# Controlled/Living Cyclopolymerization of *tert*-Butyl α-(Hydroxymethyl) Acrylate Ether Dimer via Reversible Addition Fragmentation Chain Transfer Polymerization

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ABSTRACT: Reversible addition fragmentation chain transfer (RAFT) polymerization was used in the cyclopolymerization of a symmetrical difunctional monomer, *tert*-butyl α-(hydroxymethyl)acrylate ether dimer. Cumyl dithiobenzoate (CDB) was chosen as the RAFT agent and *N*,*N*′-azobis(isobutyronitrile) (AIBN) was employed as the initiator. Polymerizations were carried out in xylene at 70 °C. Under tuned conditions, cyclic soluble polymers with six-membered tetrahydropyran repeat units were obtained. Polydispersities of the polymers were relatively low and molecular weights were close to the theoretical values. Factors affecting the RAFT mediated cyclopolymerization were investigated. The results indicate that initial monomer concentration, [CDB]/[AIBN] ratios, and reaction temperatures change the rate and the control of the RAFT cyclopolymerization. The livingness of the cyclopolymers was shown through successful block copolymerization with *n*-butyl acrylate where the formers were used as the macro-chain transfer agents.

## Introduction

Controlled/Living radical polymerization involving reversible addition fragmentation chain transfer (RAFT) has increasingly gained popularity because of its ease of application. The method requires the addition of a chain transfer agent (CTA), commonly referred as the RAFT agent, to a conventional radical polymerization mixture which contains a radical initiator such as *N*,*N*′-azobis(isobutyronitrile) (AIBN) and a monomer.[1−4] The RAFT polymerization has been applied to a wide range of monomers (i.e., styrene, acrylates, methacrylates, acrylamides, and functional monomers) at various reaction conditions.[5−12] Among many RAFT agents, thiocarbonylthio-derivatives were found to be the most versatile agents and were employed with variety of monomers.[13−16]

The literature reports on the RAFT polymerization have been mostly limited to monomers that contain a single polymerizable double bond. Bifunctional monomers such as diacrylates, dienes which upon polymerization result in polymers with cyclic repeat units and linearlike backbones are not studied much. Only recently, Li et al. reported the formation of ring structures in the preparation of hyperbranched polymers from asymmetric divinyl monomers such as allyl methacrylates in low yields.[17] Then, Agarwal et al. reported the first studies on RAFT mediated cyclopolymerizations in which alkyl ammonium dienes were used in the preparation of cyclopolymers with five membered heterocyclic repeat units.[18,19] In a broader sense, there are only few examples of cyclopolymers obtained by the controlled living radical polymerization techniques.[17−22] Therefore, the cyclopolymers reported have been limited to high polydispersity homopolymers with uncontrolled molecular weights and most importantly dead end groups.

In this paper, we present the second study on the RAFT mediated controlled living cyclopolymerization. *tert*-Butyl α-(hydroxymethyl)acrylate (TBHMA) ether dimer was employed as the difunctional acrylate (Figure 1). To the best of our knowledge, this is the first time a diacrylate monomer is used in the RAFT mediated cyclopolymerization. Aliphatic cyclopolymers derived from alkyl α-(hydroxymethyl)acrylate

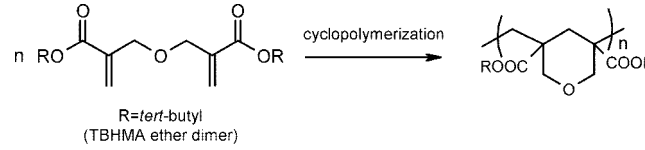


**Figure 1.** Cyclopolymerization of *tert*-butyl α-(hydroxymethyl)acrylate (TBHMA) ether dimer.

(RHMA) ether dimers have been previously synthesized by conventional radical polymerization technique.[23−25] We recently reported the successful cyclopolymerization of the TBHMA ether dimer via atom transfer radical polymerization (ATRP).[20] The cyclopolymers derived from the RHMA ether dimers exhibit high glass transition temperatures, and therefore can be considered as alternatives to acrylate/methacrylate derived polymers for higher temperature applications such as automotive part and coatings where dimensional stability is important.[20] The cyclopolymerization is known to proceed through sequential intramolecular cyclization and intermolecular propagation reactions which leads to the formation of cyclopolymers with six-membered tetrahydropyran repeat units. The main challenge in the cyclopolymerization is the synthesis of cyclopolymers with linearlike backbone since incomplete cyclization leads to pendent group unsaturation which may act as in bound-plasticizer or cross-linking sites (Figure 2). Previous studies with similar difunctional monomers showed that large R-groups such as *tert*-butyl and high temperatures favor cyclization.[23]

Thus, in this study, TBHMA ether dimer was employed as the bulky difunctional acrylate since previous conventional radical and atom transfer radical polymerizations of this monomer resulted in high cyclization efficiencies.[20,23] Factors affecting the RAFT cyclopolymerization of TBHMA ether dimer were investigated. The livingness of the corresponding cyclopolymers was examined through chain extension/block copolymerization studies.

## Experimental Section

**Materials.** Xylenes (*extra pure*, mixture of isomers, Merck) was purified by distillation over Na and benzophenone. *tert*-Butyl acrylate (Acros Organics, 99%), paraformaldehyde (Sigma-Aldrich), 1,4-diazabicyclo[2.2.2]octane (DABCO; Fluka, ≥95.0%), *tert*-butyl

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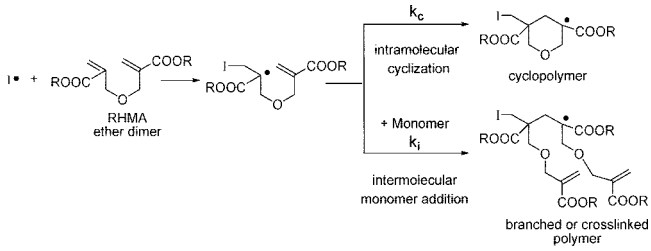


**Figure 2.** Intra- and intermolecular reactions leading to cyclization and cross-linking.

**Table 1. Results from the RAFT Cyclopolymerization of TBHMA Ether Dimer at 70 °C[a,b]**

| entry | [M]/[CDB] | [M] (mol/L) | time (h) | conv.[c] (%) | $M_{n,th}$ ($10^3$ g/mol) | $M_{n,sec}$ ($10^3$ g/mol) | $M_w/M_n$[d] |
|---|---|---|---|---|---|---|---|
| 1 | 200:1 | 1 | 2 | 42.0 | 25.3 | 20.6 | 1.36 |
| 2 | 200:1 | 1 | 4 | 72.2 | 43.3 | 39.7 | 1.48 |
| 3 | 100:1 | 1 | 2 | 36.6 | 11.2 | 10.8 | 1.31 |
| 4 | 100:1 | 1 | 4 | 77.1 | 23.2 | 23.8 | 1.39 |
| 5 | 50:1 | 1 | 2 | 38.7 | 6.0 | 5.3 | 1.25 |
| 6 | 50:1 | 1 | 4 | 78.8 | 12.0 | 12.4 | 1.30 |
| 7 | 150:1 | 1.5 | 2 | 45.0 | 20.4 | 16.4 | 1.35 |
| 8 | 150:1 | 1.5 | 3 | 70.3 | 31.7 | 26.4 | 1.53 |
| 9 | 150:1 | 1.5 | 4 | 82.9 | 37.3 | 35.6 | 1.90 |
| 10 | 50:1 | 1.5 | 2 | 43.5 | 6.8 | 6.4 | 1.33 |
| 11 | 70:1 | 1.75 | 1 | 29.4 | 6.4 | 9.1 | 1.59 |
| 12[e] | | 1 | 2 | 85.0 | 25.5 | 57.5 | 2.75 |

[a] Conditions: [CDB]/[AIBN] = 1:0.25; TBHMA = *tert*-butyl α-(hydroxymethyl)acrylate, M = monomer, CDB = cumyl dithiobenzoate, AIBN = 2,2′-azobis(isobutyronitrile). [b] All polymers were entirely soluble in methylene chloride. [c] Measured by gravimetric methods. [d] Molecular weight distribution ($M_w/M_n$) was measured by size exclusion chromatography (SEC). [e] Entry 12 was generated by conventional free radical polymerization.

alcohol (Merck, 99%), benzyl chloride (Acros Organics, 99.5+%), elemental sulfur (Acros Organics, 99.5+%), sodium methoxide (Acros Organics, 30 wt % solution in methanol), α-methylstyrene (Acros Organics, 99%), *n*-butyl acrylate (*n*-BA; Fluka, ≥99.0%) were used as received without any purification. AIBN was recrystallized from ethanol. All glassware, needles, and stirring bars were dried overnight in an oven at 150 °C and purged with nitrogen before use.

**Instrumentation.** $^1$H NMR and $^{13}$C NMR spectra were recorded on Varian 400-MHz NMR spectrometer (Varian Associates, Palo Alto, CA). Size exclusion chromatography (SEC) analyses were done using a Viscotek GPCmax VE-2001 Analysis System with a PL Gel 5 μm MIXED-C column that was calibrated against polystyrene standards.

**Synthesis of Cumyl Dithiobenzoate (CDB).** CDB was synthesized according to the published literature.[2,26] Purification was done by flash chromatography on silica with *n*-hexane as eluent to give CDB as a dark purple oil with a purity exceeding 99% ($^1$H NMR in $CDCl_3$).

**Synthesis of TBHMA Ether Dimer.** It was synthesized according to the published procedure,[23] where a final column chromatography on silica with *n*-hexane/methanol (99:1) as eluent gave the pure monomer as a clear liquid in 68% yield. $^1$H NMR δ: 1.46 (s, 18H, C$H_3$), 4.17 (s, 4H, OC$H_2$), 5.78 (s, 2H, C$H$ = C), 6.17 (s, 2H, C$H$ = C) ppm. $^{13}$C NMR δ: 28.26 (*C*$H_3$), 69.19 (O*C*$H_2$), 81.13 [*C*-(CH$_3$)$_3$], 124.69 (*C*=*C*H$_2$), 138.83 (CH$_2$=*C*), 165.26 (*C* = O) ppm.

**RAFT Solution Polymerization of TBHMA Ether Dimer (Table 1, Entry 3).** The monomer (5.03 g, 16.9 mmol), CDB (45.9 mg, 0.169 mmol), AIBN (6.9 mg, 0.042 mmol), and 11.4 mL of xylene were put in a 25 mL single neck round-bottom flask fitted with a magnetic stirring bar. The flask was sealed with rubber septa and the solution was purged with nitrogen for 45 min. Then, the flask was immersed into a preheated oil bath at 70 °C. Polymerization was carried out under nitrogen for 2 h. The final polymer was dissolved in 2 mL methylene chloride, precipitated into 60 mL of methanol/water (5/1 v/v), and dried in a vacuum oven overnight to give a pink powder (1.84 g, 36.6% yield. $M_{n,sec}$ = 10.8 × $10^3$, $M_{n,th}$ = 11.2 × $10^3$ g/mol, $M_w/M_{n,sec}$ = 1.31). The theoretical molecular weight was calculated by the equation ($M_{n,th}$) = (MW of monomer) × (conv.) × ([M]/[CTA]) + (MW of CTA).

In the $^1$H NMR characterization of poly(TBHMA ether dimer), the spectrum clearly shows characteristic aromatic peaks of CDB between 7−8 ppm.

In the $^{13}$C NMR characterization of poly(TBHMA ether dimer), the spectrum clearly shows characteristic peaks of backbone carbons, cyclic ether groups, and ester carbonyls. The backbone quaternary carbon peak is at 45.3 ppm and ether methylenes of the pyran units are at 71.0 ppm. The methyl and quaternary carbon peaks of the ester alkyls are at 28.1 and 82.1 ppm and the ester carbonyl is at 174.2 ppm. These data are consistent with previous results from our laboratory on this and related cyclopolymers.[20,23] $^1$H NMR δ: 1.40 (OC(C$H_3$)$_3$), 1.80 (*backbone* C$H_2$), 2.40−4.40 (m-br, *tetrahydropyran H's)*, 7.09 (Ar-*H*), 7.23 (Ar-*H*), 7.31 (Ar-*H*), 7.74 (Ar-*H*) ppm. $^{13}$C NMR, δ: 28.1 (OC(*C*H$_3$)$_3$), 45.3 (backbone *C*$_q$), 71.0 (O*C*H$_2$C$_q$), 82.1 (O*C*(CH$_3$)$_3$), 174.2 (C$_q$-*C*OOC(CH$_3$)$_3$) ppm.

**Conventional Free Radical Polymerization of TBHMA Ether Dimer (Table 1, Entry 12).** The monomer (2.01 g, 6.74 mmol), AIBN (11.0 mg, 0.067 mmol), and 4.6 mL of xylene were put in a 25 mL single neck round-bottom flask fitted with a magnetic stirring bar. The flask was sealed with rubber septa and the solution was purged with nitrogen for 45 min. Then, the flask was immersed into a preheated oil bath at 70 °C. Polymerization was carried out under nitrogen for 2 h. The final polymer was dissolved in 2 mL methylene chloride, precipitated into 60 mL methanol/water (5/1, v/v) and dried in a vacuum oven overnight (1.71 g, 85.0% yield. $M_{n,sec}$ = 57.5 × $10^3$, $M_{n,th}$ = 25.5 × $10^3$ g/mol, $M_w/M_{n,sec}$ = 2.75). The theoretical molecular weight was calculated by the equation ($M_{n,th}$) = (MW of monomer) × (conv.) × ([M]/[AIBN]). $^1$H NMR δ: 1.40 (OC(C$H_3$)$_3$), 1.85 (br, *backbone* C$H_2$5002 > s), 2.40−4.40 (m-br, *tetrahydropyran H's)*. $^{13}$C NMR, δ: 28.1 (OC(*C*H$_3$)$_3$), 45.3 (backbone *C*$_q$), 71.0 (O*C*H$_2$C$_q$), 82.1 (O*C*(CH$_3$)$_3$), 174.2 (C$_q$-*C*OOC(CH$_3$)$_3$) ppm.

**Bulk Block Copolymerization of Poly(TBHMA Ether Dimer) with *n*-BA (Table 4, Entry 4).** The copolymerization was conducted in a single neck round-bottom flask fitted with a stirring bar which had been sealed with rubber septa and purged with nitrogen for 15 min. In a separate vial, the solid macroCTA poly(TBHMA ether dimer) ($M_{n,sec}$ = 4572, 0.150 g, 0.033 mmol) and AIBN (2.7 mg, 0.016 mmol) was dissolved in 8 mL *n*-BA (7.20 g, 56.3 mmol). The solution was transferred to the reaction flask by syringe and degassed with nitrogen for 30 min. Then the flask was immersed into a preheated oil bath at 60 °C. Polymerization was carried out under nitrogen for 4 h. The final polymer was dissolved in 2 mL methylene chloride, precipitated into 60 mL methanol/water (5/1) and dried in a vacuum oven overnight (0.69 g, 7.5% yield. $M_{n,sec}$ = 31940 g/mol, $M_w/M_{n,sec}$ = 1.33). $^1$H NMR δ: 0.86 (t, OCH$_2$CH$_2$CH$_2$C*H*$_3$), 1.30 (m, OCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.40 (s-br, OC(C*H*$_3$)$_3$), 1.52 (br, OCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.84 (br, backbone C*H*$_2$-CH), 2.21 (br, backbone CH$_2$−C*H*), 3.96 (t, OC*H*$_2$CH$_2$CH$_2$CH$_3$) ppm. $^{13}$C NMR δ: 13.9 (OCH$_2$CH$_2$CH$_2$*C*H$_3$), 19.3 (OCH$_2$CH$_2$*C*H$_2$CH$_3$), 28.1 (OC(*C*H$_3$)$_3$), 30.8 (OCH$_2$*C*H$_2$CH$_2$CH$_3$), 34.5−36.8 (*n*-BA-backbone *C*H$_2$−CH) 41.6 (*n*-BA-backbone CH$_2$-*C*H), 45.3 (cyclopolymer backbone *C*$_q$), 64.6 (OCH$_2$CH$_2$-CH$_2$CH$_3$), 82.1 (O*C*(CH$_3$)$_3$), 174.7 (*C*OO) ppm.

## Results and Discussion

It is known that the success of the RAFT process with a given monomer depends on the proper selection of the CTA and reaction conditions. In the cyclopolymerization of TBHMA ether dimer, CDB[15,27,28] was chosen as the chain transfer agent and AIBN was used as the initiator. The concentration of the monomer, [M]/[CDB] and [CDB]/[AIBN] ratios in polymerization mixtures and the polymerization temperature were changed to investigate the effect of the individual RAFT

components and to find out the optimum RAFT cyclopolymerization conditions.

**RAFT Cyclopolymerization of the TBHMA Ether Dimer.** The initial polymerizations were carried out at 70 °C at various [M]/[CDB] ratios where [CDB]/[AIBN] ratio was kept constant (1:0.25; Table 1). This ratio, according to the literature, appeared to be a good compromise between a fast polymerization rate and a well controlled radical polymerization process for acrylic monomers.[5] The monomer concentrations were fixed to 1 M initially, CDB and thus accordingly the AIBN concentrations were changed and polymers with various molecular weights were obtained (Table 1, entries 1−6). All resulting polymers were soluble in organic solvents such as methylene chloride, which indicated that cyclizations were efficient enough to prevent cross-linking. The polydispersities of the polymers were relatively low (1.25−1.50) and the molecular weights were close to the theoretical values. The $^1$H and $^{13}$C NMR analysis of the polymers showed no peaks corresponding to pendent group unsaturation which may result from incomplete cyclization. Kinetic experiments were carried out at 1 M monomer concentration and three different [M]/[CDB] ratios (Figure 3). An induction period of one hour was detected for all the polymerizations. As shown in Figure 3, a linear first-order rate plot was observed for conversions up to 80−90% at three different [M]/[CDB] ratios, which indicated a constant free radical concentration during polymerizations. The number average molecular weights increased linearly with monomer conversions while the polydispersities remained relatively low throughout the polymerizations only with a small increase at higher conversions (>80%). These results indicate that the RAFT cyclopolymerizations of the TBHMA ether dimer proceeded in a controlled manner. The control experiment carried out in the absence of the CTA resulted in polymers with high polydispersities (Table 1, entry 12), proving the effect of the CTA in the RAFT cyclopolymerization. The first-order rate plots also show that the overall polymerization rates were close to each other even though different initiator concentrations were used. We believe that, as previously reported in the literature, the expected increase in polymerization rate which should be observed as a result of the increased AIBN concentration (i.e., [M]/[CDB] = 50 vs [M]/[CDB] = 100, the former contains twice of the initiator since [CDB]/[AIBN] ratio is constant) is compensated by the higher retardation effect of the CDB whose concentration had to be increased to the same extent as AIBN.[10]

Cyclopolymerizations carried out at more concentrated solutions resulted in polymers with higher polydispersities (Table 1, entries 7−11). Similar results were reported by Agarwal et al.[18] at higher monomer concentrations (4.2 M) and the increase in polydispersity was attributed to diffusion problems and/or changing kinetic parameters. Because the monomer concentrations in the present work were much lower (1.50−1.75 M) than the reported ones, it is most probable that the higher polydispersities are due to the changing kinetic parameters corresponding to intramolecular cyclization and intermolecular branching reactions.

**Effect of CDB and AIBN Concentrations.** To see the effect of the CDB concentration, initially, the monomer and AIBN concentrations were kept constant, and CDB concentration was changed. Increasing the CDB concentration as observed in previous reports[5,9] resulted in lower conversions at similar polymerization times (Table 2, entries 1 and 2). To demonstrate this effect better, kinetic studies were done. Figure 4 shows the pseudofirst-order rate plots of the cyclopolymerizations carried out at constant monomer concentration but various CDB and AIBN concentrations. The results show that when the [CDB]/[AIBN] ratio was kept constant but the absolute concentrations of CDB and AIBN were increased, the polymerization rate remained unchanged (Figure 4, [CDB]/[AIBN] = 10:2.5 mM and 20:5 mM). These results are in accordance with the results

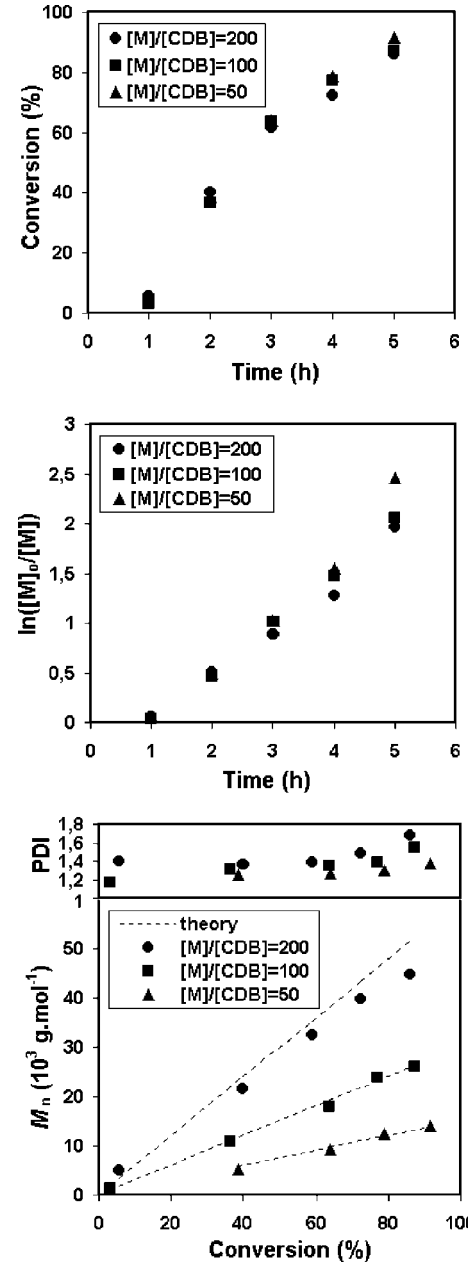


**Figure 3.** Kinetic studies of the RAFT cyclopolymerization of TBHMA ether dimer in xylene at 70 °C and various [M]/[CDB] ratios ([M] = 1 mol·L$^{-1}$; [CDB]/[AIBN] = 1:0.25; TBHMA = *tert*-butyl α-(hydroxymethyl)acrylate, M = monomer, CDB = cumyl dithiobenzoate, AIBN = 2,2′-azobis(isobutyronitrile)).

**Table 2. Effect of CDB and AIBN Concentrations on the RAFT Cyclopolymerization of TBHMA Ether Dimer in Xylene at 70 °C[a,b]**

| entry | [M]/[CDB]/[AIBN] | conv.[c] (%) | $M_{n,th}$ ($10^3$ g/mol) | $M_{n,sec}$ ($10^3$ g/mol) | $M_w/M_n$[d] |
|---|---|---|---|---|---|
| 1 | 1000:10:2.5 | 77.1 | 23.2 | 23.8 | 1.39 |
| 2 | 1000:20:2.5 | 48.8 | 7.5 | 4.7 | 1.26 |
| 3 | 1000:20:5 | 78.8 | 12.0 | 12.4 | 1.30 |
| 4 | 1000:20:10 | 98.3 | 14.9 | 9.9 | 1.44 |

[a] Conditions: [M] = 1 mol·L$^{-1}$; polymerization time = 4 h; TBHMA = *tert*-butyl α-(hydroxymethyl)acrylate; M = monomer, CDB = cumyl dithiobenzoate, AIBN = 2,2′-azobis(isobutyronitrile). [b] All polymers were entirely soluble in methylene chloride. [c] Measured by gravimetric methods. [d] Molecular weight distribution ($M_w/M_n$) was measured by size exclusion chromatography (SEC).

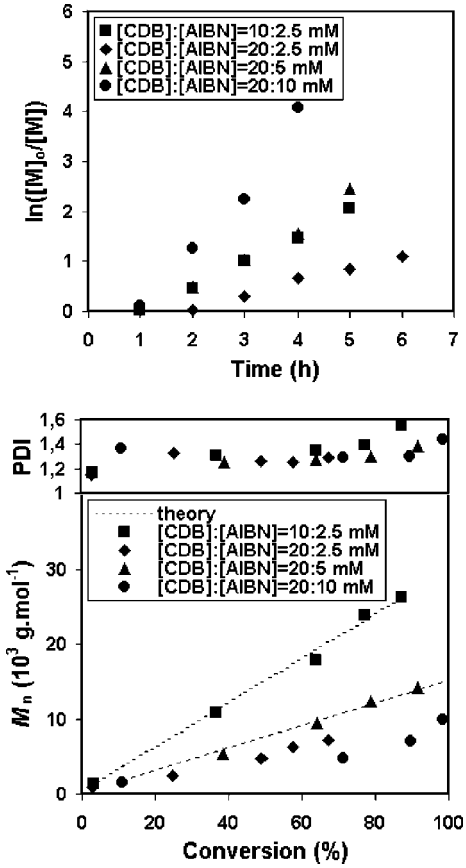


**Figure 4.** Kinetic studies of the RAFT cyclopolymerization of TBHMA ether dimer in xylene at 70 °C and various CDB and AIBN concentrations ([M] = 1 mol·L$^{-1}$; TBHMA = *tert*-butyl α-(hydroxymethyl)-acrylate, M = monomer, CDB = cumyl dithiobenzoate, AIBN = 2,2′-azobis(isobutyronitrile)).

discussed in Figure 3. However, increasing the CDB concentration relative to the AIBN concentration decreases the polymerization rate considerably ([CDB]/[AIBN] = 10:2.5 mM compared to 20:2.5 mM). Higher concentrations of AIBN at constant CDB and monomer concentrations resulted in faster polymerizations (Figure 4, [CDB]/[AIBN] = 20:10 mM compared to 20:5 mM and 20:2.5 mM) but at the expense of higher polydispersities (Table 2, entry 4 compared to 2 and 3) and deviation from theoretical molecular weights. When all polymerizations are compared, as expected, the slowest polymerization rate is observed with the lowest AIBN concentration but highest CDB concentration ([CDB]/[AIBN] = 20:2.5 mM); whereas, the highest polymerization rate is observed with the highest initiator concentration but lowest CDB concentration. A good balance between a fast polymerization rate and control of the RAFT process is attained at 4:1 [CDB]/[AIBN] ratio.

**Effect of Temperature.** In the conventional free radical polymerization, it is known that high temperatures favor the cyclization process. Previously, we reported that in the ATRP cyclopolymerization of the TBHMA ether dimer an optimum temperature range is present (70−80 °C).[20] Below this temperature, the branching/cross-linking reactions become significant. On the other hand, when the temperature exceeds these optimum values, a less controlled ATRP process takes place.

To investigate the effect of temperature on the RAFT cyclopolymerization of TBHMA ether dimer, experiments were carried out at various temperatures (60−90 °C, Table 3). All resulting polymers were soluble in organic solvents such as methylene chloride, indicating that the intramolecular cyclization was still the dominant pathway. The cyclopolymers obtained

**Table 3. Effect of Temperature on the RAFT Cyclopolymerization of TBHMA Ether Dimer in Xylene[a,b]**

| entry | [M]/[CDB] | [M] (mol/L) | temp. (°C) | time (h) | conv.[c] (%) | $M_{n,th}$ ($10^3$ g/mol) | $M_{n,sec}$ ($10^3$ g/mol) | $M_w/M_n$[d] |
|---|---|---|---|---|---|---|---|---|
| 1 | 100:1 | 0.75 | 60 | 7 | 9.6 | 3.1 | 2.7 | 1.50 |
| 2 | 100:1 | 0.75 | 60 | 29 | 83.6 | 25.2 | 22.3 | 1.78 |
| 3 | 200:1 | 1.5 | 60 | 3 | 5.2 | 3.4 | 5.1 | 3.20 |
| 4 | 100:1 | 1 | 70 | 2 | 42.0 | 12.8 | 9.2 | 1.32 |
| 5 | 100:1 | 1 | 80 | 1 | 49.0 | 14.9 | 13.3 | 1.30 |
| 6 | 100:1 | 1 | 80 | 2 | 80.9 | 24.4 | 24.0 | 1.45 |
| 7 | 100:2 | 1 | 90 | 2 | 85.6 | 13.0 | 15.1 | 2.23 |

[a] Conditions: [CDB]/[AIBN] = 1:0.25; TBHMA = *tert*-butyl α-(hydroxymethyl)acrylate, M = monomer, CDB = cumyl dithiobenzoate, AIBN = 2,2′-azobis(isobutyronitrile). [b] All polymers were entirely soluble in methylene chloride. [c] Measured by gravimetric methods. [d] Molecular weight distribution ($M_w/M_n$) was measured by size exclusion chromatography (SEC).

**Table 4. Synthesis of Block Copolymers in Bulk Using the TBHMA Ether Dimer Derived Cyclopolymers as the MacroCTAs and *n*-Butyl Acrylate as the Co-Monomer[a,b]**

| | macroCTA | | block copolymer | | |
|---|---|---|---|---|---|
| entry | $M_{n,sec}$ (g/mol) | $M_w/M_n$ | time (h) | $M_{n,sec}$ (g/mol) | $M_w/M_n$[c] |
| 1 | 4561 | 1.30 | 6 | 92272 | 1.55 |
| 2 | 4572 | 1.35 | 1 | 6023 | 1.28 |
| 3 | 4572 | 1.35 | 2 | 25864 | 1.37 |
| 4 | 4572 | 1.35 | 4 | 31940 | 1.33 |
| 5 | 5297 | 1.33 | 2 | 20835 | 1.37 |

[a] Conditions: [macroCTA]/[AIBN] = 1:0.50 for entries 1−4 and [macroCTA]/[AIBN] = 1:0.25 for entry 5; temp = 60 °C; TBHMA = *tert*-butyl α-(hydroxymethyl)acrylate, AIBN = 2,2′-azobis(isobutyronitrile). [b] All polymers were entirely soluble in methylene chloride. [c] Molecular weight distribution ($M_w/M_n$) was measured by size exclusion chromatography (SEC).

at 60 °C had broader molecular weight distributions than the ones obtained at 70 and 80 °C, even under more dilute conditions (Table 3, entries 1 and 2). We believe that, at lower temperatures, the intermolecular branching reactions become more competitive with the desired intramolecular cyclization reactions that require higher temperatures to overcome the energy of activation for the cyclization. The amount of intermolecular branching reactions increased with the increasing monomer concentration giving rise to polymers with higher polydispersities (Table 3, entry 3). When the polymerizations at 70 and 80 °C were compared, faster rates of polymerization were observed at 80 °C as evidenced by the shorter polymerization times (Table 3, entries 4−6) and the first-order rate plots (Figure 5). Both polymerizations proceeded in a controlled manner; polydispersities were low and comparable, the molecular weights increased with conversions linearly. Inhibition time, as expected, decreased with increasing temperature. Finally, when the polymerization temperature was increased further to 90 °C, higher molecular weight distributions were obtained indicating a less controlled RAFT process (Table 3, entry 7). This is most probably due to the changing equilibrium constants involved in the RAFT process.

As a result, similar to the ATRP cyclopolymerization of TBHMA ether dimer,[20] an optimum temperature (70−80 °C) range seems to exist for the RAFT cyclopolymerization as well.

**Copolymerization Studies.** The livingness of the cyclopolymer end groups was investigated through chain extension/block copolymerization studies where the cyclopolymers obtained were used as macroCTAs. The copolymerizations were carried out at 60 °C in bulk with *n*-butyl acrylate as the comonomer (Table 4). SEC traces of the block copolymers showed unimodal molecular weight distributions with no evidence of unreacted macroCTA (Figure 6), which proved the high efficiency of the macroCTA, and thus the livingness of the cyclopolymers obtained by the RAFT technique. Changing the [macroCTA]/[AIBN] ratio from 1:0.50 to 1:0.25 (Table 4, entry 5) had no

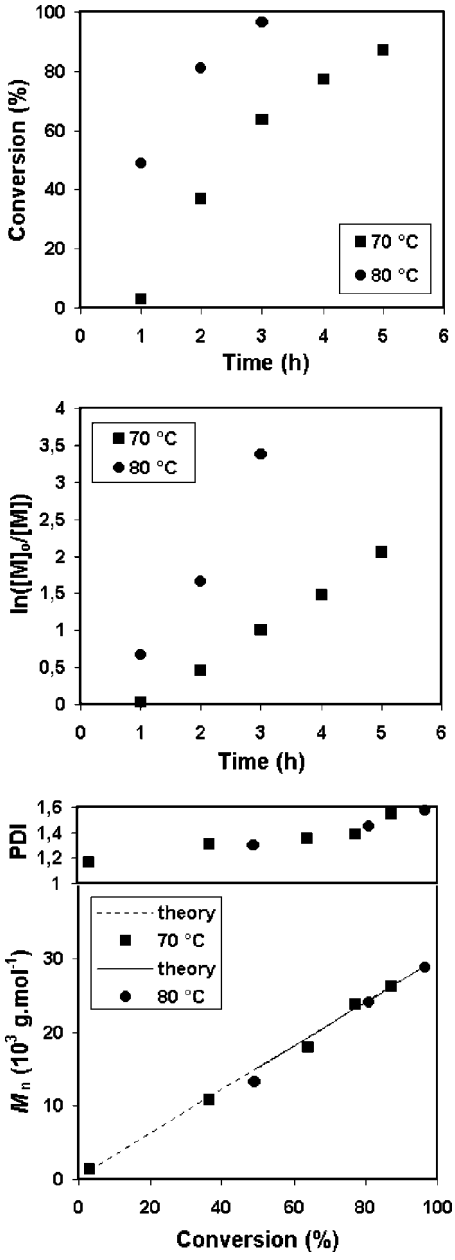


**Figure 5.** Kinetic studies of the RAFT cyclopolymerization of TBHMA ether dimer in xylene at 70 and 80 °C ([M] = 1 mol·L$^{-1}$; [M]/[CDB]/[AIBN] = 100:1:0.25; TBHMA = *tert*-butyl α-(hydroxymethyl)acrylate, M = monomer, CDB = cumyl dithiobenzoate, AIBN = 2,2′-azobis(isobutyronitrile)).

significant effect on the polydispersities obtained, but the copolymerization rate was slightly lower than the ones carried out at 1:0.50 [macroCTA]/[AIBN] ratio (Table 4, entry 3) as evidenced by the lower molecular weights obtained at similar copolymerization times.

## Conclusions

The results indicate that the RAFT process can be applied successfully to the synthesis of cyclopolymers with six-membered tetrahydropyran repeat units using a diacrylate monomer such as the TBHMA ether dimer. An optimum polymerization temperature is attained around 70−80 °C, below and above which the controlled RAFT cyclopolymerization process becomes less efficient. Cyclopolymers with tunable molecular weights, low polydispersities, and most importantly, living end groups were obtained under tuned conditions. The

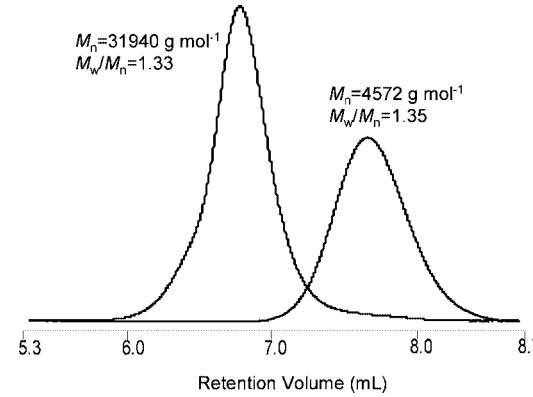


**Figure 6.** Size-exclusion chromatography (SEC) traces of the copolymerization study in bulk using *tert*-butyl α-(hydroxymethyl)acrylate (TBHMA) ether dimer derived cyclopolymer as the macroCTA and *n*-butyl acrylate as the comonomer (Table 4, entry 4).

cyclopolymers showed living character that allowed the synthesis of block copolymers. As a future perspective, we believe that the RAFT cyclopolymerization of the RHMA ether dimers may allow the synthesis of telechelic homo- and copolymers, which may not be accessible by the other living polymerization techniques.

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