Macromolecules **2006,** *39,* 8936−8942

Cyclopolymerization of *tert*-Butyl α-(Hydroxymethyl) Acrylate (TBHMA) Ether Dimer via Atom Transfer Radical Polymerization (ATRP)

Selda Erkoc,[†] Lon J. Mathias,[‡] and A. Ersin Acar*,[†]

Department of Chemistry, Bogazici University, Bebek, 34342, Istanbul, Turkey, and Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi 39406

Received August 15, 2006; Revised Manuscript Received October 19, 2006

ABSTRACT: Atom transfer radical polymerization (ATRP) was used in the cyclopolymerizaton of a symmetrical dimethacrylate, the ether dimer of *tert*-butyl α-(hydroxymethyl)acrylate (TBHMA). The cyclopolymerization was succesfully carried out with high cyclization efficiency in xylene using CuBr/PMDETA at 70 °C. Cyclopolymers with six membered tetrahydropyran repeat units were obtained in high conversions with controlled molecular weights and low polydispersities. It was found that at higher temperatures (100 °C), the polymerization became less controlled and polydispersities increased slightly whereas at lower temperatures (50 °C) the intermolecular reactions lead to pendent vinyl groups and cross-linking. The livingness of the propagating cyclopolymers was shown through successful block copolymerization with *tert*-butyl acrylate where the former was used as macroinitiator. The physical properties of the cyclopolymers were investigated and it was found that ring microstructures and polymer polydispersities affected the glass transition temperatures of the polymers obtained.

Introduction

Aliphatic polymers are good candidates for outdoor applications since they do not contain strong ultraviolet chromophores which are often responsible for the photodegradation of polymeric materials. Unfortunately, most aliphatic polymers have low glass transition temperatures and/or poor mechanical properties which make them unsuitable for applications where dimensional and mechanical stabilities are important. Thus, there is a need for new aliphatic polymers with high glass transition temperatures (i.e., >110 °C) that possess other desirable properties.

We have been interested for a number of years in polymers obtained from the cyclopolymerization of alkyl α-(hydroxymethyl)acrylate (RHMA) ether dimers (Figure 1). The polymers obtained possess high degrees of cyclization and thus display high glass transition temperatures (>135 °C) and reduced shrinkage during polymerization compared to noncyclic linear analogs.[1,2] All literature reports of such cyclopolymers involve conventional free radical polymerization[3−8] and the polymerization has been shown to occur through sequential intermolecular propagation and intramolecular cyclization which result in the formation of a polymer with six-membered tetrahydropyran repeat units. Major problems in the polymerization may involve imperfect cyclization which leads to pendent group unsaturation which can act as a bound plasticizer or lead to cross-linking and formation of intractable product (Figure 2). To overcome this problem, parameters affecting the cyclization efficiency have been well studied.[3,9] The bulkiness of the ester substituent seems to be a major parameter as shown for the relatively large *tert*-butyl group which increases the cyclization efficiency and leads to almost complete formation of cyclic repeat units. The enhancement of cyclization by bulky substituents was also reported in the cyclopolymerization of *N*-allylmethacrylamide and *N*-allylacrylamide which resulted in fully cyclized polymers for the *N*-*tert*-butyl derivatives.[10,11] In these studies it has also been reported that higher polymerization temperatures favor the cyclization process.

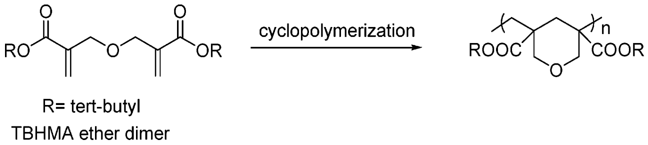


Figure 1. Cyclopolymerization of TBHMA ether dimer.

It has also been shown that the substituent alters the cyclopolymer microstructure depending on size and electronic structure. The internal ring stereochemistry can be *trans* or *cis* (Figure 3) and the relative ring configurations between adjacent rings can be *racemic* or *meso*; both are affected by the size of the substituents. Bulky groups in general favor a *trans*−*racemic* combination.[3]

All the studies mentioned above were carried out via conventional free radical polymerization techniques. Therefore, the resulting polymers did not have well-defined molecular weights, narrow polydispersities, and, most importantly, living end groups which could be used later for copolymerization or functionalization studies. As a consequence the synthesized cyclopolymers have been limited to cyclic homopolymers and random copolymers. In this paper, we report the results of the first living and controlled radical cyclopolymerization of the *tert*-butyl ester derivative of the hydroxymethyl acrylate ether dimers. For the present study, atom transfer radical polymerization (ATRP) was employed since it is one of the most successful controlled living radical polymerization techniques.[12−19] It allows the preparation of a wide range of polymeric materials with predictable molecular weights, low polydispersities, and living end groups.[20−26] The published literature on ATRP mostly contains monomers with only one polymerizable double bond, resulting in linear polymers with simple vinyl backbones. Until recently, ATRP had not been applied to difunctional monomers such as dimethacrylates, diacrylates, and imide dimers, which

---

* Corresponding author. Telephone: 0090-212-359-7390. E-mail: ersin.acar@boun.edu.tr.

[†] Department of Chemistry, Bogazici University.

[‡] Department of Polymer Science, University of Southern Mississippi.

10.1021/ma061876e CCC: $33.50

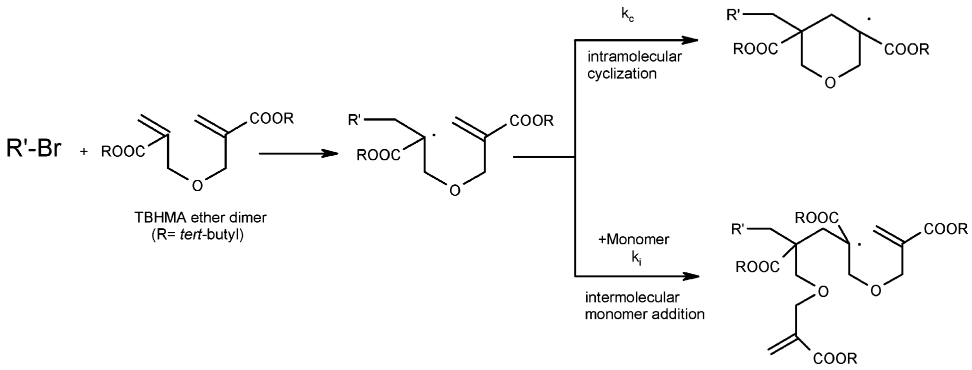
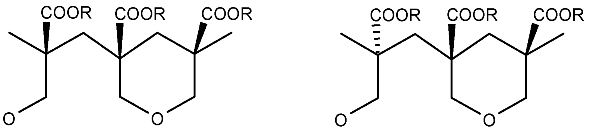
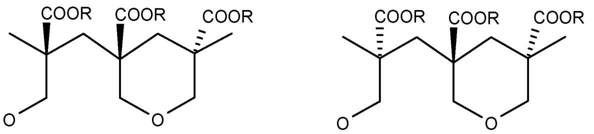


Figure 2. Intra- and intermolecular reactions leading to cyclization and cross-linking respectively.



meso-cis racemic-cis



meso-trans racemic-trans

Figure 3. Four possible ring microstructures.

may allow the synthesis of linear cyclopolymers. Very recently, the enantiomer selective cyclopolymerization of *rac*-2,4-pentanediyl dimethacrylate was reported where ten-membered rings were synthesized using the ATRP method.[27,28] To the best of our knowledge, neither the cyclopolymers nor their corresponding copolymers containing six-membered tetrahydropyran repeat units have been synthesized by ATRP techniques or other controlled radical polymerization techniques.

Here we are reporting the results obtained from the ATRP cyclopolymerizaton of *tert*-butyl α-(hydroxymethyl)acrylate (TBHMA) ether dimer. The goal of this work was, first, to apply ATRP successfully to the synthesis of tetrahydropyran-containing cyclopolymers in high conversions with controlled molecular weights and low polydispersities and, second, to demonstrate livingness of the cyclopolymer−ATRP system by synthesizing block copolymers. Finally, this project involved evaluation of the physical properties of the cyclopolymers in comparison with those of polymers obtained by conventional free radical polymerization.

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 alcohol (Merck, 99%), ethyl-2-bromoisobutyrate (Fluka, ≥97.0%), copper(I) bromide (CuBr) (Aldrich, 99.999%), copper(I) chloride (CuCl) (Aldrich, 99.995%), and pentamethyldiethylene triamine (PMDETA) (Aldrich, 99%) were used as received. 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). SEC analyses were done using an Agilent 1100 Series GPC−SEC Analysis System with a PL Gel 5 μm MIXED-C Column that was calibrated against polystyrene standards. T_g values were determined with a TA Instruments differential scanning calorimeter (DSC Q100). TGA scans were performed under nitrogen flow using a TA Q50 at a heating rate of 10 °C/min. All polymer samples were purified by passing through basic aluminum oxide columns to remove the copper catalyst followed by two reprecipitations before NMR, SEC, DSC, and TGA analyses.

Synthesis of TBHMA Ether Dimer. *tert*-Butyl acrylate (64 g, 0.5 mol), paraformaldehyde (15 g, 0.5 mol), 1,4-diazabicyclo[2.2.2]-octane (DABCO) (2.5 g, 0.02 mol), and *tert*-butyl alcohol (5 mL, 0.05 mol) were added to a 250 mL three-necked round-bottom flask fitted with a condenser and magnetic stirring bar. The mixture was stirred at 95 °C for 4 days. The reaction progress was monitored by TLC. The mixture was then diluted with 150 mL of methylene chloride and washed three times with 100 mL of 3% HCl and three times with 100 mL of water. The organic layer was separated and solvent was evaporated under reduced pressure to give 63.9 g of crude monomer in 86% yield. Vacuum distillation gave the pure monomer as a clear liquid in 37% yield. ^{1}H NMR, δ: 1.46 (s, 18H, CH_3), 4.17 (s, 4H, OCH_2), 5.78 (s, 2H, CH=C), 6.17 (s, 2H, CH=C) ppm. ^{13}C NMR, δ: 28.26 (CH$_3$), 69.19 (OCH$_2$), 81.13 [C-(CH$_3$)$_3$], 124.69 (C=CH$_2$), 138.83 (CH$_2$=C), 165.26 (C=O) ppm.

Solution Polymerization of TBHMA Ether Dimer by ATRP. All liquid chemicals were purged with nitrogen for at least 20 min prior to use. The polymerization of TBHMA ether dimer was conducted in a three-necked round-bottom flask using xylene as the solvent. The empty reaction flask was fitted with a magnetic stirring bar, sealed with rubber septa and purged with nitrogen for 15 min. TBHMA ether dimer (2.01 g, 6.7 mmol) dissolved in 7 mL of xylene was transferred into the reaction flask by syringe. The solution was purged with nitrogen for an additional 30 min. The flask was immersed in a preheated oil bath at 70 °C. From the reaction solution, 2 mL was taken via syringe and added to solid CuBr (9.6 mg, 0.067 mmol), which had been sealed with a rubber septum in a vial and purged with nitrogen for 15 min prior to the addition. PMDETA (16 μL, 0.076 mmol) was then added to the same vial. The resulting mixture was stirred and heated until the CuBr dissolved. The solution was transferred into the three-necked reaction flask by syringe. Ethyl-α-bromoisobutyrate (10 μL, 0.067 mmol) was introduced into the reaction flask by microsyringe. Polymerization was carried out under nitrogen in a preheated oil bath (e.g.,70 °C) for the given polymerization time (e.g., 2 h). The final polymer was dissolved in methylene chloride, precipitated into methanol/water (5/1) and dried in a vacuum oven overnight.

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 ppm and ether methylenes of the pyran units are at 71 ppm. The methyl and quaternary carbon peaks of the ester alkyls are at 28 and 82 ppm and the ester carbonyl is at 174 ppm. These data are consistent with previous results from our lab on this and related cyclopolymers.

^{13}C NMR, δ: 28.1 (OC(CH$_3$)$_3$), 45.3 (backbone C_q), 71.0 (OCH$_2$C$_q$), 82.1 (OC(CH$_3$)$_3$), 174.2 (C$_q$$C$OOC(CH$_3$)$_3$) ppm.

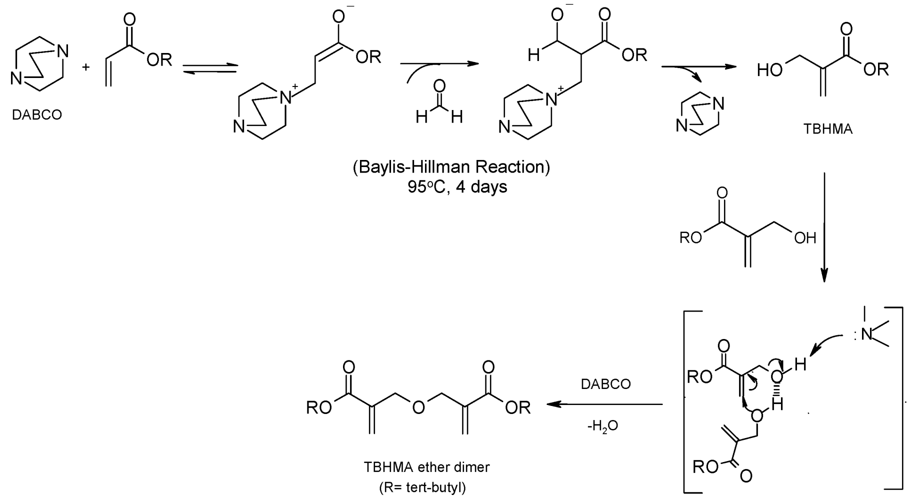


Figure 4. DABCO-catalyzed synthesis of TBHMA ether dimer.

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

entry	$[M]_0$:$[I]_0$:$[Cat]_o$	time (h)	conv[c] (%)	$M_{n,cal}$ (10^3 g/mol)	$M_{n,sec}$ (10^3 g/mol)	M_w/M_n
1	100:1:1	2	29	8.6	8.6	1.05
2	100:1:1	8	36	10.7	10.9	1.19
3	100:1:1	18	76	22.6	24.2	1.30
4	100:1:2	4	98	29.2	27.6	1.97
5	200:1:1	18	43	25.6	16.4	1.16
6	50:1:1	6	63	9.4	5.8	1.17
7	50:1:1	6	68	10.2	10.9	1.21
8	50:1:1	4	81	12.0	12.0	1.23
9	50:1:1	2	64	9.5	8.7	1.17
10	100:0:0	24	0			

[a] Conditions: $[M]_o = 0.96$ M in xylene. [b] All polymers were entirely soluble in methylene chloride. [c] Measured by gravimetric methods.

Conventional Free Radical Polymerization of TBHMA Ether Dimer. The polymerization was conducted in a round-bottom flask using xylene as the solvent. The reaction flask was fitted with a magnetic stirring bar, sealed with rubber septa and purged with nitrogen for 15 min. The monomer (1.02 g, 3.42 mmol) dissolved in 4 mL of xylene was transferred into the reaction flask by syringe. The solution was purged with nitrogen for an addiitional 30 min and the flask was immersed in a preheated oil bath at 70 °C. AIBN (5.6 mg, 0.034 mmol) in 2 mL of xylene (purged for 30 min with nitrogen) was added to the reaction flask by syringe. Polymerization was carried out under nitrogen at 70 °C for 2 h. The final polymer was dissolved in methylene chloride and precipitated into methanol/water and then dried in a vacuum oven overnight.

Bulk Copolymerization of Poly(TBHMA Ether Dimer) with *t*-BA. All liquid chemicals were purged with nitrogen for at least 20 min prior to use. The copolymerization was conducted in a three-necked round-bottom flask. The solid macroinitiator poly(TBHMA ether dimer) (0.16 g, 0.028 mmol) was added to a reaction flask fitted with a stirring bar and which had been sealed with rubber septa and purged with nitrogen for 15 min. *tert*-BA (4 mL) was added to the reaction flask by syringe. The resulting mixture was stirred and degassed until the macroinitiator dissolved. Then, the solution was degassed for an additional 30 min and immersed into a preheated oil bath at 80 °C. CuBr (8.1 mg, 0.056 mmol) was put in a separate vial sealed with a rubber septum and 2 mL of *tert*-BA was added to the CuBr and purged with nitrogen for 20 min. PMDETA (12 μL, 0.057 mmol) was added to the vial and the resulting mixture was stirred and heated until the CuBr dissolved. The resulting solution was then transferred into the reaction flask by syringe. Polymerization was carried out under nitrogen at 80 °C for 6 h. The final polymer was dissolved in methylene chloride, precipitated into methanol/water (5/1) and dried in a vacuum oven overnight.

Table 2. Results from the ATRP of TBHMA Ether Dimer at 100 °C[a,b]

entry	$[M]_0$:$[I]_0$:$[Cat]_o$	time (h)	convn[c] (%)	$M_{n,cal}$ (10^3 g/mol)	$M_{n,sec}$ (10^3 g/mol)	M_w/M_n
1	100:1:1	2	62	18.5	17.6	1.13
2	100:1:1	8	60	17.9	19.1	1.44
3	100:1:1	18	71	21.2	18.5	1.48
4	100:1:2	0.2	77	22.9	35.1	2.05

[a] Conditions: $[M]_o = 0.96$ M in xylene. [b] All polymers were soluble in methylene chloride. [c] Measured by gravimetric methods.

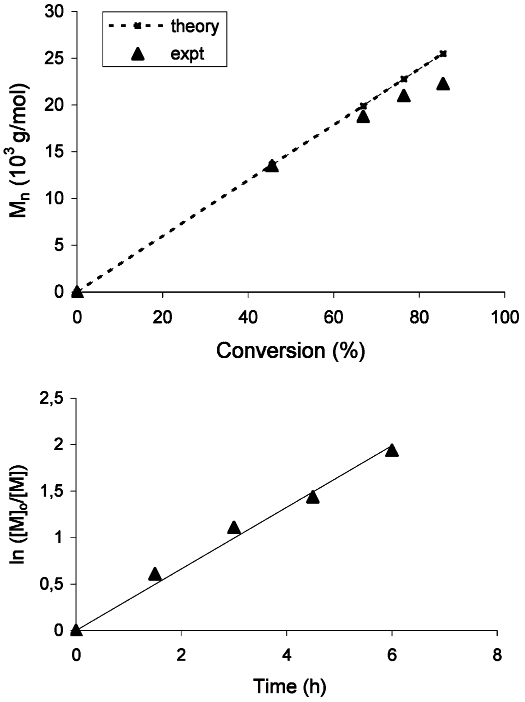


Figure 5. Kinetic study of TBHMA ether dimer cyclopolymerization at 70 °C by ATRP.

^{13}C NMR, δ: 28.3 ($OC(CH_3)_3$), 36.0 (backbone CH_2), 42.0−42.5 (backbone CH), 45.3 (backbone C_q), 80.6 ($CHCOOC(CH_3)_3$), 82.1 ($C_qCOOC(CH_3)_3$), 174.2(COO) ppm.

Results and Discussion

The TBHMA ether dimer was synthesized in one pot from *tert*-butyl acrylate using the Baylis−Hillman reaction followed by dimerization of the Baylis−Hillman adduct at high temper-

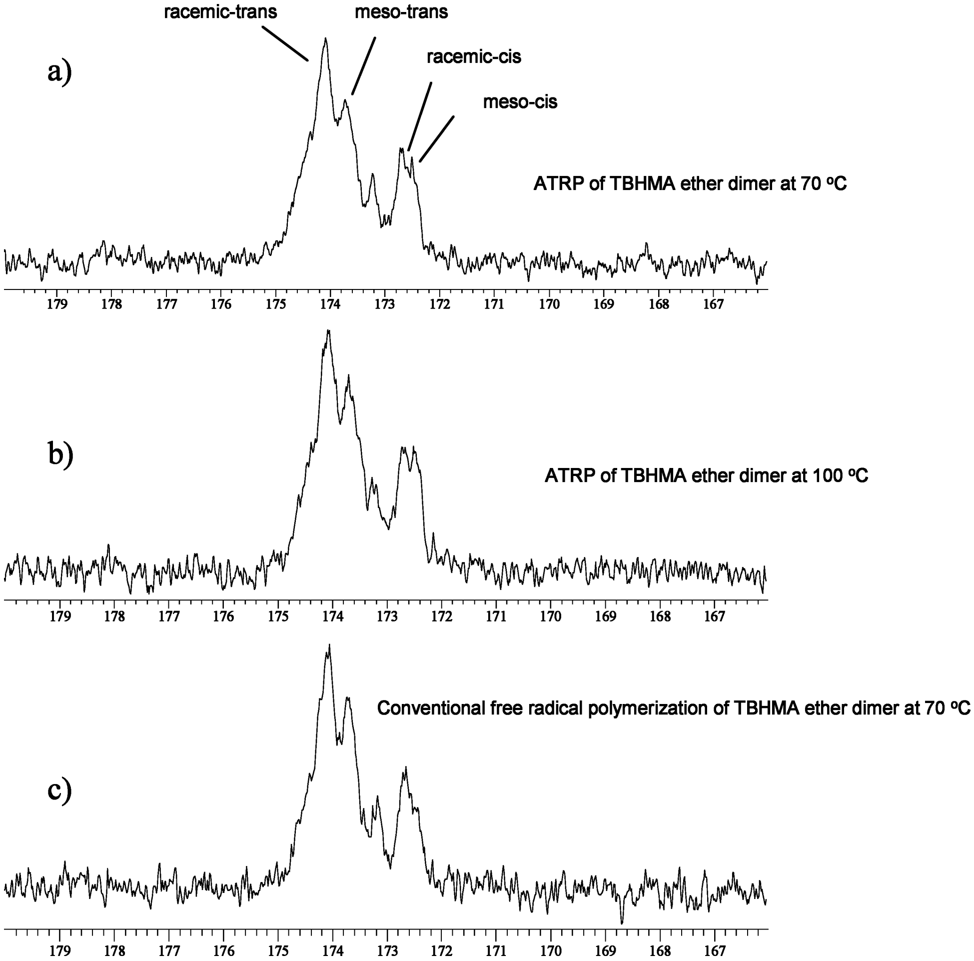


Figure 6. (a) ^{13}C NMR carbonyl region of the cyclopolymer obtained by ATRP of TBHMA ether dimer at 70 °C. (b) ATRP at 100 °C. (c) Conventional radical polymerization at 70 °C.

Table 3. Synthesis of Copolymers by ATRP in Bulk at 70 °C Using the TBHMA Ether Dimer−Cyclopolymers as Macroinitiators[a,b]

	macroinitiator		block copolymer					
entry	$M_{n,sec}$ (g/mol)	M_w/M_n	monomer	time (h)	CuX	$M_{n,cal}$[c] (g/mol)	$M_{n,sec}$ (g/mol)	M_w/M_n
1	5815	1.17	*tert*-BA	7	CuBr	39 472	59 871	1.24
2	24 085	1.21	*n*-BA	24	CuBr	37 001	38 247	1.24
3	19 064	1.44	*tert*-BA	6	CuCl	23 927	34 512	1.49
4	12 032	1.23	*tert*-BA	0.5	CuBr	15 476	16 840	1.29

[a] Conditions: $[I]_0$:$[CuX]_0$:[PMDETA] = 1:2:2. [b] Macroinitiators were −Br terminated. [c] Calculated by using conversion values (2%−18%) that were obtained by gravimetric methods.

ature (95 °C) (Figure 4).[7] Special attention was paid to the monomer purification since the main impurity, a dimer in which the TBHMA alchohol groups were coupled through an acetal bond, could potentially have a different cyclization efficiency and a much greater tendency to give cross-linked polymers.

TBHMA ether dimer was then polymerized in xylene at 70 °C using CuBr/PMDETA as the catalyst complex and ethyl α-bromoisobutyrate (EB*i*B) as the initiator (Table 1). The concentration of the monomer in polymerization mixture was about 0.96 M similar to the concentrations of monofunctional acrylates or methacrylates in conventional solution polymerizations. In other words, polymerizations were not carried out under high dilutions which favor cyclization reactions but at normal concentrations. The first indication that cyclizations were efficient was that all the resulting polymers were soluble in organic solvents such as methylene chloride. In addition, the rate data showed first-order kinetics (Figure 5), while molecular weights increased with conversion linearly and polydispersities remained low even at high conversions. Most importantly, up to 75% conversion was reached in the ATRP process without cross-linking or increasing the polydispersity. In all polymerizations, a small amount of catalyst precipitation was observed as the conversion increased, most probably indicating the irreversible oxidation and precipitation of the copper complex. We believe that this heterogeneity is responsible for the observed variation of polymerization times and conversions (Table 1). When the catalyst concentration was doubled (entry 4) with respect to the initiator concentration, the polydispersity increased and the calculated molecular weights were different from those observed, indicating that the ATRP process was less controlled at higher radical concentrations.

Effect of Temperature on ATRP Cyclopolymerization and Cyclopolymer Microstructure. In the conventional free radical cyclopolymerization of the TBHMA dimer, it is known that temperature affects the course of the cylopolymerization, with higher temperatures favoring the intramolecular cyclization process. An investigation on the effect of temperature on the ATRP cyclopolymerization was carried out where the temper-

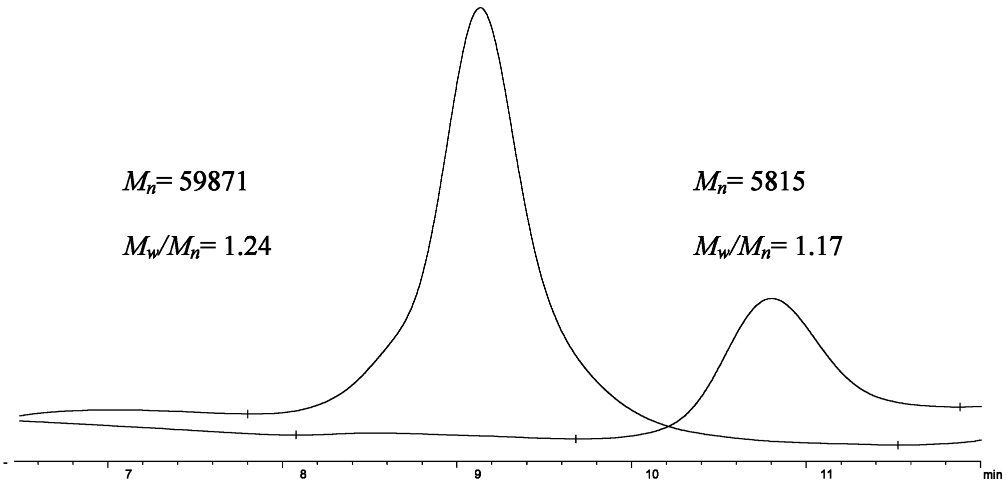


Figure 7. SEC traces of the copolymerization study showing macroinitiator (right) and the obtained block copolymer (left).

ature was changed to 50 and 100 °C from the regular polymerization temperature of 70 °C. ATRP of the TBHMA ether dimer at the lower temperature, 50 °C, always resulted in insoluble polymers, indicating that cross-linked polymer networks were formed due to competititve intermolecular ATRP reaction. At this temperature, the system most probably did not have enough energy to efficiently promote cyclization, which has a higher activation energy than intermolecular radical addition, allowing the latter to occur to a sufficient extent to cause cross-linking.

When the polymerization of TBHMA ether dimer was carried out at higher temperature, 100 °C, only soluble polymers were obtained (Table 2). Polymerization times were shorter with respect to polymerizations carried out at 70 °C, but the obtained polymers generally had slightly higher polydispersities. At this temperature, the difference between the rate of intramolecular cyclization and intermolecular addition may decrease slightly leading to some minor branching which may show up as higher polydsipersity. The higher polydispersity may also be the result of the changing equilibrium constant of the ATRP system which depends on activation/deactivation rate constants which are expected to be temperature dependent. When the catalyst concentration was doubled with respect to the initiator concentration, the polydispersity increased to give similar results as those obtained at 70 °C (Table 2, Entry 4).

A temperature effect was also observed in the microstructures of the polymers obtained. As discussed earlier, there are four possible ring-plus-repeat unit structures that can be formed during the course of the cyclopolymerization process (Figure 3). Figure 6 shows the carbonyl region of the ^{13}C NMR spectra of the polymers obtained by ATRP at 70 and 100 °C. The peak assignments of the carbonyl region were previously reported for the different ring-plus-repeat unit microstructures.[3] Comparison of the peaks clearly indicates that the relative amounts of the two *meso* products increased at higher temperature. In addition, the microstructures of the polymers obtained by the ATRP and conventional radical polymerization processes were also compared (Figure 6). The ^{13}C NMR analyses of the polymers indicates that under similar conditions and polymerization temperatures, similar microstructures are observed. Only a slightly higher proportion is observed in rings with the *meso-trans* configuration in the cyclopolymers obtained by conventional radical polymerization method.

Table 4. Glass Transition Temperatures of the Cyclopolymers with Various Molecular Weights and Polydispersities Synthesized at 70 and 100 °C by ATRP[a]

entry	temp (˚C)	$M_{n,sec}$ (10^3g/mol)	M_w/M_n	T_g (˚C)
1	70	8.7	1.17	145.3
2	70	26.0	1.42	138.8
3	70	24.2	1.30	148.9
4	70	10.9	1.19	147.3
5	70	5.8	1.17	129.9
6	70	27.6	1.97	116.5
7	100	19.1	1.44	119.0
8	100	30.6	3.26	118.6
9	70	57.5	2.75	158.7

[a] Entry 9 was generated by conventional free radical polymerization.

Copolymerization Studies. Copolymerization evaluations were carried out to evaluate the livingness of the terminal groups of the cyclopolymers obtained by the ATRP method. The copolymerizations were carried out with the CuBr/PMDETA catalyst complex at 70 °C in bulk and using preformed cyclopolymers as macroinitiators. The second monomer, *tert*-butyl acrylate (*t*-BA) or *n*-butyl acrylate (*n*-BA), was used as the solvent (Table 3). In the SEC trace, the peaks corresponding to macroinitiator disappeared completely and new peaks with relatively narrow polydispersities were observed for block copolymers generated (Figure 7). One example of polymerization using the halogen exchange method was examined in which CuCl was used as the copper halide (bromine end group on the macroinitiator) (entry 3); there was no significant effect on the polymerization. Thus, the combined results suggest that the cyclopolymers obtained by the ATRP method were fully living and capable of being used to synthesize block copolymers and perhaps telechelic cyclopolymers.

Physical Properties of the Cyclopolymers. The glass transition temperatures of the polymers obtained ranged from 120 to 140 °C (Table 4). The results indicate that when the polydispersity increased at a given molecular weight, the T_g decreased (entries 2 and 3). In addition, a T_g difference was observed between the cyclopolymers obtained at 70 and 100 °C, the former giving a higher T_g at a given molecular weight. This is most probably due to the difference in the relative amounts of various ring and repeat unit configurations that the polymers contained in their microstructure (Figure 6). When compared to cyclopolymers obtained by conventional radical polymerization, however, there were no significant T_g differences, indicating that the observed T_g differences for the ATRP systems was due almost entirely to temperature induced effects.

Thermogravimetric analyses (TGA) of the polymers were carried out to determine the thermal stability of the polymers (Figure 8). The onset decomposition temperature was observed in the range 175−200 °C depending somewhat on the molecular

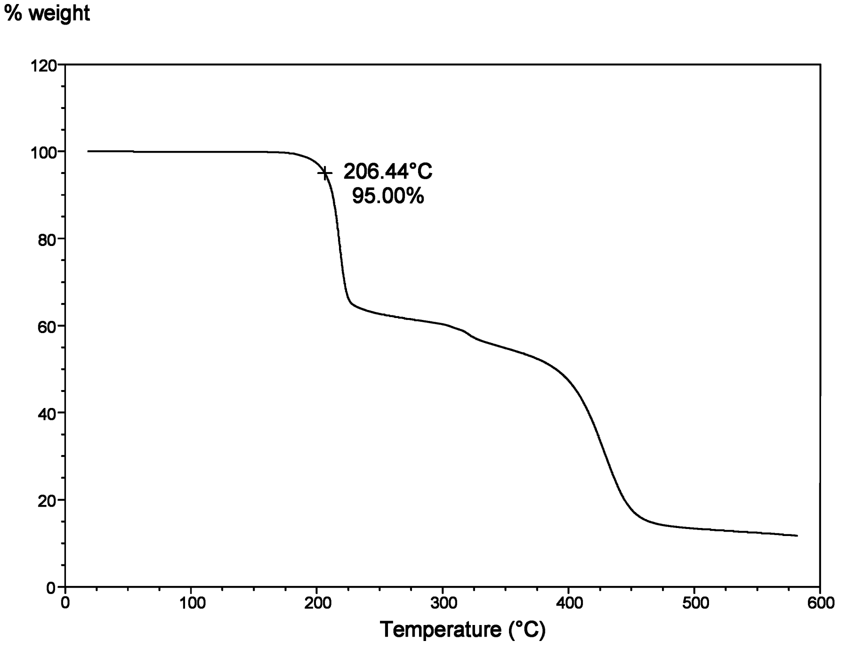


Figure 8. TGA trace of the TBHMA−cyclopolymers (Table 5, entry 3).

Table 5. Thermal Gravimetric Analysis of TBHMA Ether Dimer Polymers[a]

entry	temp (˚C)	$M_{n,sec}$ (10^3g/mol)	M_w/M_n	temp (˚C) at %5 dec
1	70	13.5	1.12	174.8
2	70	22.3	1.19	192.2
3	70	24.2	1.30	206.4
4	100	17.6	1.13	189.4
5	100	19.1	1.44	201.1
6	70	57.5	2.75	212.8

[a] All polymers were generated by ATRP except entry 6. Entry 6 was generated by conventional free radical polymerization.

weight (Table 5), indicating that the end groups might be involved in the first step of the decomposition process. The major decomposition seems to be the loss of the *tert*-butyl group followed by ring decomposition and/or depolymerization. The decomposition behavior and the onset decomposition temperatures are very similar to those of the cyclopolymers obtained by conventional radical cyclopolymerizations (Table 5, entry 6).

Conclusions

Overall, these results show that the cyclopolymerizations of TBHMA ether dimer by ATRP are consistent with the living or controlled nature expected of the polymerization. Cyclopolymers with six-membered tetrahydropyran repeat units were obtained with high conversions, low polydispersities and desired molecular weights. Increasing the polymerization temperature may reduce the controlled behavior of the polymerization and also cause a slight change in the microstructure of the cyclopolymer. This change in microstructure was shown to slightly alter the glass transition temperature of the cylopolymers at a given molecular weight. A difference in the microstructure was also seen between the polymers obtained by conventional and ATRP methods under similar reaction conditions. Most importantly, for the first time, cyclopolymers based on alkyl α-(hydroxymethyl)acrylate (RHMA) ether dimers were obtained as living cyclopolymers with still-reactive end groups which allowed the synthesis of block copolymers. This result opens up new possibilities for these polymers to be used as telechelic cyclopolymers to generate controlled structures and tailored properties. In a larger perspective, this study demonstrates the ability to synthesize an aliphatic cyclopolymer with high glass transition temperature which can be used as a telechelic polymer.

Acknowledgment. This research was funded by Bogazici University Scientific Research Funds (BAP, Project No: 04HB505) and TUBITAK (Project No:104M261), and in part, by the University of Southern Mississippi. The authors thank Assistant Prof. Funda H. Yagci ACAR at Koç University, Istanbul, Turkey, for the SEC analyses of the polymers.

References and Notes

(1) Butler, G. B. *Cyclopolymerization and Cyclocopolymerization*; Marcel Dekker: New York, 1992.
(2) Lee, H. J.; Kodaira, T.; Urushisaki, M.; Hashimoto, T. Cyclopolymerization. Part XXXII Radical Polymerization of α-(2-Phenylallyloxy)methylstyrene: Synthesis of Highly Cyclized Polymers with High Glass Transition Temperatures and Thermal Stability. *Polymer* **2004**, *45*, 7505.
(3) Tsuda, T.; Mathias, L. J. Cyclopolymerization of Ether Dimers of α-(hydroxymethyl)acrylic Acid and its Alkyl Esters: Substituent Effect on Cyclization Efficiency and Microstructures. *Polymer* **1994**, *35*, 3317.
(4) Mathias, L. J.; Warren, R. M.; Huang, S. *tert*-Butyl α-(Hydroxymethyl)acrylate and Its Ether Dimer: Multifunctional Monomers Giving Polymers with Easily Cleaved Ester Groups. *Macromolecules* **1991**, *24*, 2036.
(5) Avci, D.; Lemopulo, K.; Mathias, L. J. Cyclopolymerization of Allyl-Acrylate Quaternary Ammonium Salts with Diallyldimethylammonium Chloride. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 640.
(6) Avci, D.; Haynes, C.; Mathias, L. J. Cyclopolymerization of Amine-Linked Diacrylate Monomers. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2111.
(7) Mathias, L. J.; Kusefoglu, S. H.; Kress, A. O.; Lee, S.; Dickerson, C. W.; Thames, S. F. New Acrylate-Containing Dimers and Oligomers for Crosslinking Vinyl Polymers. *Polymer News* **1992**, *17*, 36.
(8) Mathias, L. J.; Küsefo’’lu, S. H.; Ingram, J. E. Cyclopolymerization of the Ether of Methyl α-(hydroxymethyl)acrylate. *Macromolecules* **1988**, *21*, 545.
(9) Stansbury, J. W. Difunctional and Multifunctional Monomers Capable of Cyclopolymerization. *Macromolecules* **1991**, *24*, 2029.
(10) Kodaira, T.; Okumura, M.; Urushisaki, M.; Isa, K. Effect of *N*-Substituents on Cyclopolymerizability of N-Allylmethacrylamides. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 169.
(11) Fukuda, W.; Suzuki, Y.; Kakiuchi, H.; Novel synthesis of poly(1-t-butylpyrrolidin-2-one-3,4-diylethylene) by Cyclopolymerization of N-t-Butyl-N-Allylacrylamide. *J. Polym. Sci., Polym. Lett. Ed.* **1988**, *26*, 305.

(12) Matyjaszewski, K.; Xia, J. Atom Transfer Radical Polymerization. *Chem. Rev.* **2001**, *101*, 2921.

(13) Kamigaito, M.; Ando, T.; Sawamoto, M. Metal-Catalyzed Living Radical Polymerization. *Chem. Rev.* **2001**, *101*, 3689.

(14) Nanda, A. K.; Matyjaszewski, K. Effect of [PMDETA]/[Cu(I)] Ratio, Monomer, Solvent, Counterion, Ligand, and Alkyl Bromide on the Activation Rate Constants in Atom Transfer Radical Polymerization. *Macromolecules* **2003**, *36*, 1487.

(15) Uegaki, H.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. $NiBr_2(Pn\text{-}Bu_3)_2$-Mediated Living Radical Polymerization of Methacrylates and Acrylates and Their Block or Random Copolymerizations. *Macromolecules* **1998**, *31*, 6756.

(16) Haddleton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J. Atom Transfer Radical Polymerization of Methyl Methacrylate Initiated by Alkyl Bromide and 2-Pyridinecarbaldehyde Imine Copper(I) Complexes. *Macromolecules* **1997**, *30*, 2190.

(17) Chambard, G.; Klumperman, B.; German, A. L. Effect of Solvent on the Activation Rate Parameters for Polystyrene and Poly(butyl acrylate) Macroinitiators in Atom Transfer Radical Polymerization. *Macromolecules* **2000**, *33*, 4417.

(18) Inoue, Y.; Matyjaszewski, K. New Amine-Based Tripodal Copper Cataysts for Atom Transfer Radical Polymerization. *Macromolecules* **2004**, *37*, 4014.

(19) Acar, A. E.; Yagci, M. B.; Mathias, L. J. Adventitious Effect of Air in Atom Transfer Radical Polymerization: Air-Induced (Reverse) Atom Transfer Radical Polymerization of Methacrylates in the Absence of an Added Initiator. *Macromolecules* **2000**, *33*, 7700.

(20) Gao, H.; Matyjaszewski, K. Synthesis of Star Polymers by a Combination of ATRP and the “Click” Coupling Method. *Macromolecules* **2006**, *39*, 4960.

(21) Sarbu, T.; Lin, K.; Spanswick, J.; Gil, R. R.; Siegwart, D. J.; Matyjaszewski, K. Synthesis of Hydroxy-Telechelic Poly(methyl acrylate) and Polystyrene by Atom Transfer Radical Coupling. *Macromolecules* **2004**, *37*, 9694.

(22) He, T.; Li, D.; Sheng, X.; Zhao, B. Synthesis of ABC 3-Miktoarm Star Terpolymers from a Trifunctional Initiator by Combining Ring-Opening Polymerization, Atom Transfer Radical Polymerization, and Nitroxide-Mediated Radical Polymerization. *Macromolecules* **2004**, *37*, 3128.

(23) Altintas, O.; Yilmaz, I.; Hizal, G.; Tunca, U. Synthesis of poly(methyl methacrylate)-*b*-polystyrene containing a crown ether unit at the junction point via combination of atom transfer radical polymerization and nitroxide mediated radical polymerization routes. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 3242.

(24) Shemper, B. S.; Acar, A. E.; Mathias, L. J. Synthesis of Linear and Starlike Polymers from Poly(propylene glycol) Methacrylate Using Controlled Radical Polymerization. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 334.

(25) Zhang, H.; Jiang, X.; Linde, R. Synthesis and Characterisation of Hydroxyl End-Capped Telechelic Polymers with Poly(methyl methacrylate)-*block*-poly*(n*-butyl acrylate) Backbones via Atom Transfer Radical Polymerisation. *Polymer* **2004**, *45*, 1455.

(26) Cai, Y.; Armes, S. P. Synthesis of Well-Defined Y-Shaped Zwitterionic Block Copolymers via Atom-Transfer Radical Polymerization. *Macromolecules* **2005**, *38*, 271.

(27) Tsuji, M.; Sakai, R.; Satoh, T.; Kaga, H.; Kakuchi, T. Enantiomer-Selective Radical Cyclopolymerization of *rac*-2,4-Pentanediyl Dimethacrylate Using ATRP Initiating System with Chiral Amine Ligand. *Macromolecules* **2002**, *35*, 8255.

(28) Tsuji, M.; Aoki, T.; Sakai, R.; Satoh, T.; Kaga, H.; Kakuchi, T. Enantiomer-Selective Radical Cyclopolymerization of *rac*-2,4-Pentanediyl Dimethacrylate Using a Ruthenium-Mediated Chiral Atom Transfer Radical Polymerization Initiating System. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4563.

MA061876E