

Reversible Addition–Fragmentation Chain Transfer Polymerization of *N*-Isopropylacrylamide: A Comparison between a Conventional and a Fast Initiator

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Received: June 5, 2007; In Final Form: July 28, 2007

The reversible addition–fragmentation chain transfer (RAFT) polymerization of *N*-isopropylacrylamide (NIPAM) was studied to determine the reasons for deviation of experimental molecular weights to lower molecular weight at high monomer conversion when *S*-1-dodecyl-*S*-(α,α' -dimethyl- α'' -acetic acid)trithiocarbonate (CTAm) and *S,S*-bis(α,α' -dimethyl- α'' -acetic acid)trithiocarbonate (CTAd) were used as RAFT agents at 65 °C. For this purpose, experiments were performed in *N,N'*-dimethylformamide (DMF) at the NIPAM/CTA ratio of 200 with initiators capable of yielding fast and slow initiation, respectively by photochemical and thermal process, either at ambient temperature or at 65 °C. When the polymerization of NIPAM was conducted under these conditions with Irgacure-2959 (IRGC) as photoinitiator, a continuing supply of primary radicals by incremental initiator addition was required to achieve reasonably high conversion. This effect was also apparent by the loss of linearity of the first-order kinetic plot with a conventional initiator (4,4'-azobis(4-cyanovaleric acid) (ACVA) as azo-initiator, 10h (t_{1/2}) decomposition at 65 °C) indicating that steady-state concentration of the macroradical decreases significantly with the initiator consumption. Nevertheless, polymers with predictable number-average molecular weight M_n (i.e., based on [monomer]/([CTA] + [initiator]) ratio) and narrow polydispersities were obtained (PDIs \ll 1.2) with CTAm indicating that the process of chain growth was controlled. When CTAd was used, instead of CTAm, the polymers obtained were characterized by a larger polydispersity (1.2 < PDIs < 1.3). The so-called “living steady-state concentration” in chain equilibration together with the linear dependence of M_n vs conversion was observed only when the 200/1 NIPAM/CTA mixture in DMF was subjected to a permanent photoirradiation at 65 °C. With ACVA, the deviation of the experimentally measured molecular weights at high conversion was accounted for by the simultaneous self-initiated polymerization of NIPAM with the controlled process in the presence of CTA at 65 °C. Similar drift from the linear dependence M_n vs conversion was also observed at 65 °C when a significant number of low molecular weight polymer chains were generated intentionally by photodecomposition of IRGC.

Introduction

The reversible addition–fragmentation chain transfer (RAFT) process¹ has emerged as an important radical polymerization technique for producing polymers of controlled architecture (e.g., block and star) for a wide range of monomer (e.g., *N*-isopropylacrylamide (NIPAM)^{2–16}) and experimental conditions (e.g., water, organic solvent, and bulk). The mechanism given in the Scheme 1 relies on the chain transfer of growing radical, P_n^\bullet , to the RAFT agent, $R-X$, followed by the fragmentation of the intermediate, $P_n-X^\bullet-R$, to liberate the living group, R^\bullet , which then reinitiates the polymerization. Once the RAFT agent has been consumed, chain equilibration is established between active and dormant species and, in the presence of a suitable RAFT agent, polymers with predictable number average molecular weights (M_n) and narrow polydispersities (PDIs) < 1.3 can be produced during the course of the polymerization. In these systems, the stationary state kinetics, $-d\ln[M]/dt = k_p(R_i/k_t)^{1/2}$, are governed by the rate of conventional initiation (R_i), the concentration of monomer ([M]), and the rate constants of propagation and termination (k_p and k_t , respectively).

At present, there are several reports detailing the RAFT polymerization of NIPAM. For example, Ganachaud et al.,² who first reported the RAFT polymerization of NIPAM, showed that the use of benzyl dithiobenzoate (in benzene) or cumyl dithiobenzoate (in 1,4-dioxane) as RAFT agent in conjunction with 2,2'-azobis-isobutyronitrile (AIBN) as azo-initiator at 60 °C yields a wide range of polymers with polydispersities (PDIs) < 1.4. Despite the THF-based gel permeation chromatography (GPC) characterization problems encountered with the aggregation of PNIPAM in THF, the authors were able to determine the number average molecular weight (M_n) and molecular weight distributions (MWDs) by combining intrinsic viscosity and MALDI-TOF data. By this approach, it has been shown that the system was indeed controlled and that M_n increases linearly with conversion with a broadening of the MWDs. Similar results were reported by Schilli et al., who used benzyl 1-pyrrolocarbodithiate and cumyl 1-pyrrolocarbodithiate as RAFT agents at 65 °C in 1,4-dioxane.³ Although low molecular weight products formed by disproportionation and direct initiation/termination from the isobutyronitrile radicals were observed by MALDI-TOF, none of the aforementioned authors^{2,3} or other researchers in the field^{9–13} reported any deviation of the experimental molecular weights resulting from

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Initiation

Initiator \xrightarrow{M} P_n^\bullet + $S=C(S-R)_2$

Chains growth ($X-R$)

$P_n^\bullet + S=C(S-R)_2 \xrightleftharpoons[k_{fr}]{k_{add}} P_n-S-C(S-R)_2^\bullet \xrightleftharpoons[k_{add}]{k_{fr}} P_n-S-C(S-R)=S + R^\bullet$

Chains growth (P_n-X)

$Z = CH_3, Ph, R-S, OEt, NEt_2, \text{ etc... fragment}$
 $R = \text{initially a radical and subsequently a macroradical leaving fragment}$

Termination

$P_n^\bullet + P_m^\bullet \rightarrow \text{dead polymer}$

The aim of this paper is to examine the control over M_n and PDI of a model RAFT polymerization system when low molecular weight polymer chains are intentionally produced during the course of the polymerization. For this purpose, the RAFT polymerization of NIPAM in DMF with *S*-1-dodecyl-*S*-(α,α' -dimethyl- α'' -acetic acid)trithiocarbonate (CTAm) and *S,S*-bis(α,α' -dimethyl- α'' -acetic acid)trithiocarbonate (CTAd) as RAFT agent, was studied with initiators capable of yielding fast (Irgacure-2959, IRGC) and slow (4,4'-azobis(4-cyanovaleric acid), ACVA) production of primary radicals respectively by

In a typical polymerization experiment of 33 w/v % solution of *N*-isopropylacrylamide in DMF, 1 g of NIPAM, 2 mL of DMF, 1 mL of stock solution in DMF of ACVA (2.5 mg, 10 mL), and the required amount of RAFT agent (16.953 mg of CTAm or 11.53 mg of CTAd) were prepared and mixed vigorously at ambient temperature in a Schlenk tube fitted with a glass stopper. The solutions were subsequently subjected to 3–4 freeze–pump–thaw cycles. The polymerizations were then carried out under nitrogen atmosphere in an oil bath at 65 °C. The initial concentrations were the following: [NIPAM]₀ = 2.95 M, [CTA]₀ = 14.75 mM, and [ACVA]₀ = 2.95 mM. After proper time intervals, samples of ~0.1 mL of the polymerizing

solution were taken with use of an anaerobic sampling technique and then quenched by a solution of 10^{-3} M of hydroquinone in DMF. The fraction of unreacted monomer was determined by ^1H NMR spectroscopy in $\text{DMSO}-d_6$ solution: 200 MHz ^1H ($\text{DMSO}-d_6$) δ 0.8–1.5 ppm (2H, $-\text{CH}_2-$), 1.5–2 ppm (1H, $-\text{CHCO}-$), 5.2–5.4 ppm (2H, $\text{CH}_2=$), 5.8–6 ppm (1H, $=\text{CHCO}-$), 3.4–3.8 ppm (1H, CH), 0.8–1 ppm (6H, $\text{C}(\text{CH}_3)_2$). The integration of the monomer resonance peaks at around 5.8–6 ppm and at around 5.2–5.4 ppm was compared with the mixture of monomer/polymer resonance peaks at around 3.4–3.8 ppm and at around 0.8–2 ppm. As an example, the results with CTAm and CTAd as RAFT agent for $\sim 60\%$ monomer conversion were as followed: $t = 60$ min, $M_{n(\text{GPC})} = 13\,210$ g/mol and $M_w/M_n = 1.09$ (CTAm, polymer sample S1.5); $t = 45$ min, $M_{n(\text{GPC})} = 13\,995$ g/mol and $M_w/M_n = 1.227$ (CTAd, polymer sample S2.4).

RAFT Photopolymerization of NIPAM in the Presence of IRGC (350 nm). In a typical photopolymerization experiment of 33 w/v % solution of NIPAM in DMF, using CTAm as RAFT agent, 1 g of NIPAM and 16.953 mg of CTAm in 3 mL of DMF were mixed vigorously at ambient temperature in a Schlenk tube fitted with a glass stopper. Then 10–75 μL of IRGC stock solution in DMF (66 mg, 58.9 mM) was added. The solutions were subsequently subjected to 3–4 freeze–pump–thaw cycles. The initial concentrations were the following: $[\text{NIPAM}]_0 = 2.95$ M, $[\text{CTAm}]_0 = 14.75$ mM, and $[\text{IRGC}]_0 \leq 2.94$ mM ($[\text{CTAm}]/[\text{IRGC}] \leq 5$). The photopolymerization was carried out under nitrogen atmosphere in a Rayonet photoreactor (Southern N.E. Ultraviolet Co.), using 16 75W UV lamps having a 350 nm wavelength. The photoinitiation was carried out at either ambient temperature or 65°C . After a proper time of irradiation (t_i), the polymerization was stopped by cooling into liquid nitrogen and an ~ 0.1 mL sample of the polymer solution was taken. The fraction of unreacted monomer was determined by ^1H NMR spectroscopy in $\text{DMSO}-d_6$ solution. As an example, for polymer sample S8.1, results obtained at ambient temperature with $[\text{IRGC}]_0 = 588.7$ μM (introduction of 30 μL of 58.93 mM IRGC stock solution) were as follows: conversion = 21.4% ($t_i = 20$ min), $M_{n(\text{GPC})} = 4827$ g/mol, and $M_w/M_n = 1.147$.

The polymer solution containing the monomer was further polymerized by the incremental photoinitiator addition technique. As an example, the second incremental photoinitiator addition, polymer sample S8.2, was carried out by introduction of 30 μL of IRGC stock solution in DMF (66 mg, 58.9 mM) into the Schlenk tube containing the remaining ~ 2.9 mL polymer/monomer solution in DMF. The Schlenk tube sealed with a glass stopper was subsequently subjected to 3–4 freeze–pump–thaw cycles. The photoinitiation was carried out under nitrogen atmosphere at ambient temperature as highlighted above. The results were as follow: conversion = 37.5% ($t_i = 20$ min), $M_{n(\text{GPC})} = 6860$ g/mol, and $M_w/M_n = 1.07$.

RAFT Photopolymerization of NIPAM without IRGC. Photopolymerization of a 33 w/v % solution of NIPAM in DMF in the presence of CTA was carried out as described above at either ambient temperature or 65°C . The initial concentrations were the following: $[\text{NIPAM}]_0 = 2.95$ M and $[\text{CTAm}]_0 = 14.75$ mM. After a predetermined time of irradiation (t_i), the polymerization was stopped by cooling with liquid nitrogen and samples of ~ 0.1 mL were taken. The polymer solution containing the monomers was further photopolymerized at 350 nm at the same temperature after being subjected to 3–4 freeze–pump–thaw cycles. As an example, results obtained for a time of irradiation of 7 min at 65°C with $[\text{NIPAM}]_0 = 2.95$

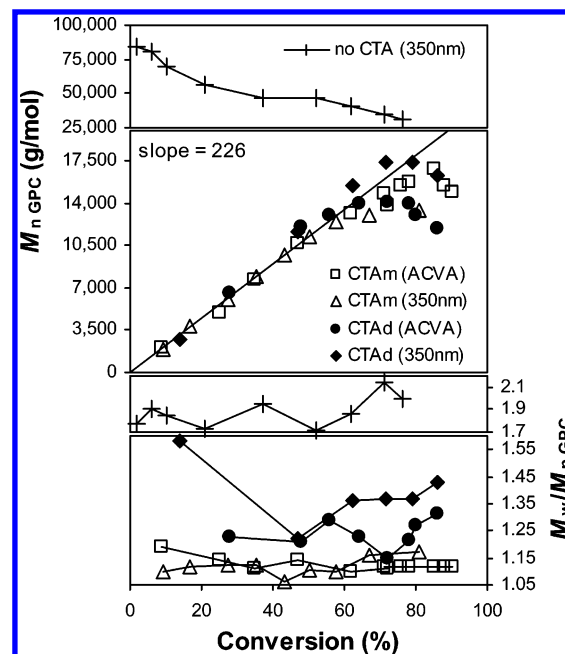


Figure 1. $M_{n(\text{GPC})}$ (number-average molecular weight) and $M_w/M_{n(\text{GPC})}$ (molecular weight distribution) vs conversion dependences for the NIPAM (2.95 M in DMF) polymerization with 4,4-azobis(4-cyanovaleic acid) (ACVA) (2.95 mM) as initiator (\square , \bullet) and for the NIPAM (2.95 M in DMF) photopolymerization at 350 nm (Δ , \blacklozenge) at 65°C in the absence (+) and in the presence of trithiocarbonate R-S(CS)S-C(CH₃)₂COOH (14.75 M) with R = C(CH₃)₂COOH (\bullet , \blacklozenge) and C₅H₁₂– (Δ , \square). For additional experimental details see Table 1–4 (series S1–5) in the Supporting Information. Targeted $M_n = 22\,600$ g/mol; (—) is the theoretical dependences of M_n vs conversion (%) calculated on the bases of mole of NIPAM converted into polymers for 100% CTAm and IRGC efficiency. (For GPC RI traces see Figures S1–5 in the Supporting Information.)

M and $[\text{CTAm}]_0 = 14.75$ mM in 3 mL of DMF, series S5, were as follows: conversion = 9% ($M_n = 1980$ g/mol and PDI = 1.1); conversion = 16.7% ($M_n = 3780$ g/mol and PDI = 1.1).

Results and Discussions

In all experiments, the polymerization of 33% w/v of NIPAM in DMF was conducted either at room temperature or at 65°C , using 8.85 mmol of NIPAM, 3 mL of DMF, 44.25 μmol of RAFT agent (CTAm or CTAd), and the required amount of initiator (IRGC or ACVA).

Polymerization of NIPAM with ACVA at 65°C . When S-1-dodecyl-S-(α,α' -dimethyl- α'' -acetic acid)trithiocarbonate (CTAm) was used as RAFT agent, polymers with predictable number average molecular weight $M_{n(\text{GPC})}$ (i.e., based on the moles of NIPAM converted into polymer for 100% CTA efficiency) and narrow molecular weight distributions (MWDs) ($1.05 < M_w/M_n < 1.15$) were obtained. $M_{n(\text{GPC})}$ values increase linearly with conversion and then, as soon as $\sim 78\%$ of monomer was consumed, the $M_{n(\text{GPC})}$ decreases with a broadening of the MWDs (see Figures 1 and 2).

The examination of the GPC traces of PNIPAM (Figure 2) at 90% conversion ($t = 72$ h: $M_{n(\text{GPC})} = 14\,870$ g/mol and PDI = 1.18) showed a tail that was not observed at 78% monomer conversion ($t = 4$ h: $M_{n(\text{GPC})} = 15\,480$ g/mol and PDI = 1.1) indicating that termination reactions were taking place together with the formation of new growing polymer chains. When a 33 w/v % solution of NIPAM in DMF was heated at 65°C , high molecular weight polymer chains with large polydispersity ($M_{n(\text{GPC})} = 72\,450$ g/mol and PDI = 1.9) were formed after

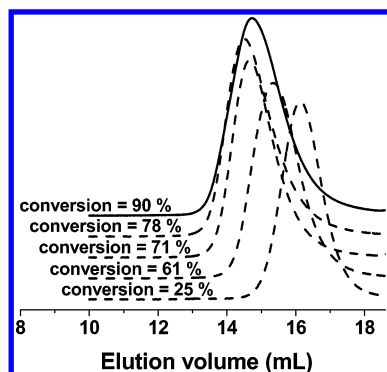


Figure 2. GPC RI traces of PNIPAM in the polymerization of NIPAM with *S*-1-dodecyl-*S*-(α,α' -dimethyl- α'' -acetic acid)trithiocarbonate (CTAm) and 4-azobis(4-cyanovaleric acid) (ACVA) at 65 °C in DMF; [NIPAM]₀ = 2.95 M, [CTAm]₀ = 14.75 M, and [ACVA]₀ = 2.95 mM. (For additional experimental details see Table 1 (series S1) in the Supporting Information.)

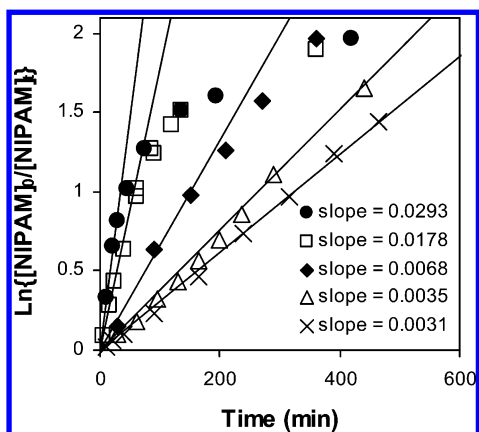


Figure 3. Evolution of $\ln\{[NIPAM]_0/[NIPAM]_t\}$ against time for the NIPAM (2.95 M in DMF) polymerization with 4,4'-azobis(4-cyanovaleric acid) (ACVA) (2.95 mM) as initiator (\square , \bullet) and for the NIPAM (2.95 M in DMF) photopolymerization at 350 nm (Δ , \blacklozenge , \times) at 65 °C (Δ , \blacklozenge , \times , \square , \bullet) in the absence (\times) and in the presence of trithiocarbonate R-S(CS)₂-S-C(CH₃)₂-COOH (14.75 mM) with R = C(CH₃)₂-COOH (\bullet , \blacklozenge) and C₅H₁₂- (Δ , \square). (For experimental details see Table 1-4 (series S1–5) in the Supporting Information.)

17 h (conversion = 11%) indicating that the self-initiated polymerization of NIPAM occurred. In the presence of CTAm and without any initiator, the yield at 65 °C after 17 h was slightly lower (conversion = 8–9%) and polymer with predictable number average molecular weight (i.e., based on $[NIPAM]/[CTA]$) and narrow polydispersity ($M_{n(GPC)} = 2100$ g/mol and $PDI = 1.18$) was obtained. When *S,S*-bis(α,α' -dimethyl- α'' -acetic acid)trithiocarbonate (CTAd) (14.75 mM) was used instead of CTAm for the controlled polymerization of 2.95 M NIPAM in DMF with 2.95 mM ACVA at 65 °C, the polymer obtained was characterized by a broader MWDs ($1.23 < M_w/M_n < 1.31$) and the loss of the control over $M_{n(GPC)}$ was observed at lower conversion: 64% against 78% when CTAd was used instead of CTAm. (The data from this study are listed in the Tables 1 and 2 in the Supporting Information.)

In the Figure 3, the curvature of the slope plot of $\ln\{[NIPAM]_0/[NIPAM]_t\}$ against time as well as the decrease of the $k_{app,CTAd}/k_{app,CTAm}$ ratio from ~ 2 to 1 were then accounted for by the significant decrease of the steady-state concentration of the propagating macroradical during the process of chain growth. Similar deviation was also observed by Convertine et al.⁶ when CTAm in conjunction with AIBN was used in the ambient temperature RAFT polymerization of NIPAM in DMF.

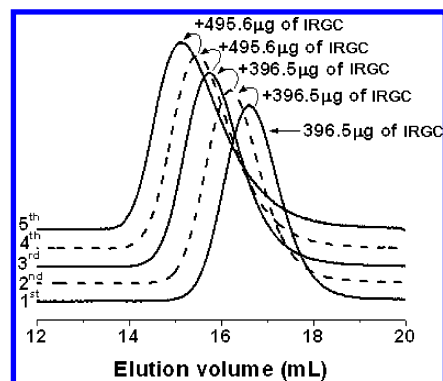


Figure 4. GPC RI traces of PNIPAM in the RAFT polymerization of NIPAM with CTAm in DMF studies by the incremental photoinitiator (IRGC) addition technique at ambient temperature; [NIPAM]₀ = 2.95 M, [CTAm]₀ = 14.75 mM, and [IRGC]₀ = 583 μ M. For a time of photoirradiation of 20 min at 350 nm (1.2 KW/s²) the concentration of each increment of IRGC and results were the following: (first) 396.5 (583) μ g (μ M), $M_n = 4827$ g/mol, $PDI = 1.147$; (second) 396.5 (603) μ g (μ M), $M_n = 6860$ g/mol, $PDI = 1.07$; (third) 396.5 (625) μ g (μ M), $M_n = 9675$ g/mol, $PDI = 1.085$; (fourth) 495.6 (820) μ g (μ M), $M_n = 11\,824$ g/mol, $PDI = 1.124$; (fifth) 495.6 (852) μ g (μ M), $M_n = 13\,544$, $PDI = 1.167$. (For additional experimental details see Table 5 (series S7) in the Supporting Information.)

Polymerization of NIPAM with IRGC at Ambient Temperature. To minimize the broadening of the MWDs arising from the slow decomposition of ACVA (10 h ($t_{1/2}$) decomposition at 65 °C) and the self-initiated polymerization of NIPAM at 65 °C, IRGC (preferred to AIBN initiator: 10 h ($t_{1/2}$) decomposition at 37 °C) was then used as fast initiator as it can be photodecomposed quantitatively (no irreversible terminations by “cage effect”)¹⁸ within 5–7 min (16.75 W/s² UV lamps with wavelength of 350 nm) at ambient temperature. When the polymerization of 33 w/v % NIPAM solution in DMF was carried out at ambient temperature in the presence of CTAm (14.75 mM) and IRGC (162 μ g < IRGC < 990 μ g) as photoinitiator, the polymerization stopped once the time required for the quantitative photochemical decomposition of the initiator at 350 nm was passed.¹⁹ Indeed, for a time of irradiation of 20 min (> 7 min), the use of 196, 395.6, 530, 660, and 990 μ g yields 6.9%, 20.6%, 35.4%, 37.9%, 45.2% conversion, respectively. However, polymers with predictable number average molecular weight and narrow polydispersities ($1.1 < PDIs < 1.2$) were obtained, indicating that the process of chain growth was controlled. On the other hand, the use of 1.9 mg of IRGC ($[ACVA]_0/[IRGC]_0 = 5$) leads to a quantitative polymerization ($\sim 94\%$) and the production of polymer with a large polydispersity ($M_n = 19\,980$ g/mol, $PDI = 1.98$). These experiments show that chain equilibration in the *reversible addition–fragmentation* process required a continuing supply of primary radicals. This decrease of the rate of initiation supports the curvature of the first-order plots of $\ln\{[NIPAM]_0/[NIPAM]_t\}$ against time that was observed when ACVA was used as the initiator for the polymerization of NIPAM in the presence of CTA (CTAm and CTAd) at 65 °C. The data from this study are listed in Table 5 in the Supporting Information.

To complete the polymerization, the macro-CTA solution containing the monomer was further polymerized by using the incremental photoinitiator addition technique. When three increments of 396.5 μ g were followed by two increments of 495.6 μ g of IRGC, Figure 4 series S7, the M_n of the existing polymer chains increased proportionally to the monomer conversion after each addition. In Figure 5, it can be seen that $M_{n(GPC)}$ of the resulting polymer (conversion = 75% ($t_i = 5 \times 20$ min), $M_{n(GPC)} = 13\,514$ g/mol, $PDI = 1.167$) is close to $M_{n(th)}$,

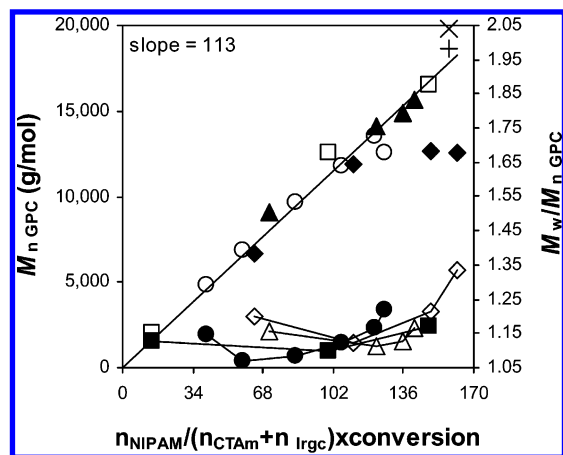


Figure 5. $M_{n(\text{GPC})}$ (number-average molecular weight) (\square , \bullet , Δ , \blacklozenge , \times) and $M_w/M_{n(\text{GPC})}$ (molecular weight distribution) (\blacksquare , \circ , \blacktriangle , \blacklozenge , $+$) vs $n_{\text{NIPAM}}/(n_{\text{CTA}} + n_{\text{IRGC}}) \times \text{conversion}$ dependences for the poly(NIPAM) chain extension polymerization studies by incremental photoinitiator (IRGC) addition technique at ambient temperature in the presence of *S*-1-dodecyl-*S*-(α,α' -dimethyl- α' -acetic acid)trithiocarbonate (CTAm). The initial concentrations in DMF were the following: $[\text{NIPAM}]_0 = 2.95 \text{ M}$ and $[\text{CTAm}]_0 = 14.75 \text{ mM}$. For a time of photoirradiation of 20 min at 350 nm (1.2 KW) the concentrations of IRGC were the following: S9, 196 (292) μg (μM) (first), 990 (1.526) μg (mM) (second), 990 (1.578) μg (mM) (third) (\square , \blacksquare); S6, 660 (966) μg (μM) (first), 660 (998) μg (μM) (second), 132 (210) μg (μM) (third), 132 (217) μg (μM) (fourth) (Δ , \blacktriangle); S8, 395.6 (588) μg (μM) (first), 395.6 (609) μg (μM) (second), 395.6 (630) μg (μM) (third), 496.5 (820) μg (μM) (fourth), 496.5 (852) μg (μM) (fifth), 990 (1.767) μg (mM) (sixth) (\bullet , \circ); S7, 530 (775) μg (μM) (first), 990 (1.485) μg (mM) (second), 990 (1.537) μg (mM) (third), 990 (1.592) μg (mM) (fourth) (\blacklozenge , \diamond); (\times , $+$) 990 (1.472) μg (mM). For additional experimental details see Table 5 (series S6–9) in the Supporting Information. Targeted $M_n = 22\,600 \text{ g/mol}$ targeted $M_n = 22\,600 \text{ g/mol}$; (—) is the theoretical dependences of M_n vs $n_{\text{NIPAM}}/(n_{\text{CTAm}} + n_{\text{IRGC}}) \times \text{conversion}$ calculated on the bases of moles of NIPAM converted into polymers for 100% CTAm and IRGC efficiency. (For GPC RI traces see Figure S6 (series S7) and Figures S6–8 (series 6, 8, and 9) in the Supporting Information.)

a theoretical molecular weight calculated on the base of the mole of NIPAM converted into polymer chains for 100% CTA and IRGC efficiency. Here, the growing macroradical generated after each initiation step led to the formation of low molecular weight polymer chains responsible of the broadening of the MWDs after every chain extension polymerization experiment. Additionally, the chain extension with 990 μg of IRGC increased the yield from 75% to 87% but failed to extend correspondingly the polymer chains; $M_{n(\text{GPC})}$ decreases indicating that large proportions of polymer chains initially produced (or produce at low conversion of monomer to polymer) are dead because of the existence of chain termination reactions (in particular primary termination reactions) during the photodecomposition of the initiator. Thus, all growing radicals formed during the last steps of initiation (at high conversion of monomer to polymer) contribute in the decrease of the M_n .

Therefore, when a larger proportion of photoinitiator was added into a low conversion of monomer to polymer solution, it was then possible to reduce the number of chain extension polymerization experiments required to reach high conversion from 6 to 3. As an example, in Figure 5 series S9, when 196 and 2 increments of 990 μg of IRGC were used in that order, 87.3% of monomers were consumed and a polymer with narrow MWDs and predictable number average molecular weight ($M_{n(\text{GPC})} = 16\,520 \text{ g/mol}$, $\text{PDI} = 1.17$) was obtained. On the other hand, the use of two increments of 990 μg after one increment of 530 μg , series S7, resulted in the formation of polymer with $M_{n(\text{GPC})} < M_{n(\text{th})}$ indicating that termination

reactions have occurred significantly. A further chain extension polymerization experiment carried out at 85.8% monomer conversion with 990 μg of IRGC broadens the MWDs of the resulting polymers and the number average molecular weights remain unchanged. The photoirradiation of the polymerizing solutions resulted only in little initial color change, from light yellow to yellow during the first 20 min. Thereafter, no color change was observed.

Polymerization of NIPAM with IRGC at 65 °C. The photopolymerization of NIPAM (2.95 M) in DMF in the presence of CTAm (14.75 mM) was further examined at 65 °C. (The data from this study are summarized in the Tables 3–5 in the Supporting Information.) When 33 w/v % of NIPAM in DMF was subjected to irradiation at 65 °C, series S5, after 2 min, high molecular weight polymer chains with large polydispersity ($M_{n(\text{GPC})} = 84\,178 \text{ g/mol}$ and $\text{PDI} = 1.9$, conversion = 1.9%) were obtained. In the presence of 14.75 mM CTAm, series S3, the polymerization was slightly faster (Figure 1), indicating that CTAm can act as a photoinitiator. This was demonstrated by the fact that the use of CTAd (difunctional trithiocarbonate) instead of CTAm (monofunctional trithiocarbonate) increases the initial rate of monomer consumption by a factor of ~ 2 whereas with ACVA as initiator the $k_{\text{app,CTAd}}/k_{\text{app,CTAm}}$ ratio of 1.7 (inferior to 2) was initially observed for a short period of time (Figure 1 series S4) due to the decrease of the radicals steady-state concentration. The photopolymerization of the monomer shows that the alternative explanation offered by Hong et al.^{20,21} for a living behavior via the so-called *reversible intermediate termination* applies here for the formation of “stable” trithiocarbonyl dodecyl radicals. These radicals, if they occur, cannot initiate or dissociate via the RAFT process as described by Davis and co-workers.^{22,23} The dependence $M_{n(\text{GPC})}$ on conversion was then examined and it was found, as shown in Figure 2, that the $M_{n(\text{GPC})}$ increases linearly with conversion but as soon as $\sim 57.8\%$ of the monomer was consumed ($t_i = 235 \text{ min}$), the $M_{n(\text{GPC})}$ decreased with a broadening of the MWDs most likely due to the possible photochemical production of growing radical from the monomer and probably by the decomposition of the transfer site at the polymer chain end.²⁴ The polymerization was faster with CTAd and polymers with predictable number average molecular weight and large PDIs ($1.2 < M_w/M_{n(\text{GPC})} < 1.37$) were formed up to 79.2% conversion of monomer, after which $M_{n(\text{GPC})}$ starts to decrease. This shows that the production of new macroradicals during the process of chain growth does not significantly affect the linear dependence $M_{n(\text{GPC})}$ vs $n_{\text{NIPAM}}/(n_{\text{IRGC}} + n_{\text{CTA}}) \times \text{conversion}$ as long as primary termination reactions are not breaking a significant proportion of polymer chains initially produced. (The data from this study are listed in Tables 1.3 and 1–4 in the Supporting Information.)

Therefore, in the presence of CTAm, the chain extension polymerization by incremental photoinitiator additions technique was carried out for a time of irradiation of 7 min, the time at which 2.1% of monomer can be photopolymerized in the absence of CTAm. As shown in Figure 6 series S11, after four increments of 264 μg of IRGC, series S11, polymers with predictable number average molecular weight and narrow polydispersity ($M_{n(\text{GPC})} = 10\,827 \text{ g/mol}$ and $\text{PDI} = 1.17$) were obtained indicating that the process of chain growth was controlled. Two further chain extension polymerization experiments with 396.5 and 660 μg of IRGC led to a broadening of MWDs and to a decrease of M_n because termination reactions occur together with the formation of new polymer chains of lower molecular weight. The use of 660 and 395.6 μg of IRGC

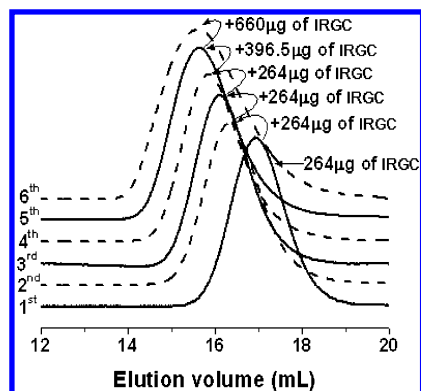


Figure 6. RI traces of PNIPAM in the RAFT polymerization of NIPAM with CTAm in DMF studies by incremental photoinitiator (IRGC) addition technique at 65 °C; [NIPAM]₀ = 2.95 M, [CTAm]₀ = 14.75 mM, and [IRGC]₀ = μM. For a time of photoirradiation of 20 min at 350 nm (1.2 KW/s²) the concentration of each increment of IRGC and results were the following: (first) 264 (390) μg (μM), M_n = 4221, PDI = 1.126; (second) 264 (403) μg (μM), M_n = 7140 g/mol, PDI = 1.15; (third) 264 (418) μg (μM), M_n = 9504 g/mol, PDI = 1.163; (fourth) 264 (432) μg (μM), M_n = 10 827 g/mol, PDI = 1.197; (fifth) 396.5 (681) μg (μM), M_n = 11 835 PDI = 1.21; (sixth) 660 (1.178) μg (μM), M_n = 10 950, PDI = 1.127. For additional experimental details see Table 6 (series S11) in the Supporting Information.

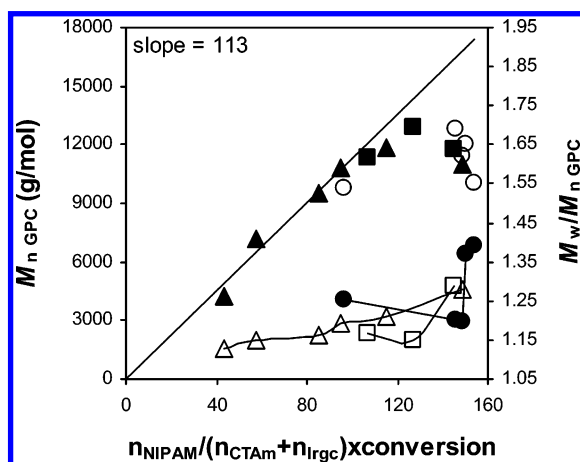


Figure 7. M_n (GPC) (number-average molecular weight) (○, ■, ▲) and M_w/M_n (GPC) (molecular weight distribution) (●, □, △) vs $n_{\text{NIPAM}}/(n_{\text{CTAm}} + n_{\text{IRGC}}) \times \text{conversion}$ dependences for the PNIPAM chain extension polymerization studies by incremental photoinitiator addition technique at 65 °C temperature in the presence of *S*-1-dodecyl-*S*-(α,α' -dimethyl- α'' -acetic acid)trithiocarbonate (CTAm). The initial concentrations were the following: [NIPAM]₀ = 2.95 M and [CTAm]₀ = 14.75 mM. For a time of photoirradiation of 7 min (□, ■, △) and 30 min (●, ○) at 350 nm (1.2 KW) the concentrations of IRGC were the following: S13, 495.6 (737) μg (μM) (first), 495.6 (763) μg (μM) (second), 264 (421) μg (μM) (third), 132 (218) μg (μM) (fourth), 264 (453) μg (μM) (fifth) (●, ○); S11, 264 (393) μg (μM) (first), 264 (406) μg (μM) (second), 264 (421) μg (μM) (third), 264 (436) μg (μM) (fourth), 396.5 (681) μg (μM) (fifth), 660 (1.178) μg (μM) (sixth) (△, ▲); S12, 660 (982) μg (μM) (first), 396.5 (610) μg (μM) (second), 395.6 (632) μg (μM) (third) (□, ■). For experimental details see Table 6 (series S11 and S12) in the Supporting Information. Targeted M_n = 22 600 g/mol; (—) is the theoretical dependence of M_n vs $n_{\text{NIPAM}}/(n_{\text{CTAm}} + n_{\text{IRGC}}) \times \text{conversion}$ calculated on the bases of moles of NIPAM converted into polymers for 100% CTAm and IRGC efficiency. (For GPC RI traces see Figure S6 (series S11) and Figure S9 (series S12) in the Supporting Information.)

as increment, Figure 7 series S12, yields 56.1% and 70.3% conversion, respectively, and the resulting polymer showed M_n (GPC) slightly inferior to M_n (th) (M_n (GPC) = 12 875 g/mol and PDI = 1.149 for M_n (th) = 14 330 g/mol). A further addition of

396.5 μg of IRGC leads to a decrease of M_n (GPC) band broadening of the MWDs.

When the time of irradiation was extended to 30 min, the time at which 8.9% of monomer can be photopolymerized in the absence of CTAm, two increments of 495.6 μg of IRGC lead to an increase of M_n (GPC) but not in direct proportion with the fraction of monomers consumed. Further additions of IRGC decreased the M_n (GPC) from its theoretical value with a broadening of the MWDs, indicating that primary radical termination reactions occur predominantly.

Conclusion

Clearly, the intentional production of new growing chains during the course of the polymerization can be an important issue in RAFT polymerization. However, living characteristics (linear evolution of M_n (GPC) with $n_{\text{NIPAM}}/(n_{\text{IRGC}} + n_{\text{CTA}}) \times \text{conversion}$, narrow polydispersities, and good adherence to theoretical molecular weight) can be observed up to 80% monomer conversion at ambient and 50% monomer conversion at 65 °C, as long as a significant number of chains initially produced are not irreversibly terminated via primary termination reactions. On the other hand, we showed that a redistribution of the MWDs can occur at high conversion (>78%) when the RAFT polymerization of NIPAM in DMF, using trithiocarbonyl ester (CTAm and CTAd) in conjunction with ACVA, was carried out at 65 °C.

Acknowledgment. The authors of this paper would like to thank Natural Sciences and Engineering Research Council (NSERC) and Ontario Centres of Excellence (OCE) Emerging Materials and Knowledge for financial support of this research.

Supporting Information Available: Tables and GPC RI traces of PNIPAM obtained in DMF; at different times using CTAm (series S1, Table 1, Figure S1) and CTAd (series S2, Table 2, Figure S2) as CTA agents in conjunction with ACVA with [NIPAM]₀ = 2.95 M, [CTA]₀ = 14.75 M, [ACVA]₀ = 2.95 mM, and T = 65 °C; at different times using CTAm (series S3, Table 3, Figure S3) and CTAd (series S4, Table 3, Figure S4) as CTA agents in conjunction with IRGC with [NIPAM]₀ = 2.95 M, [CTA]₀ = 14.75 M, [ACVA]₀ = 2.95 mM, and T = 65 °C; at different times without CTA agent (series S5, Table 4, Figure S5) with [NIPAM]₀ = 2.95 M and [ACVA]₀ = 2.95 mM, and T = 65 °C; in incremental IRGC addition (series S6–S9, Table 5, Figures S6–8) at ambient temperature with [NIPAM]₀ = 2.95 M and [CTAm]₀ = 14.75 M; in incremental IRGC addition (series S6–S9, Table 6, Figures S6–8) at 65 °C with [NIPAM]₀ = 2.95 M and [CTAm]₀ = 14.75 M. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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