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Living Radical Polymerization of Acrylates Initiated and Controlled by Organocobalt Porphyrin Complexes

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ABSTRACT: (Tetramesitylporphyrinato)cobalt(II) ((TMP)Co$^\bullet$) and the octabromo derivative ((Br$_8$TMP)Co$^\bullet$) mediate an effective living radical polymerization of acrylate monomers through the formation of dormant organocobalt complexes ((por)Co−PA) with the growing acrylate polymer radical ($^\bullet$PA). Radical polymerization of methyl acrylate controlled by (Br$_8$TMP)Co$^\bullet$ is substantially faster than that for (TMP)Co$^\bullet$ because of the higher concentration of radicals resulting from greater dissociation of the dormant organocobalt complex. Unusually large molecular weight low polydispersity acrylate homopolymers and block copolymers have been obtained by this method. Kinetic studies for the conversion of methyl acrylate (MA) to poly(methyl acrylate) (PMA) initiated and controlled by (TMP)Co−PMA are fully compatable with a living radical process mediated by the metallo radical ((TMP)Co$^\bullet$). Overall apparent activation parameters for the polymerization process ($\Delta H^\ddagger_{\mathrm{app}} = 28 \pm 2$ kcal mol^{-1}; $\Delta S^\ddagger_{\mathrm{app}} = 4 \pm 1$ cal K^{-1} mol^{-1}) are interpreted as sums of the activation parameters for radical propagation ($\Delta H^\ddagger_{\mathrm{p}} \sim 4$ kcal mol^{-1}; $\Delta S^\ddagger_{\mathrm{p}} \sim 25$ cal K^{-1} mol^{-1}) and thermodynamic values for homolytic dissociation of (TMP)Co−PMA ($\Delta H^\circ \sim 24$ kcal mol^{-1}; $\Delta S^\circ \sim 29$ cal K^{-1} mol^{-1}).

Introduction

Several approaches have recently been developed to obtain living character in radical polymerizations.[1−10] All methods to achieve a living radical polymerization depend on controlling the radical concentration through equilibria with a dormant species that suppresses inherent bimolecular radical termination relative to polymer propagation. Our studies[10] have been focused on developing organometal complexes (M−R) as both a source of organic radicals (R$^\bullet$) that initiate radical polymerization and stable metal-centered radicals (M$^\bullet$) that exclusively inhibit irreversible radical termination through the persistent radical effect.[11] We have previously reported that (tetramesitylporphyrinato)cobalt(III) organo complexes ((TMP)Co−R) initiate and control a living polymerization process for acrylate monomers, as evidenced by the formation of relatively low polydispersity polymers ($\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}} < 1.25$) where the number average molecular weight increases linearly with monomer conversion (eqs 1−3).[10] (TMP)Co$^\bullet$ serves as a prototype complex to illustrate the potential efficacy of persistent metalloradicals to achieve living radical polymerization through reversible binding with the growing acrylate polymer radical ($^\bullet$PA) (eq 3). This article reports on the formation of relatively high molecular weight acrylate homopolymers and block copolymers using (TMP)Co−CH(CH$_3$)CO$_2$CH$_3$ as an initiator and enhanced polymerization rates obtained with the octabromo derivative of TMP, (Br$_8$TMP)Co−R). Kinetic studies are also presented that substantiate the primary features for this metalloradical-controlled effective living radical polymerization of acrylates.

$$\mathrm{(TMP)Co{-}R} \rightleftharpoons \mathrm{(TMP)Co^\bullet} + {}^\bullet\mathrm{R} \tag{1}$$

$$n\mathrm{CH_2{=}CH(CO_2R')} + {}^\bullet\mathrm{R} \rightarrow {}^\bullet\mathrm{PA} \tag{2}$$

$$\mathrm{(TMP)Co^\bullet} + {}^\bullet\mathrm{PA} \rightleftharpoons \mathrm{(TMP)Co{-}PA} \tag{3}$$

Results and Discussion

Bulk polymerization of methyl acrylate (MA) initiated by (TMP)Co−CH(CH$_3$)CO$_2$CH$_3$ (**1**) is capable of producing high molecular weight, low polydispersity poly(methyl acrylate) (PMA) (Table 1). Formation of methyl acrylate homopolymers with $\bar{M}_{\mathrm{n}} = 5.5 \times 10^5$ and $\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}} = 1.15$ indicates that a large fraction of the initial polymer radical chains are still growing after about 6400 propagation events. These results demonstrate that the rate of polymer propagation is at least 4 orders of magnitude larger than the sum of the rates for events that terminate chain growth. This further infers that low-polydispersity living polymer chains with molecular weights of several million could be fabricated by this method. The living character of this polymerization process is also illustrated by the utilization of **1** to form relatively low polydispersity block copolymers by sequential addition of MA and butyl acrylate (BA) (Figure 1).

Polymerization of acrylates using (octabromotetramesitylporphyrinato)cobalt(III) organo complexes ((Br$_8$TMP)Co−R) is illustrated in Table 2 and Figure 2. The formation of relatively low polydispersity homopolymers and block copolymers using (Br$_8$TMP)Co−R is comparable to that for the (TMP)Co system, but the rate of polymerization with the (Br$_8$TMP)Co system is substantially greater (Table 3).

The rate of monomer (M) conversion to polymer in a radical polymerization is first order in both the polymeric radical (P$^\bullet$) and the monomer (M) ($-\mathrm{d[M]}/\mathrm{d}t = k_{\mathrm{p}}[\mathrm{P}^\bullet][\mathrm{M}]$). In a cobalt(II) metalloradical (Co$^\bullet$) mediated living radical polymerization, the polymer radical concentration is maintained effectively constant by an

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Table 1. Bulk Polymerization of MA by (TMP)Co−CH(CO$_2$CH$_3$)CH$_3$[a]

time (h)	% conversion	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
0.75	3.5	177 000	1.15
2.0	10.5	554 000	1.13

[a] $[(TMP)Co{-}CH(CO_2CH_3)CH_3]_0 = 1.75 \times 10^{-4}$ M; $[CH_2{=}CH(CO_2CH_3)]_0 = 10.5$ M; $[(TMP)Co^\bullet]_0 = 3.1 \times 10^{-5}$ M; solvent = MA; $T = 60$ °C.

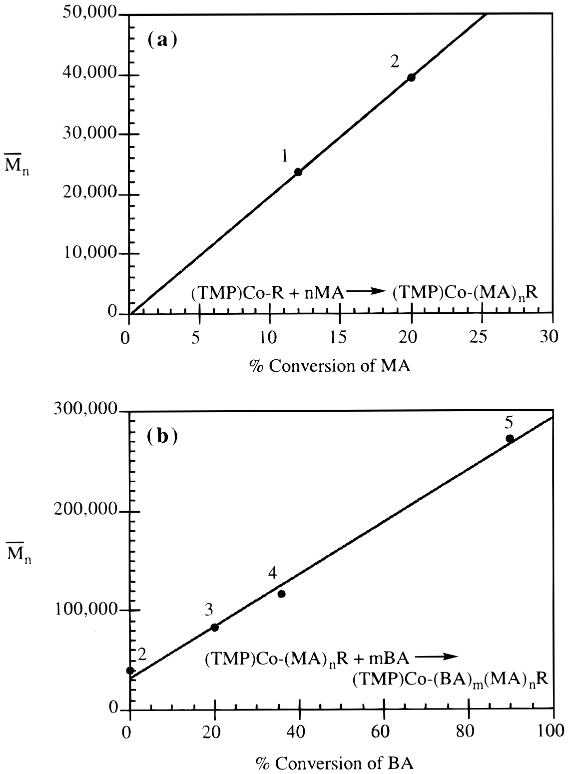

Figure 1. Block copolymerization of MA and BA by (TMP)-Co−CH(CH$_3$)CO$_2$CH$_3$ in C$_6$D$_6$ at 60 °C. $[(TMP)Co{-}CH(CH_3)CO_2CH_3]_0 = 1.15 \times 10^{-3}$ M. (TMP)Co−PMA block $\bar{M}_n(1) = 24\,000$ ($\bar{M}_w/\bar{M}_n = 1.09$), $\bar{M}_n(2) = 39\,500$ (1.15). (TMP)Co−PBA−PMA block copolymer: $[BA]_0 = 2.5$ M, $\bar{M}_n(3) = 85\,000$ (1.15), $\bar{M}_n(4) = 120\,000$ (1.17), $\bar{M}_n(5) = 270\,000$ (1.23).

Table 2. Polymerization of MA Controlled by (Br$_8$TMP)Co$^\bullet$ [a]

% conversion	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
32	77 000	1.09
53	120 000	1.09
70	160 000	1.09
83	180 000	1.11

[a] $[(Br_8TMP)Co{-}R]_0 = 9.6 \times 10^{-4}$ M; $[MA]_0 = 2.5$ M; solvent = C$_6$D$_6$; $T = 25$ °C.

equilibrium with the dormant organocobalt complex (K_d(Co−P) = [Co$^\bullet$][P$^\bullet$]/[Co−P]; [P$^\bullet$] = K_d[Co−P]/[Co$^\bullet$]). The rate of monomer polymerization is thus given by the expression $-d[M]/dt = k_p(K_d[Co{-}P]/[Co^\bullet])[M]$ where k_p is the propagation constant for radical polymerization of the monomer (M) and K_d is the equilibrium constant for homolytic dissociation of the Co−P organometallic complex. The slope for linear plots of $([Co^\bullet]/[Co{-}P])\ln([M]_0/[M]_t)$ versus time gives the overall apparent first-order rate constant (k_{app}), which for a living radical process is the product of k_p and K_d ($k_{app} = k_pK_d$) (Figures 2 and 3).

Comparative kinetic studies for the polymerization of methylacrylate (MA) by (TMP)Co−PMA and (Br$_8$TMP)-Co−PMA at 323 K are shown in Figure 2. The apparent first-order rate constant (k_{app}(323 K)) for MA polymerization using (Br$_8$TMP)Co−PMA is more than 30 times larger than the k_{app}(323 K) for the (TMP)Co−PMA system (Table 3, Figure 2). Substitution of bromine for hydrogen at the porphyrin pyrrole positions stabilizes cobalt(II) and reduces the (Br$_8$TMP)Co−PMA homolytic dissociation enthalpy, resulting in larger polymer radical concentrations relative to that for the same initial concentration of (TMP)Co−PMA.

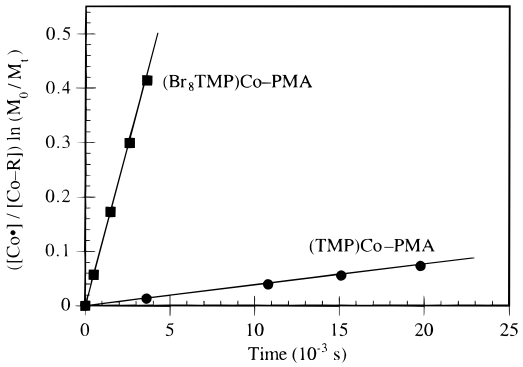

Figure 2. First-order rate plots comparing the polymerization rates of MA initiated and controlled by (TMP)Co−PMA and (Br$_8$TMP)Co−PMA. [MA] = 2.5M in C$_6$D$_6$; [Co−R] = (1−2) × 10^{-3} M; [Co$^\bullet$] = (1−3) × 10^{-4} M.

Table 3. Comparison of Kinetic Parameters for the (por)Co$^\bullet$ Mediated Polymerization of MA[a]

(por)Co$^\bullet$	K_dk_p[b]	K_d (323 K)	$\Delta G°$(323 K)[c]
(TMP)Co$^\bullet$	3.7×10^{-6}	4.2×10^{-10}	14
(Br$_8$TMP)Co$^\bullet$	1.2×10^{-4}	1.3×10^{-8}	12

[a] $[MA]_0 = 2.5$ M in C$_6$D$_6$. K_d = homolytic dissociation constant for (por)Co−PMA complexes. [b] k_p(MA)(323 K) = 8900 M^{-1} s^{-1} (ref 14), $T = 50$ °C. [c] $\Delta G°$ in kcal mol^{-1}.

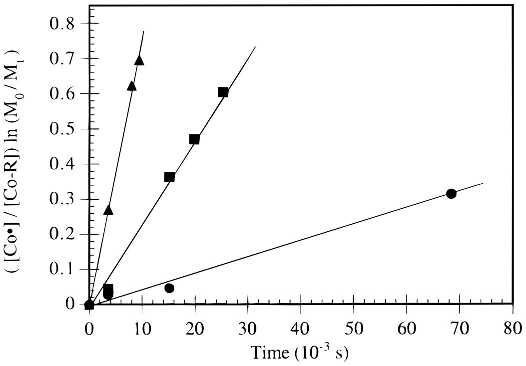

Figure 3. Modified-first order rate plot for the polymerization of MA by (TMP)Co−PMA where the slope equals k_pK_d. k_p = radical propagation rate constant, K_d = [(TMP)Co$^\bullet$][$^\bullet$PMA]/[(TMP)Co−PMA] (▲ = 60 °C; ■ = 50 °C; ● = 40 °C).

Representative results from kinetic studies for the polymerization of MA initiated and controlled by (TMP)-Co−PMA at a series of temperatures are illustrated in Figure 3. The temperature dependence of the apparent first-order rate constant ($k_{app} = K_dk_p$) for MA polymerization gives the overall apparent activation parameters ($\Delta H^\ddagger_{app}$; $\Delta S^\ddagger_{app}$), which are composite sums of the activation parameters for the radical propagation ($\Delta H^\ddagger_p$, $\Delta S^\ddagger_p$) and the thermodynamic parameters ($\Delta H°$, $\Delta S°$) for the dissociation of (TMP)Co−PMA (Figure 4). Thermodynamic values for the homolytic dissociation of (TMP)-Co−PMA ($\Delta H° \cong 24$ kcal mol^{-1}; $\Delta S° \cong 29$ cal K^{-1} mol^{-1}) are estimated by assuming that the activation parameters for radical propagation for MA are comparable to those determined for butyl acrylate ($\Delta H^\ddagger_p \approx 4$ kcal mol^{-1}; $\Delta S^\ddagger_p \approx -25$ cal K^{-1} mol^{-1}).[12] The thermody-

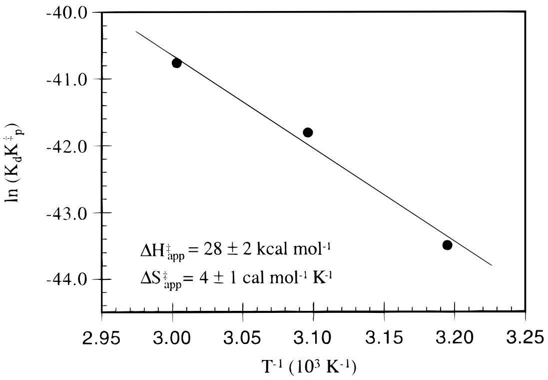

Figure 4. Effective activation parameters for polymerization of MA by (TMP)Co−PMA. ($K^‡\ K_d = k_p(h/kT)K_d$; $\Delta H^‡_{app} = \Delta H° + \Delta H^‡_p = 28 \pm 2$ kcal mol^{-1}, $\Delta S^‡_{app} = \Delta S° + \Delta S^‡_p = 4 \pm 1$ cal K^{-1} mol^{-1}.

namic values derived for the dissociation of (TMP)Co−PMA ($\Delta H° = 24$ kcal mol^{-1}; $\Delta S° = 29$ cal K^{-1} mol^{-1}) from the overall apparent activation parameters for MA polymerization ($\Delta H^‡_{app}$; $\Delta S^‡_{app}$) compare favorably with values for the dissociation of the analogous tetraanisylporphyrin derivative ((TAP)Co−CH(CH$_3$)CO$_2$CH$_3$) determined by direct methods ($\Delta H° = 25.0 \pm 0.4$ kcal mol^{-1}; $\Delta S° = 34 \pm 1$ cal K^{-1} mol^{-1}).[13] The internal consistency of these reactivity, kinetic, and thermodynamic results provides confidence that the living polymerization process mediated by ((TMP)Co$^•$) is well behaved and accurately described by eqs 2 and 3.

Conclusions

Polymerization of acrylates induced and controlled by organocobalt porphyrin complexes is envisioned to occur through a reaction sequence like that given by eqs 1−3. Bond homolysis of (por)Co−R produces a carbon-centered radical (R$^•$) (eq 1) that initiates polymerization by reacting with an acrylate monomer to form a radical that further propagates to form an acrylate polymer radical ($^•$PA) (eq 2). The acrylate polymer radical either combines reversibly with [(por)Co^{II}]$^•$ (eq 3) or reacts with additional acrylate monomers to form a larger polymer radical that subsequently combines reversibly with [(por)Co^{II}]$^•$. Repetition of these events without radical termination or chain transfer would result in a fully living radical polymerization. The actual polymerization process cannot fulfill the criteria of an ideally living process because of inherent bimolecular radical termination and chain transfer reactions with monomer, polymer, solvent, and [(por)Co^{II}]$^•$ that yeild nonliving polymer chains. Despite the processes that can limit polymer chain growth, observation of linear increases in the number average molecular weight with conversion, formation of block copolymers, and relatively small polydispersities clearly demonstrates that organocobalt porphryin complexes ((TMP)Co−R; (Br$_8$TMP)Co−R) initiate and control an effictive living radical polymerization of acrylates. The metalloradicals (TMP)Co$^•$ and (Br$_8$TMP)Co$^•$ fulfill the criteria for mediating the living polymerization because they function exclusively to bind reversibly with the polymer radical. These metallo radicals do not react with the monomer or solvent and the ligand steric requirements prohibit both dimerization by M−M bonding and β-H abstraction from the polymer radical.

Recognition of the general criteria to obtain living radical polymerization is guiding our effort to expand the range of metal-centered radicals and monomers that can be used in living radical polymerizations.

Experimental Section

Materials: Tetramesitylporphyrin, (TMP)H$_2$, and octabromotetramesitylporphyrin, (Br$_8$TMP)H$_2$, were synthesized following literature methods.[15,16] All reactions were carried out under vacuum or inert atmosphere unless otherwise noted. Deuterated solvents were degassed through freeze−pump−thaw cycles and acrylate monomers were vacuum distilled to remove polymerization inhibitors.

(TMP)Co and (Br$_8$TMP)Co. (TMP)H$_2$ (0.038 mmol, 1 equiv) and cobalt acetate (0.077 mmol, 2 equiv) were refluxed in DMF overnight under nitrogen. When the reaction was complete, the solvent was removed. The product was then dissolved in chloroform and washed with water. A similar procedure was used to synthesize (Br$_8$TMP)Co. (TMP)Co ^{1}H NMR (CDCl$_3$, 200 MHz) δ 3.46 (24H, *o*-CH$_3$), 3.92 (12H, *p*-CH$_3$), 9.28 (8H, *m*-H), 15.24 (8H, pyrrole-H). (Br$_8$TMP)Co ^{1}H NMR (CDCl$_3$, 200 MHz): δ 3.88 (24H, *o*-CH$_3$), 5.74 (12H, *p*-CH$_3$), 9.19 (8H, m-H).

Organocobalt Porphyrin Complexes. (a) (TMP)Co−R. (TMP)Co^{II} was reduced with a slight excess of sodium amalgam in THF. The solvent was removed and the (TMP)-Co^I (1 equiv) was reacted with excess RBr (R = CH(CH$_3$)(CO$_2$-CH$_3$), CH$_2$C(CH$_3$)$_3$) (1.3 equiv) in benzene. The reaction mixture was filtered in the inert atmosphere box to remove the excess amalgam and the solvent, and excess RBr was evacuated to isolate the product. The product was identified by ^{1}H NMR. The ratio of Co−R to Co$^•$ was assayed by integration of the ^{1}H NMR peaks for the (TMP)Co$^•$ *m*-H and the (TMP)Co−R pyrrole-H. (TMP)Co−CH(CH$_3$)(CO$_2$CH$_3$) ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ −4.61 (d, 3H, CH(CH$_3$)(CO$_2$CH$_3$), $^3J_{H-H}$ = 7.2 Hz), −2.74 (q, 1H, CH(CH$_3$)(CO$_2$CH$_3$), $^3J_{H-H}$ = 7.2), 8.72 (d, 4H, pyrrole-H, $^3J_{H-H}$ = 4.8 Hz), 8.77 (d, 4H, pyrrole-H, $^3J_{H-H}$ = 4.8 Hz). (TMP)Co−CH$_2$C(CH$_3$)$_3$ ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ −3.24 (br s, 2H, CH$_2$), −1.88 (s, 9H, C(CH$_3$)$_3$), 8.66 (s, 8H, pyrrole).

(b) Poly(methyl acrylate) oligomer complexes of cobalt porphyrin complexes ((por)Co−PMA) were prepared using V-70 (2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile)) to initiate the radical polymerization of methyl acrylate in the presence of (por)Co$^•$ where the initial molar ratio of MA to Co$^•$ is relatively small ([MA]/[Co$^•$] ∼ 30−50). The reaction is carried out at 295 K for 10 half-lives of V-70 in order to ensure complete reaction of the V-70. The (por)Co−PMA is identified by characteristic high-field resonances and the ratio of [Co−PMA]/[Co$^•$] determined by integration of the ^{1}H NMR resonances. In a typical preparation of the oligomer complex (TMP)Co−PMA, (TMP)Co (6.3 × 10^{-3} mmol, 1 equiv), MA (28.3 μL, 50 equiv) and V-70 (1.45 mg, 0.75 equiv) reacted in deuterated benzene (0.72 mL) at room temperature for 4 days. The product complex was collected as a solid by removing the solvent and unreacted MA under vacuum. (TMP)Co−PMA, ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ −4.6 (1H), −4.3 (1H), −3.3 (1H), −2.9 (3H), 8.72 (d, 4H, pyrrole, $^3J_{H-H}$ = 4.8 Hz), 8.76 (d, 4H, pyrrole, $^3J_{H-H}$ = 4.8 Hz).

Acrylate Polymerizations. In a typical polymerization reaction a stock solution of the organocobalt porphyrin initiator ((TMP)Co−R) (6.3 × 10^{-3} mmol) in benzene (0.72 mL) was prepared in an inert atmosphere box. Aliquots (50 μL) of the initiator solution were added to vacuum-adapted NMR tubes. The sample was evacuated to remove solvents, and 0.42 mL of a 2.5 M methyl acrylate solution in deuterated benzene was added. The NMR sample tube was then sealed under vacuum and placed in a constant temperature bath. The fraction of monomer conversion at a series of time intervals was determined by integration of the ^{1}H NMR. The polymerization was halted at various percent monomer conversion and the polymer molecular weight evaluated by GPC analysis.

Bulk Polymerization of Methyl Acrylate. To a vacuum-adapted NMR tube were added (TMP)Co−CH(CH$_3$)CO$_2$CH$_3$ (1.75 10^{-4} M) and methyl acrylate (10.5 M). The tube was sealed under vacuum and placed in a constant temperature bath at 60 °C. At the desired percent conversion the sample was opened and exposed to air to stop the polymerization process. The unreacted methyl acrylate was removed under vacuum, and the sample was analyzed by GPC.

Block Copolymerization of Butyl Acrylate and Methyl Acrylate. A sample of poly(methyl acrylate) appended to (TMP)Co$^\bullet$ or (Br$_8$TMP)Co$^\bullet$ was prepared as previously described. The sample was opened in the inert atmosphere box and added to a vacuum-adapted NMR tube. The unreacted monomer was removed under vacuum, and butyl acrylate (2.5 M in C_6D_6) was added. The sample was sealed under vacuum and heated to 60 °C to continue the polymerization. Samples were removed for GPC analysis at 1, 4, and 24 h intervals.

Polymerization Kinetic Studies. The ratio of [Co−PMA]/[Co$^\bullet$] can be adjusted by addition of [Co$^\bullet$]. The ratio of [Co−R]/[Co$^\bullet$] as determined by ^{1}H NMR does not change to an observable extent up to 85% conversion. Samples were prepared in a similar manner to those for regular polymerization reactions. The sealed tubes were placed in either 40, 50, or 60 °C temperature baths, and the fraction of momomer conversion was monitored as a function of time by ^{1}H NMR.

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