Monomers under Mild Long-Wave Radiation. As shown in Figure 7a, the GPC traces of PVBC polymers synthesized via the RAFT polymerization of VBC monomer at $[VBC]_0$:$[DDMAT]_0$:$[TPO]_0$ = 450:1:0.4 under mild long-wave radiation at 30 °C clearly shifted with increasing monomer conversion, with monomodal distribution and remarkably symmetrical characteristics from 10% monomer conversion onward. This suggested the well-controlled behavior of this RAFT polymerization. Moreover, as shown in Figure 7b, the M_n of PVBC exhibited clearly a linear evolution with the VBC monomer conversion for the complete duration of the RAFT polymerization. The polydispersity index (M_w/M_n) of PVBC was 1.59 at 5% monomer conversion, indicating that DDMAT exerted reasonable control over this radical polymerization at low monomer conversions, which gradually decreased to 1.20 at 35% monomer conversion. These results confirm the well-controlled behavior of this RAFT polymerization.

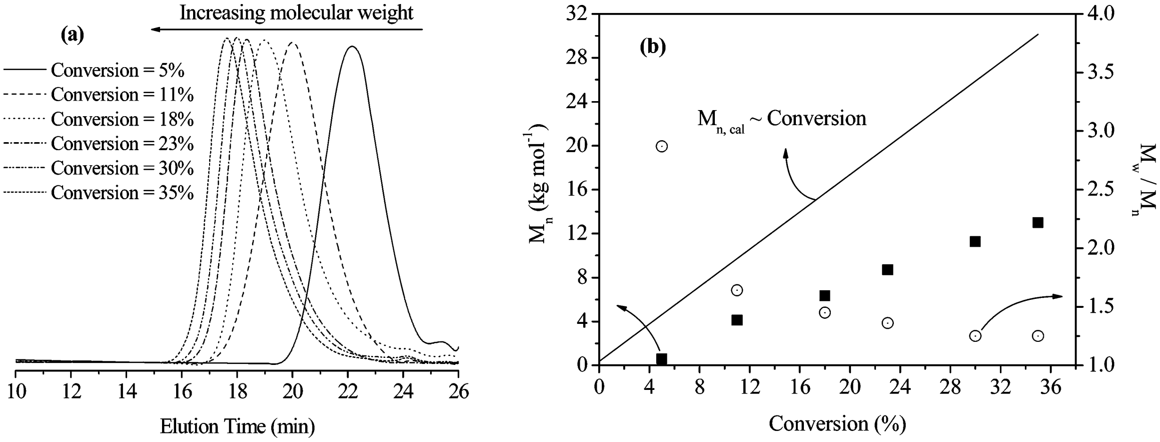

Figure 8. (a) GPC trace evolution trends of poly(*N*,*N*-diethyl vinylbenzylamine) synthesized via bulk RAFT polymerization of DEVBA monomer at $[DEVBA]_0:[DDMAT]_0:[TPO]_0 = 450:1:0.4$ under long-wave radiation with 100 μW cm^{-2} at 365 nm and 80 μW cm^{-2} at 420 nm at 30 °C. (b) Number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of PDEVBA as a function of monomer conversion. $M_{n,cal}$ was calculated according to the following equation: $M_{n,cal} = M_{DEVBA} \times \text{Conversion} \times [DEVBA]_0/[DDMAT]_0 + M_{DDMAT}$.

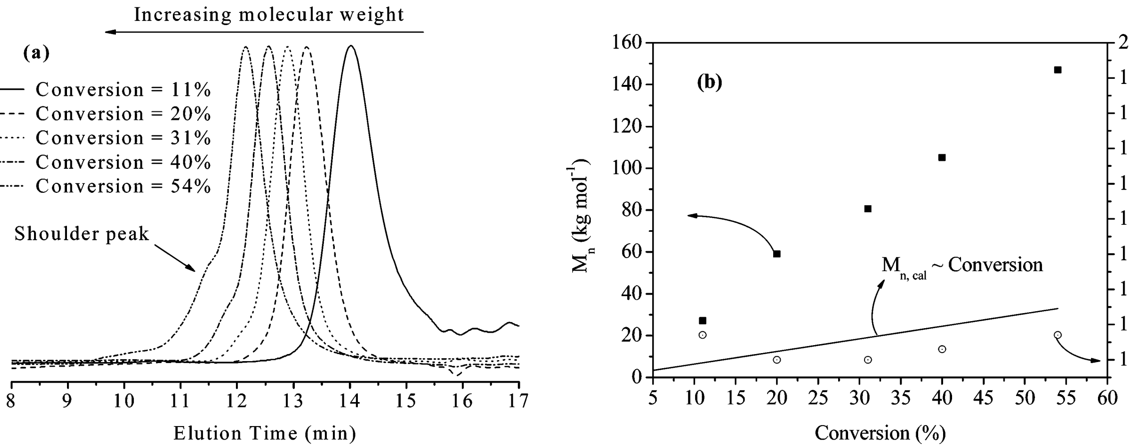

Figure 9. (a) GPC trace evolution trends of poly(4-vinylbenzyl alcohol) synthesized via bulk RAFT polymerization of VBA monomer at $[VBA]_0:[DDMAT]_0:[TPO]_0 = 450:1:0.4$ under long-wave radiation with 100 μW cm^{-2} at 365 nm and 80 μW cm^{-2} at 420 nm at 30 °C. (b) Number-average molecular weights (M_n) and polydispersity indices (M_w/M_n) of PVBA polymers as a function of monomer conversions. $M_{n,cal}$ was calculated according to the following equation: $M_{n,cal} = M_{VBA} \times \text{Conversion} \times [VBA]_0/[DDMAT]_0 + M_{DDMAT}$.

On comparison, the GPC traces of PDEVBA synthesized via RAFT polymerization of DEVBA monomer under the same conditions as described above (Figure 8a) also clearly showed a shift to the higher molecular weight side with increasing monomer conversion. However, the monomodal distribution and the symmetrical GPC traces could be only detected at low conversions, up to 11%. Thereafter, a slight peak tail on the lower molecular weight side was detected. As shown in Figure 8b, M_n of PDEVBA exhibited a linear evolution with monomer conversion for the duration of the RAFT polymerization. M_w/M_n of PDEVBA was 1.64 at 11% monomer conversion, indicating that DDMAT exerted reasonable control over this polymerization at low monomer conversions, which gradually decreased to 1.25 at 30% monomer conversion.

As shown in Figure 9a, the GPC traces of PVBA polymers synthesized via RAFT polymerization of the VBA monomer (the most reactive monomer among the styrenic-based monomers) under the same conditions as described above are quite different. On one hand, the GPC traces of PVBA also clearly shifted with increasing monomer conversion. On the other hand, the monomodal and symmetrical GPC traces could be only detected up to 20% monomer conversion. Thereafter, a slight peak tail on the higher molecular weight side was detected at 31% monomer conversion, presumably caused by the irreversible termination reaction of intermediate radicals.[14−18] This peak tail finally evolved into a shoulder at 54% monomer conversion, leading to wider molecular weight distributions.

As shown in Figure 9b, M_n of PVBA polymers exhibited a roughly linear evolution with VBA monomer conversions for the complete duration of the RAFT polymerization. M_w/M_n of PVBA was 1.10 at 31% monomer conversion, indicating that DDMAT exerted good control over this radical polymerization. Thereafter, it gradually increased up to 1.17 at 54% monomer conversion due to the shoulder peak generated on the higher molecular weight side.

It was also noted that the M_n values of PVBA assessed by GPC measurements were strikingly overestimated, due to the remarkably larger polarity of PVBA compared to the polystyrene standards. However, the molecular weight evolution tendency of these polymers should be reliable despite these system errors. In order to minimize the calibration errors caused by the strong polarity of the VBA units, the hydroxyl groups of the below discussed PVBA-based block copolymers were essentially capped by acetic anhydride.

Synthesis of All-Styrenic-Based Block Copolymers via Ambient-Temperature RAFT Polymerization under Mild Long-Wave Radiation. In order to clarify the living behavior of ambient-temperature RAFT polymerization of the styrenic-based monomers under mild long-wave radiation, the block copolymerization of VBC monomer was conducted, selecting

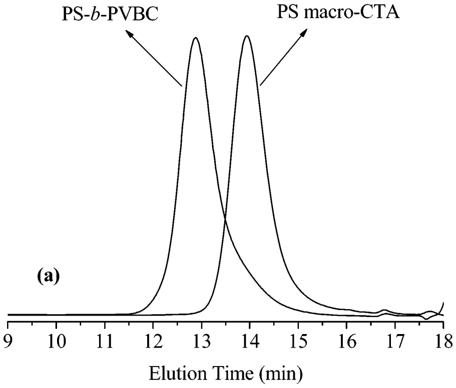

Figure 10. GPC traces of PS macro-CTA (UV−vis spectrophotometry, 7% of S═C groups lost; ^{1}H NMR, 14% monomer conversion; GPC, $M_n = 4.6$ kg mol^{-1} and $M_w/M_n = 1.24$) and its corresponding chain-extended PS-*b*-PVBC diblock copolymer. Copolymerization conditions: $[VBC]_0$:[PS macro-CTA]$_0$:$[TPO]_0 = 260:1:0.17$ in 20 wt % *N*,*N*-dimethylformamide under long-wave radiation with 100 μW cm^{-2} at 365 nm and 80 μW cm^{-2} at 420 nm at 30 °C for 7.5 h. ^{1}H NMR, 21% VBC monomer conversion; GPC, M_n =13.7 kg mol^{-1} and M_w/M_n =1.35.

an above synthesized PS as a macro-CTA (UV−vis spectrophotometry, ca. 7% of S═C groups lost; ^{1}H NMR, 14% styrene monomer conversion; GPC, $M_n = 4.6$ kg mol^{-1}, $M_w/M_n = 1.24$). This PS macro-CTA was synthesized via DDMAT-mediated ambient-temperature RAFT polymerization of styrene monomer under mild long-wave radiation.

Figure 10 shows the GPC traces of the PS macro-CTA and its corresponding chain-extended PS-*b*-PVBC diblock copolymer. This PS-*b*-PVBC diblock copolymer was synthesized via RAFT polymerization of VBC monomer under the following conditions: $[VBC]_0$:[PS macro-CTA]$_0$:$[TPO]_0 = 260:1:0.17$ in 20 vol % DMF under mild long-wave radiation at 30 °C for 7.5 h. A 21% VBC monomer conversion was detected at the end of the polymerization. The observation of a monomodal and reasonably symmetrical GPC trace of the chain-extended block copolymer evidenced the living character of this chain extension RAFT polymerization. Moreover, the GPC trace clearly shifted to the higher molecular weight side, with a reasonable M_n of 13.7 kg mol^{-1} and M_w/M_n of 1.35. Only a slight peak tail on the lower molecular weight side was detected. This slight peak tail is attributed to the ∼7% "dead" PS in PS macro-CTA as well as to the premature terminations during the chain extension RAFT polymerization. The fact that only a weak peak tail was observed confirmed the living character of this chain extension RAFT polymerization under long-wave radiation.

In order to clarify this GPC peak tail on the low molecular weight side, a PS synthesized at relatively low monomer conversion, e.g., 10% monomer conversion, was employed as a macro-CTA, where the PS had ca. 3% of S═C groups lost, $M_n = 2.7$ kg mol^{-1}, and $M_w/M_n = 1.26$. VBA monomer was selected for this block copolymerization. Under the conditions of $[VBA]_0$:[PS macro-CTA]$_0$:$[TPO]_0 = 150:1:0.1$ in 20 vol % DMF under mild long-wave radiation at 30 °C for 6 h, 28% of the VBA monomer was polymerized, based on ^{1}H NMR assessment. As shown in Figure 11, the peak tail on the lower molecular weight side was clearly eliminated. Please note that the hydroxyl groups of the PS-*b*-PVBA diblock copolymer were essentially capped by acetic anhydride prior to the GPC measurement (see Supporting Information Figure S1) to keep the polarity of the two blocks comparable.

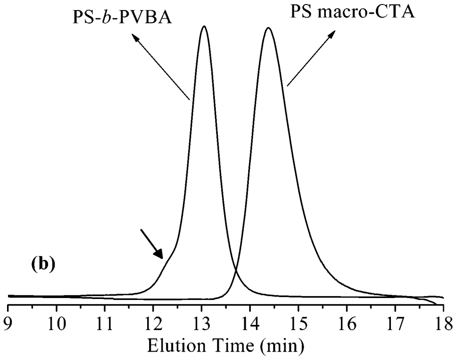

Figure 11. GPC traces of PS macro-CTA (UV−vis spectrophotometry, 3% of S═C groups lost; ^{1}H NMR, 10% monomer conversion; GPC, M_n= 2.7 kg mol^{-1} and $M_w/M_n = 1.26$) and its corresponding chain-extended PS-*b*-PVBA diblock copolymer ($M_n = 15.5$ kg mol^{-1}, $M_w/M_n = 1.15$), where the hydroxyl groups of PS-*b*-PVBA were essentially capped by acetic anhydride (see Supporting Information Figure S1) prior to GPC measurement. Copolymerization conditions: $[VBA]_0$:[PS macro-CTA]$_0$:$[TPO]_0 = 150:1:0.1$ in 20 wt % *N*,*N*-dimethylformamide under long-wave radiation as above at 30 °C for 6 h. ^{1}H NMR: 28% VBA monomer conversion.

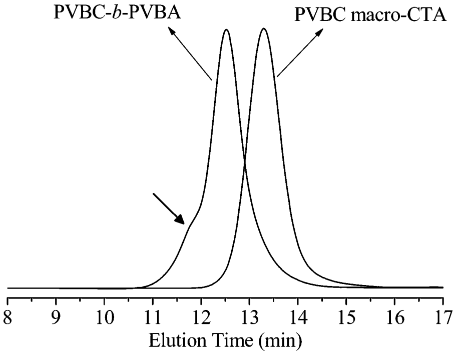

Figure 12. GPC traces of PVBC macro-CTA (UV−vis spectrophotometry, 3% of S═C groups lost; ^{1}H NMR, 23% monomer conversion; GPC, $M_n = 10.5$ kg mol^{-1} and $M_w/M_n = 1.20$) and its corresponding chain-extended PVBC-*b*-PVBA, where the hydroxyl groups of PVBC-*b*-PVBA were essentially capped by acetic anhydride (see Supporting Information Figure S1) prior to GPC measurement (GPC: $M_n = 25.6$ kg mol^{-1} and $M_w/M_n = 1.34$). Copolymerization conditions: $[VBA]_0$:[PVBC macro-CTA]$_0$:$[TPO]_0 = 170:1:0.1$ in 20 wt % *N*,*N*-dimethylformamide under long-wave radiation with 100 μW cm^{-2} at 365 nm and 80 μW cm^{-2} at 420 nm at 30 °C for 5 h. ^{1}H NMR: 36% VBA monomer conversion.

A PVBC synthesized via ambient-temperature RAFT polymerization under mild long-wave radiation at 23% monomer conversion was also employed as a macro-CTA. As shown in Figure 12, under the conditions $[VBA]_0$:[PVBC macro-CTA]$_0$:$[TPO]_0 = 170:1:0.1$ in 20 vol % DMF under mild long-wave radiation at 30 °C for 5 h, 36% of the VBA monomer was polymerized, on the basis of ^{1}H NMR assessment. The hydroxyl groups of the PS-*b*-PVBA diblock copolymer were essentially capped by acetic anhydride prior to GPC measurement (see Supporting Information Figure S1) to keep the polarity of the two blocks comparable. A slight peak tail at lower molecular weight side was detected from the GPC trace of the chain-extended PVBC-*b*-PVBA diblock copolymer. Similar to what was observed in the RAFT polymerization of VBA monomer (Figure 9a), a shoulder on the higher molecular weight side was detected. This shoulder can be suppressed by ceasing the polymerization at a low VBA monomer conversion (see Figures 11 and 9a).

In summary, the living behavior of these ambient-temperature RAFT polymerizations under mild long-wave radiation facilitated the direct synthesis of well-defined all-styrenic-based block copolymers. The reactive functionalities of PVBC, PVBA, and DEVBA polymers or blocks provide the possibility for a range of further reactions for the modification of these styrenic-based polymers and block copolymers.

Conclusions

Well-defined polystyrene and its functional derivatives, poly(vinylbenzyl chloride), poly(*N*,*N*-diethyl vinylbenzylamine) and poly(vinylbenzyl alcohol), were synthesized via DDMAT-mediated ambient-temperature RAFT polymerization under mild long-wave radiation emitting separately at 365, 405, 436, 545, and 577 nm using a TPO photoinitiator. The effect of chloromethyl, hydroxymethyl, and *tert*-amino functionalities on the reactivity and controlled behavior of the ambient-temperature RAFT polymerization under these mild conditions was studied in this paper.

The results demonstrated that the photolysis of trithiocarbonate groups and the irreversible termination reactions of their intermediate radicals were significantly suppressed during the ambient-temperature RAFT polymerization under mild long-wave radiation, thus retaining the living behavior of these RAFT polymerizations. Kinetic studies confirmed the well-controlled behavior of these RAFT polymerizations. Moreover, the chloromethyl, *tert*-amino, or hydroxymethyl functionalities significantly improved the reactivity of the styrenic-based monomers, thus remarkably accelerating the process of these ambient-temperature RAFT polymerizations. Although the RAFT polymerization of DEVBA and VBC monomers proceeded at a comparable rate, the initialization period in the RAFT polymerization of DEVBA monomer was clearly longer than that of VBC monomer. VBA was the most reactive monomer among these styrenic-based monomers, and the RAFT polymerization of VBA monomer was well controlled up to 31% monomer conversion in 1.5 h.

The living behavior of these ambient-temperature RAFT polymerizations facilitated the direct synthesis of well-defined all-styrenic-based block copolymers under mild conditions. The reactive functionalities of PVBC, PVBA, and DEVBA polymers or blocks provide the possibility for a range of further reactions for the modification of these styrenic-based polymers and block copolymers.

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Supporting Information Available: ^{1}H NMR spectra of polystyrene and its corresponding polystyrene-*b*-poly(vinylbenzyl alcohol) and acetic-anhydride-capped polystyrene-*b*-poly(vinylbenzyl alcohol), poly(vinylbenzyl chloride) and its corresponding poly(vinylbenzyl chloride)-*b*-poly(vinylbenzyl alcohol) and acetic-anhydride-capped poly(vinylbenzyl chloride)-*b*-poly(vinylbenzyl alcohol); UV−vis spectra of 2.0 mol L^{-1} styrene, 4-vinylbenzyl chloride, 4-vinylbenzyl alcohol, and *N*,*N*-diethyl vinylbenzylamine in tetrahydrofuran; ^{1}H NMR spectra of (*S*)-1-dodecyl-(*S*′)-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate (DDMAT) distilled from 25 mmol L^{-1} deoxygenated DDMAT solutions in tetrahydrofuran under long-wave radiation with an intensity of 100 μW cm^{-2} at 365 nm and 80 μW cm^{-2} at 420 nm at 30 °C at predetermined intervals; ^{1}H NMR spectra of deoxygenated bulky styrene under long-wave radiation with an intensity of 100 μW cm^{-2} at 365 nm and 80 μW cm^{-2} at 420 nm at 30 °C at predetermined intervals. This information is available free of charge via the Internet at http://pubs.acs.org.

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