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Dual Roles of a Xanthate as a Radical Source and Chain Transfer Agent in the Photoinitiated RAFT Polymerization of Vinyl Acetate

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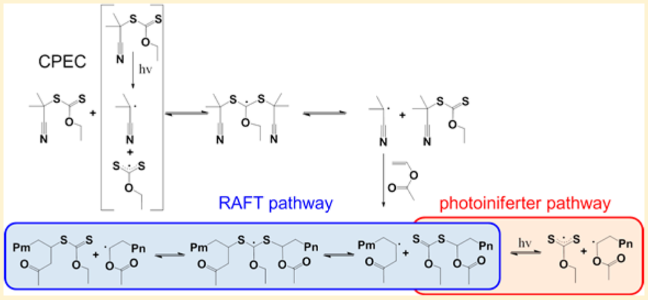
Ⓢ *Supporting Information*

ABSTRACT: A high level of control over the photoinitiated RAFT polymerization of vinyl acetate (VAc) was achieved using a specifically designed xanthate, *S*-2-cyano-2-propyl-*O*-ethyl xanthate (CPEC), which acted as a radical source and a chain transfer agent simultaneously. Unlike other RAFT processes, the present system did not use any additional radical initiator, while achieving greater control over the polymerization than the photoiniferter process. The molecular weight of the resulting polymer could be modulated by changing the initial $[VAc]_0/[CPEC]_0$ ratio, but the control over the polymerization was lost with a very low initial $[VAc]_0/[CPEC]_0$ ratio. The intensity of UV irradiation affected the polymerization by reducing the induction period and increasing the rate of polymerization but did not affect the molecular weight of the resulting polymer.



INTRODUCTION

Controlled radical polymerization (CRP) is one of the most acceptable and promising techniques developed over the last two decades for synthesizing competent functional polymers with predefined architectures, such as block, graft, and star polymers. Although several CRP techniques have been developed, systems involving atom transfer radical polymerization (ATRP),[1−5] nitroxide-mediated polymerization (NMP),[6−8] or reversible addition−fragmentation transfer (RAFT)[9−12] have received the most attention. Among these systems, the RAFT process is particularly attractive owing to its applicability for a wide range of vinyl monomers.

The majority of CRP systems are confined to thermal initiation process. Photoinitiated systems provide several advantages over thermally initiated polymerization reactions. With simple operational requirements and mild reaction conditions, photoinitiated systems permit control over the number of radicals through modulation of the light intensity.[13] In RAFT processes, the photolysis of the RAFT agent is critical for use in photoinitiation systems. Most RAFT agents bearing a thiocarbonylthio group, such as dithiobenzoate,[14] trithiocarbonate,[15,16] dithiocarbamate,[17,18] or disulfide,[19] decompose to generate additional radicals upon UV irradiation. Although this "photoiniferter" process is referred as a CRP system, it generally loses control at higher monomer conversion region due to chain end degradation upon UV exposure.[20]

Vinyl acetate (VAc) is one of the most commonly used vinyl monomers in polymer synthesis. It can be easily polymerized by radical polymerization; however achieving the CRP of VAc with control over the molecular weight (MW) and the MW distribution (MWD) has posed significant challenges for researchers because the corresponding propagating radicals are extremely reactive and tend to undergo chain transfer and chain termination reactions.[21] The CRP of VAc constitutes a major unmet need in the field of polymer science because PVAc can be easily hydrolyzed to produce poly(vinyl alcohol) (PVA), which has numerous applications. Only a few VAc CRP systems have been reported to provide controlled MW and MWD, to date.[22−28] Our group reported a photoinitiated RAFT of VAc using a conventional photoinitiator and a photolytically stable chain transfer agent (CTA). The polymerization reaction proceeded as a living polymerization, was remarkably rapid compared to the thermally initiated processes, and featured a very short induction period.[29] Unlike photoiniferter processes, the roles of the initiator and CTA were isolated to maintain control over the polymerization reaction up to the high conversion region.

This work reports a photoinitiated RAFT process using *S*-2-cyano-2-propyl-*O*-ethyl xanthate (CPEC) as both a photoinitiator and a CTA, simultaneously. CPEC can generate radicals under UV irradiation similar to conventional photoiniferters. However, as we reported in our previous report, the xanthate-derived polymer chain ends that formed after the addition of VAc units was sufficiently stable that the polymerization reaction could be controlled.[29] This differentiate our system from other photoiniferter processes. Even though there have been a few reports claiming RAFT mechanism in polymerization reactions involving thioester compounds under UV irradiation;[14,30] most of these reports dealt with the low conversion region for the polymerization

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reaction and failed to clearly differentiate these reactions from the photoiniferter process.

■ EXPERIMENTAL SECTION

Materials. VAc (98%, Aldrich) was stirred with calcium hydride overnight and distilled under reduced pressure twice before use. Methyl(ethoxycarbonothioyl)sulfanyl acetate (MESA) was synthesized according to the methods described in the literature as mentioned below.[31,32] Bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (BAPO) was received from Ciba Korea and was used without further purification. Azobis(isobutyryl nitrile) (AIBN) was recrystallized from methanol. Other materials were obtained from commercial suppliers and were used without further purification.

UV Source. Execure 4000-D (Hoya) equipped with a Hg–Xe lamp (Max power, 200 W) was used as a UV source. A filter that removed approximately 100% of the light with a wavelength below 300 nm was used. A UV light source emitting at 313, 365, 405, 436, 546, and 577 nm with an intensity of 25 μW cm^{-2} at 365 nm was obtained. The intensities were measured using a UV-A radiometer equipped with 365 and 420 nm sensors.

Synthesis of CPEC. CPEC was prepared in two steps according to the procedure by Zard and co-workers.[31]

Synthesis of O,O-Diethyl Bisxanthate. *O*,*O*-Diethyl bisxanthate was prepared by a method derived from that of Shi et al.[32] Potassium *O*-ethyl xanthate (10.80 g, 67 mmol) was dissolved in distilled water (50 mL). A solution of iodine (3.30 g) and potassium iodide (1.70 g) in distilled water (50 mL) was added dropwise. The mixture was left to stir for 48 h. Yellow/orange oil separated, which was extracted with diethyl ether (4 × 50 mL). The combined ethereal fractions were extracted with distilled water (5 × 50 mL), dried over anhydrous magnesium sulfate and the solvents were evaporated under vacuum. 6.80 g of yellow oil was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 4.69, 4H, q, ^3J = 7.1 Hz, (CH_2); 1.42, 6H, t, ^3J = 7.1 Hz, (CH_3).

Synthesis of S-2-Cyano-2-propyl-O-ethyl Xanthate. *O*,*O*-Diethyl bisxanthate (6.76 g, 28 mmol) and AIBN (5.40 g, 33 mmol) were dissolved in toluene (40 mL). The solution was degassed with argon for 30 min then placed in an oil bath at 80 °C. After 2 h an additional portion of AIBN (3.60 g, 22 mmol) was added. The reaction was stopped after 7.5 h. Solvents were evaporated under vacuum. The product was purified by column chromatography using hexane:ethyl acetate 95:5 (v/v) as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 4.74, 2H, q, ^3J = 7.2 Hz (CH_2); 1.75, 6H, s, ($C(CH_3)_2$); 1.52, 3H, t, ^3J = 7.2 Hz (CH_2CH_3).

Typical Procedure for Polymerization. The polymerization reaction was carried out in a sealed glass tube. VAc (1 mL; 10.8 M), CPEC (12.2 mg; 64.5 mM), and decalin (0.1 mL) were added to the 5 mL tube and degassed by three freeze-evacuate cycles. The tube was sealed under vacuum and placed under UV irradiation. Polymerization was performed in a thermostatically controlled chamber equipped with a UV source. The reaction tubes were placed at a certain fixed position from the UV light at desired temperatures. After the specified reaction time, the tube was removed from the thermostat and placed in liquid nitrogen to quench the polymerization reactions. The tube was then broken, and the reaction mixture was diluted with toluene. The resulting polymers were precipitated in ether, filtered, and dried overnight in a vacuum oven at 30 °C.

Determination of Monomer Conversion. The monomer conversion was determined by measuring the concentration of the remaining monomer using gas chromatography (GC). Agilent 7890A GC was performed using an instrument equipped with a flame ionization detector. A nonpolar HP-5 capillary column was used for the separation. The concentration of VAc was calculated using decalin as an internal standard. At appropriate time intervals, small aliquots were removed from the reaction mixture and placed in liquid nitrogen to stop the polymerization reaction. The quenched mixture was diluted with toluene and characterized by GC without further purification.

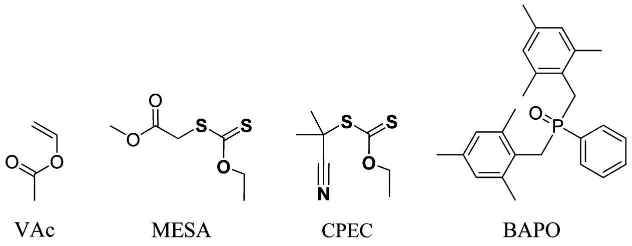
Determination of MW and MWD. Gel permeation chromatography (GPC) was performed using a Waters GPC system equipped with a refractive index detector. THF was used as the mobile phase. Samples were prepared as 0.5–2% (w/v) solutions in THF and passed through 0.45 μm filters prior to injection. Separations were performed using a series of Polymer Laboratory Mixed C columns at a flow rate of 1 mL min^{-1} at 25 °C. The column was calibrated using narrow mass dispersity polystyrene calibration standard (Polymer Laboratory, PS calibration kit, MW range 1090–419000 Da). A third-order polynomial was used to fit the log *M* versus elution volume calibration curve.

Photochemical Degradation of CPEC and BAPO. Solutions containing CPEC and BAPO in THF (3 mmol L^{-1}) were irradiated using the UV source for a given period of time. Subsequently, the UV–vis spectra of these solutions were recorded using an HP 8452A spectrometer to determine the remaining concentration of the compounds.

■ RESULTS AND DISCUSSION

The chemical structures of xanthates and photoinitiator are depicted in Scheme 1. CPEC is sensitive to UV light and can generate a tertiary carbon-centered radical that is identical to the radical formed by AIBN. The homolytic cleavage of CPEC under UV irradiation was confirmed by measuring the UV spectral changes. A plot showing the continuous decrease in the absorption spectra over the range 350–400 nm over time is presented in Figure 1a. The linear plot of ln[CPEC]$_0$/[CPEC]$_t$ vs the polymerization time indicated first order kinetics corresponding to the steady dissociation of CPEC (Figure 1b). The decomposition of CPEC was slower than that of BAPO, a conventional photoinitiator examined in our previous work. The first order decomposition rate constant (k_d) of

Scheme 1. Chemicals Used in This Study: Vinyl Acetate (VAc), Methyl(ethoxycarbonothioyl)sulfanyl Acetate (MESA), *S*-2-Cyano-2-propyl-*O*-ethyl Xanthate (CPEC), and Bis(2,4,6-trimethylbenzoyl)phenylphosphine Oxide (BAPO)



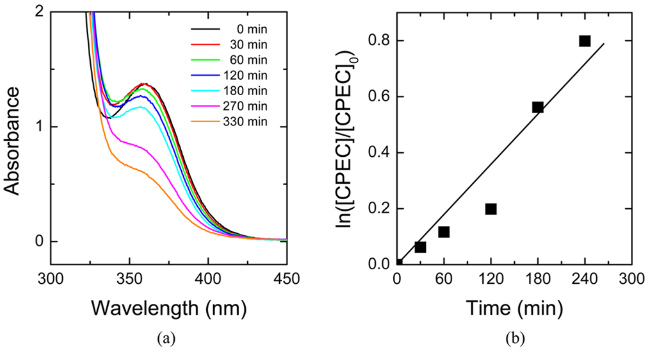
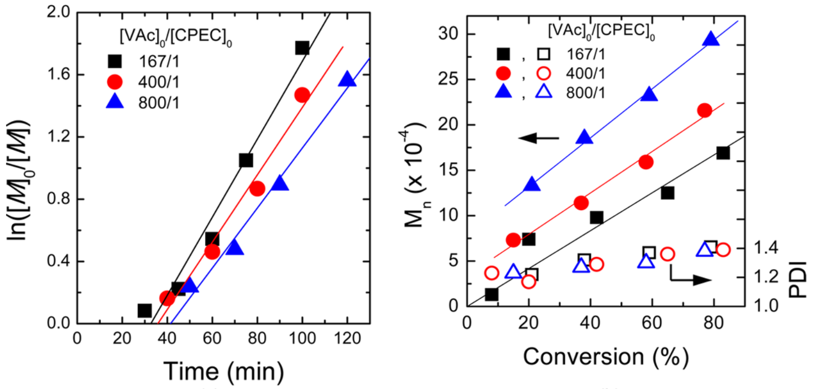


Figure 1. (a) UV–vis absorption spectra of CPEC decomposition were taken at different interval of time and (b) ln[CPEC]$_0$/[CPEC]$_t$ vs time kinetic graph. Conditions: [CPEC]$_0$ = 3 mmol L^{-1} in THF with UV irradiation at 25 μW cm^{-2} at 365 nm and 60 °C.

Table 1. Roles of CPEC in the Bulk Polymerization of VAc[a]

run	$[AIBN]_0$ (mM)	$[CPEC]_0$ (mM)	$[MESA]_0$ (mM)	time (min)	convn (%)	$M_{n,exp}$[b]	M_w/M_n
1[c]		1.5	64.5	90	81	10600	1.24
2	13.5	64.5		1440	46	5600	1.14
3[c]		64.5		100	83	16900	1.38

[a] $[VAc]_0$ = 10.8 M, all the polymerizations were performed at 60 °C. [b] Determined by GPC using polystyrene standard in THF. [c] Hg−Xe UV source using 300 nm cut off filter at 25 μW cm^{-2} intensity.



(a) (b)

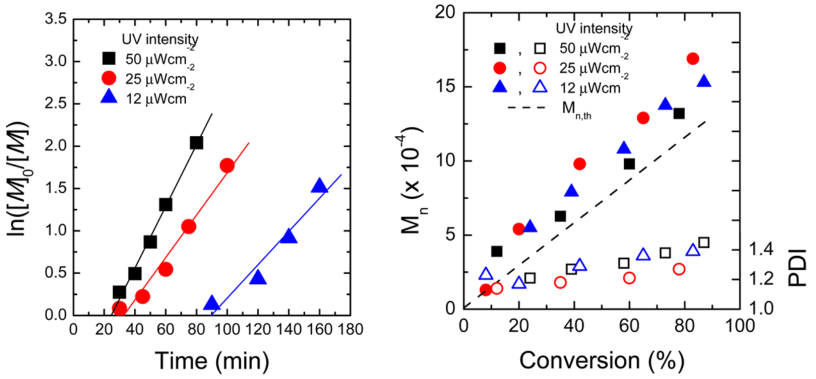
Figure 2. (a) Kinetic plots of the photoinitiated bulk polymerization of VAc, (b) Evolution of M_n (filled symbols) and MWDs (open symbols) using different molar concentration of $[VAc]_0/[CPEC]_0$. Conditions; $[VAc]_0$ = 10.8 M, all the polymerizations were performed at 60 °C under Hg−Xe UV source using 300 nm cut off filter at 25 μW cm^{-2} intensity.

CPEC was 5.7×10^{-5} s^{-1}, lower than the corresponding value for BAPO (7.4×10^{-4} s^{-1}; Supporting Information) and higher than the thermal dissociation rate constant of AIBN at 60 °C (1.3×10^{-5} s^{-1}; see Supporting Information).

The role of CPEC as a photoinitiator or a CTA in the RAFT of VAc was examined under conditions that promoted its action as a photoinitiator. CPEC was successfully employed as a photoinitiator for the polymerization of VAc using MESA as a RAFT agent. A high monomer conversion (>80%) was attained, and the resulting polymer showed a narrow MWD (Table 1, run 1). Because MESA was photochemically stable under the reaction conditions,[29] radicals were expected to be generated by the photolysis of CPEC. As expected from the UV decomposition data, the polymerization reaction was slower than the reaction involving BAPO as a photoinitiator but faster than the reaction involving AIBN as a thermal initiator.[29] The polymerization of VAc using AIBN as a thermal initiator and CPEC as a CTA in absence of UV irradiation at 60 °C underwent a long induction period during polymerization. The polymer that had formed had a narrow MWD, confirming that CPEC acted as an effective CTA for the RAFT polymerization of VAc (Table 1, run 2). Bulk polymerization of VAc using CPEC concurrently as both a photoinitiator and as a CTA proceeded smoothly to give polymers with a controlled MW and MWD (Table 1, run 3). A linear relationship between $\ln([M]_0/[M])$ and the polymerization time was maintained and the MW increased linearly as a function of the monomer conversion throughout polymerizations in all cases, demonstrating that the polymerization reaction remained under control.

The effects of the initial molar ratio of $[VAc]_0/[CPEC]_0$ were examined. The kinetic behavior of the VAc polymerizations using three different $[VAc]_0/[CPEC]_0$ ratios (800/1, 400/1, and 167/1) was studied at 60 °C. Figure 2(a) shows the linear evolution of the semilogarithmic kinetic curves, which indicated the occurrence of first order kinetics and a steady number of radicals present during the polymerizations. The rate of polymerization was found to be directly proportional to the initial $[VAc]_0/[CPEC]_0$ ratio. The apparent propagation rate constant (k_{app}) for the polymerization reactions conducted using initial $[VAc]_0/[CPEC]_0$ ratios of 800/1, 400/1, and 167/1 were found to be 4.17, 3.60, and 3.21×10^{-4} s^{-1}, respectively. These results may be due to the higher concentration of CPEC, which produced a greater number of radicals and increased the polymerization rate. As in other RAFT processes of VAc using xanthates,[33] the polymerization displayed an initial induction/retardation period before xanthate had completely converted into the single monomer adduct. The concentration of CPEC affected the induction period in two different ways. The higher concentration of radicals generated from the higher concentration of CPEC shortened the pre-equilibrium time; however, the higher concentration of CPEC required additional time to achieve total conversion to the monomer adducts. These results indicated that the induction period shortened as the concentration of CPEC increased, although the effect was small. The high radical concentration dominated the polymerization properties. It should be noted that a high monomer conversion (>80%) was achieved within a very short time span. This result is difficult to achieve in a RAFT process under UV irradiation in the absence of conventional photoinitiator,[13] dissociation combination,[14] or photoiniferter pathways.[19]

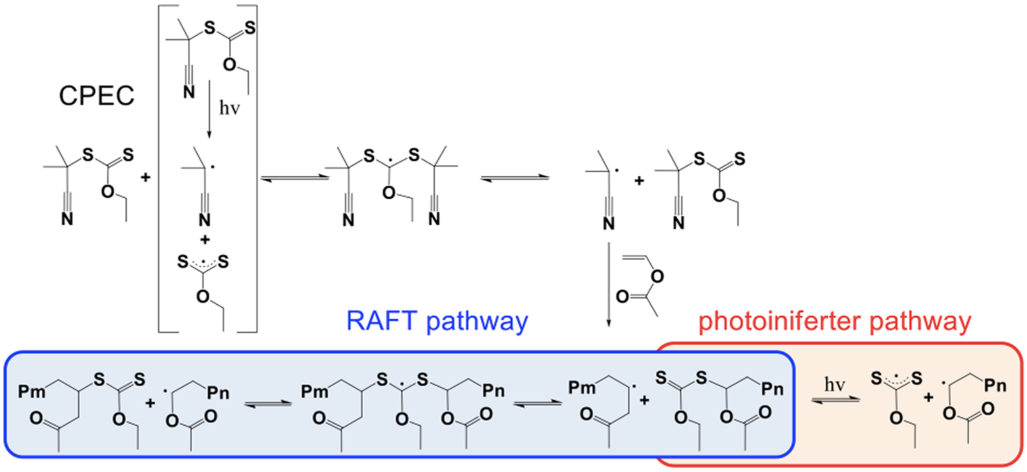
Figure 2b shows the dependence of M_n and PDI on the monomer conversion during the bulk polymerizations of VAc at 60 °C with different initial ratios of $[VAc]_0/[CPEC]_0$. The M_n of the obtained polymers varied with the initial $[VAc]_0/[CPEC]_0$ ratio and increased in direct proportion to the monomer conversion. At low $[VAc]_0/[CPEC]_0$ ratios, a plot of M_n vs the conversion followed a linear relationship. An abrupt increase in M_n was observed in the low conversion region for the polymerization reaction conducted with a high value of $[VAc]_0/[CPEC]_0$, indicating that the polymerization system lost control under a low CTA (CPEC) concentration. The PDI



(a) (b)

Figure 3. (a) Kinetic plots of the photoinitiated bulk polymerization of VAc. (b) Evolution of M_n (filled symbols) and MWDs (open symbols) using CPEC at different UV intensities. Conditions: $[VAc]_0$ = 10.8 M; $[VAc]_0/[CPEC]_0$ = 167/1 under UV irradiation at 365 nm at 60 °C.

Scheme 2. Proposed Pathway of VAc Polymerization Using CPEC under UV Irradiation



of the resulting polymers remained less than 1.4, and the lowest values were obtained even at a high monomer conversion for $[VAc]_0/[CPEC]_0$ = 167/1. However, a lack of control over the MWD (1.58) was observed in the high conversion (~72%) when $[VAc]_0/[CPEC]_0$ was as high as 7200/1, possibly because less CPEC was available as CTA under high conversion conditions.

The effects of the UV intensity on the polymerization reaction were examined. Figure 3a shows plots of the kinetic data along with the fitted curves, revealing that the number of radicals remained constant throughout the polymerization reaction. The rate of polymerization was found to be directly proportional to the intensity of the UV light. The value of k_{app} for the polymerization reactions was calculated from the slope of a linear plot of $\ln([M]_0/[M])$ vs time. UV intensities of 12, 25, and 50 μW cm^{-2} yielded k_{app} values of 3.27, 4.17, and 6.10 $\times 10^{-4}$ s^{-1}, respectively. These results revealed that the overall number of radicals could be controlled by modulating the light intensity. It should be noted that the induction time decreased as the intensity of the UV light increased, yielding induction times of 90, 30, and 25 min for UV intensities of 12, 25, and 50 μW cm^{-2}, respectively. Unlike the effects of varying the $[VAc]_0/[CPEC]_0$ ratio, modulating the UV intensity significantly affected the induction period. A higher UV intensity resulted in the generation of a greater number of radicals from CPEC and reduced the concentration of CPEC remaining in solution. A shorter induction period was, therefore, required before the polymerization reaction began. Figure 3b shows a plot of M_n and PDI as a function of the monomer conversion at different UV intensities. M_n for the polymers was found to increase continuously as the conversion proceeded, and the PDI remained below 1.4. M_n was found to remain constant at all UV intensities, indicating that M_n depended only on the initial $[VAc]_0/[CPEC]_0$ ratio. The experimentally determined values were slightly higher than the theoretically calculated values, which was determined that all polymer chains were generated from CPEC, whether through homolytic cleavage by UV irradiation or through chain transfer pathways.

A possible polymerization pathway was proposed to explain the experimental results. It is similar to the one we proposed for the photoinitiated RAFT process in our previous report,[29] except the radical generation process. During the polymerization of VAc in the presence of CPEC under UV irradiation, the weakest bonds (C−S) in the CPEC were expected to undergo facile homolytic cleavage (confirmed by the UV spectra) to form a tertiary carbon-centered radical and resonance-stabilized thiocarbonylthio radical. The radicals produced reacted with other CPEC molecules to generate another CPEC and carbon-centered radical, and these radicals could initiate polymerization according to the mechanism shown in Scheme 2. The polymerization of VAc using CPEC was thought to follow the RAFT mechanism because CPEC displayed CTA character in the thermally initiated RAFT polymerization of VAc (Table 1, entry 2). Therefore, the use of

UV light to generate radicals was unlikely to lead to a completely different polymerization mechanism;[14] however, as reported previously, the polymer chain ends were not perfectly stable under UV exposure, and they cleaved to form additional polymer radicals and thiocarbonylthio radicals (photoiniferter pathway). Because the persistent radical effects of the thiocarbonylthio radicals were not as dominant as in the nitroxide-mediated polymerization or in atom transfer radical polymerization reactions, conditions that favored the photoiniferter pathway resulted in the loss of control over the polymerization reaction. The higher degree of control afforded by the present system compared to conventional photoiniferter processes suggested that the present system mainly proceeded through a RAFT process. At this stage, it is difficult to determine the ratio of the prevalence of each pathway because the polymers generated by RAFT or photoiniferter mechanisms would yield identical structures.[34]

■ CONCLUSION

In summary, CPEC was successfully designed for the controlled radical polymerization of VAc at 60 °C in the presence of UV irradiation. The different roles of CPEC were examined in the polymerization of VAc under different reaction conditions. Kinetic studies firmly demonstrated that polymerization continued with controlled behavior. In contrast with the photoiniferter system, CPEC yielded a high monomer conversion (>80%) within a very short time span without losing control over the MWDs in all cases. The rate of polymerization under UV irradiation was very fast, with a short induction period compared to the induction period displayed by a thermal RAFT process. The MW of the resulting polymers could be modulated by changing the initial ratio of $[\mathrm{VAc}]_0/[\mathrm{CPEC}]_0$. The degree of control over the polymerization reaction decreased in the presence of very small amounts of CPEC, and it would have been difficult to obtain a very high polymer MW using the system. The intensity of the UV light increased the rate of polymerization but did not affect the MW of the resulting polymers. Even though the proposed system showed difference from the photoiniferter process, there still are remaining uncertainties in the polymerization mechanism. The chain ends are not perfectly stable under UV irradiation, and proceed through photoiniferter pathway. The relative ratio of the RAFT pathway and the photoiniferter pathway is not clear because the both pathways render the same chain end structure. Moreover, amount and fate of the thioester radicals generated by the homolytical cleavage of the chain ends have not been cleared out yet. More kinetic studies to verify those aspects need to be followed.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

UV–vis absorption spectra of CPEC and AIBN decomposition . This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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