Controlled/“Living” Reverse Atom Transfer Radical Polymerization of a Monocyclic Olefin, Methyl 1-Cyclobutenecarboxylate

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Received December 3, 2001; Revised Manuscript Received March 22, 2002

ABSTRACT: ATRP of the first cyclic olefin, methyl 1-cyclobutenecarboxylate (MCBE), by addition polymerization in a well controlled/“living” manner is described, along with a new practical method to synthesize MCBE. The polydispersity of poly(methyl 1-cyclobutenecarboxylate) (PMCBE) synthesized by a conventional ATRP initiation system was narrow ($M_w/M_n = 1.1-1.4$), but M_n was usually less than half of the theoretical number-average molecular weight. However, the polymerization of MCBE initiated by a reverse ATRP initiation system, AIBN/CuBr$_2$/dNbpy, was well controlled; the rate of polymerization was first order in monomer, and the molecular weights of the polymers were close to the designed values with very narrow polydispersities ($M_w/M_n = \sim 1.15$). The obtained polymer PMCBE can be used as a macroinitiator to further polymerize a second monomer, such as styrene.

Introduction

Since Szwarc et al.[1] first reported the concept of living polymerization in 1956, a number of living polymerization systems have been reported for anionic,[1] cationic,[2] or group transfer polymerization.[3] Generally, free radical polymerization often yields polymers with a large variety of monomers under relatively mild experimental conditions, but it is usually ill-controlled because of the facile coupling and disproportionation reactions between the propagating species. In recent years, free radical polymerization has undergone a revolutionary transformation. By “buffering” the concentration of propagating free radicals to extremely low concentration, termination has been effectively eliminated. In this way, clean polymers of defined molecular weight and low polydispersity can be obtained. These methods include atom transfer radical polymerization (ATRP)[4−6] using chloro compounds and transition metal complex catalysts, the polymerization of styrene in the presence of the 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) stable free radical,[7] and living radical polymerization by the reversible addition−fragmentation chain transfer (RAFT) process in the presence of dithioesters.[8]

Controlled/“living” radical polymerization via ATRP is an efficient way to synthesize well-defined polymers. There are two kinds of ATRP initiation systems: (conventional) ATRP and reverse ATRP (RATRP). In ATRP,[4−6] organic halides (RX) are used as initiators, transition metal compounds in their lower oxidation state as catalysts, and electron-donating compounds, such as 2,2′-bipyridine, as ligands (L). In RATRP,[9−11] a radical initiator and a higher oxidation state transition metal catalyst complex $M^{n+1}XL_m$ are used instead of the organic halides (usually toxic) and the lower oxidation state catalyst complex M^nL_m (easily oxidized by the oxygen in air). Common free radical initiators, such as AIBN[9] or BPO, are often used for RATRP.[10] Recently, the first noncommon radical initiator, 1,1,2,2-tetraphenyl-1,2-ethanediol (TPED), was successfully used as an initiator for the RATRP initiation system to polymerize MMA in a controlled /“living” process.[11]

So far, the monomers subjected to these techniques have been conventional vinyl monomers, including styrene, (meth)acrylates, vinylpyridines, etc. More recently, we have reported the first ATRP of a non-olefinic monomer, methyl 1-bicyclobutanecarboxylate, in a controlled/“living” fashion.[12]

Methyl 1-cyclobutenecarboxylate readily undergoes conventional free radical homopolymerization and copolymerization with vinyl monomers.[13a] This polymerization proceeds via addition polymerization of the double bond in the ring to give a high yield of polymer containing exclusively 1,2-linked cyclobutane rings in its backbone. Polymers having ring repeat units in the backbone often impart desirable physical properties, e.g., improved thermal, mechanical, optical, and piezoelectric properties to the materials.[13−15] These enhanced properties may qualify them for specialty, high-tech applications. In this paper we wish to report the results of ATRP of the first cyclic olefin, namely methyl 1-cyclobutenecarboxylate (MCBE), by addition polymerization in a controlled/“living” manner.

Experimental Section

Materials. Methyl 2-bromopropionate (MBP) (Aldrich, 98%) was purified by distillation. Styrene (Aldrich, 99%) was purified with a silica gel column and stored under an argon atmosphere at −15 °C. AIBN was recrystallized twice from ethanol and stored at −15 °C. Ethyl 1-bromocyclobutanecarboxylate (Aldrich, 96%), hexamethylphosphoramide (Aldrich, 99%), methyl iodide (Aldrich, 99%), potassium hydroxide (Aldrich, 85+%), diphenyl ether (Aldrich, 99+ %), CuBr (Aldrich, 99.999%), CuBr$_2$ (Aldrich, 99.999%) and 4,4′-dinonyl-2,2′-bipyridyl (dNbpy) (Aldrich, 97%) were used without any further purification.

Characterization. GPC analysis was performed using a LC-10AT Shimadzu high-performance liquid chromatography system with a set of Phenomenex columns (10^3-10^5 Å) calibrated vs polystyrene standard, THF as eluent, at 25 °C. ^{1}H NMR spectra were recorded on a Bruker DRX-500 MHz spectrometer in CDCl$_3$ at 25 °C.

Synthesis of Methyl 1-Cyclobutenecarboxylate (MCBE). A new practical method for the synthesis of methyl 1-cyclobutenecarboxylate is as follows: A mixture of 100 mL of benzene and 12 g (85%, 0.182 mol) of finely pulverized potassium hydroxide was refluxed for 2 h in a 500 mL three-

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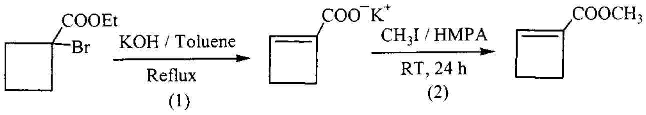
10.1021/ma012104f CCC: $22.00

Scheme 1



neck-flask. After removing the solvent by distillation, 200 mL of dry toluene was added to the dry potassium hydroxide. Under argon atmosphere, at reflux temperature and with vigorous stirring, ethyl 1-bromocyclobutanecarboxylate (10 g, 96%, 0.046 mol) was slowly added at a rate of one drop every 2 s. A vigorous exothermic reaction ensued, and solid potassium salts separated out. After completion of the addition, reflux was maintained for one additional hour. Toluene was thoroughly removed under vacuum followed by addition of 60 mL of water, 120 mL of hexamethylphosphoramide (HMPA), and 30 g (99%, 0.208 mol) of methyl iodide. The orange aqueous solution was stirred at room temperature for 24 h under an argon atmosphere. An aqueous 5% HCl solution was added until the pH of the mixture was below 7. The solution was extracted twice with 200 mL of ether. The combined ether extracts were washed twice with 50 mL of saturated NaCl solution and dried over anhydrous sodium sulfate, and the solvent was slowly evaporated at 0 °C under reduced pressure. The crystalline target product was obtained by distillation at 34−36 °C/12 mmHg while the receiver was chilled with a dry ice/acetone bath. The overall yield was 85%. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.48 (2H, m, 3-H), 2.74 (2H, t, 4-H), 3.73 (3H, s, OCH_3), 6.78 (1H, t, 2-H), which correspond to the literature values.[16a]

Polymerization. All polymerizations were performed with a Schlenk vacuum apparatus. A solution of monomer, initiator (MBP, AIBN, etc.), CuBr or $CuBr_2$, and dNbpy in a glass tube was sealed under vacuum after three freeze−pump−thaw cycles. The tube was placed in an oil bath at the desired temperature. At a specific time, cooling the tube in an ice−water bath stopped the polymerization. The polymer product was dissolved in tetrahydrofuran (THF), and the THF solution was used directly to measure $M_{n(GPC)}$, number-average molecular weight by GPC, and M_w/M_n, at 25 °C. The THF solution of the polymer product was precipitated in *n*-heptane, filtered, and dried under vacuum at 50 °C. The transition metal catalyst was removed with a silica gel column. The conversion of polymerization was determined gravimetrically.

Results and Discussion

Synthesis of MCBE. According to the previous literature,[16] MCBE was synthesized by the esterification of 1-cyclobutenecarboxylic acid (CBEA) with diazomethane. But CBEA is prone to rapid polymerization and absorption of atmospheric oxygen.[16]

Our new procedure to synthesize methyl 1-cyclobutenecarboxylate is shown in Scheme 1. Carboxylic acids can be easily converted to esters in high yield by reaction of their salts with alkyl iodides in HMPA at room temperature.[17] The stable potassium 1-cyclobutenecarboxylate was produced by the reaction of ethyl 1-bromocyclobutanecarboxylate with excess anhydrous potassium hydroxide. Reaction of potassium 1-cyclobutenecarboxylate with methyl iodide in HMPA at room temperature led to MCBE in high yield. An advantage of this procedure is that the potassium salt can be directly used for the next reaction, i.e., the esterification, without isolating the salt. In comparison with the method mentioned above, the new synthesis procedure has a relatively simple workup and can be performed under mild conditions. More importantly, the highly unstable CBEA is not an intermediate. A possible side reaction in the first step of the synthesis, i.e., the dehydrohalogenation/saponification step, is the formation of 1-(hydroxymethyl)cyclopropanecarboxylic acid, instead of potassium 1-cyclobutenecarboxylate, due to the presence of water in the potassium hydroxide.[18] To eliminate this side reaction, it is imperative to remove the water absorbed in the KOH. The water can be removed as an azeotrope with benzene by distillation. The new procedure also has good reproducibility in high overall yield (~85%).

Table 1. ATRP of Methyl 1-Cyclobutenecarboxylate (MCBE) Initiated by MBP/CuBr/dNbpy in Bulk at 100 °C[a]

no.[b]	time (h)	conv (%)	$M_{n(GPC)}$	$M_{n(th)}$[c]	M_w/M_n	f[d]
1	3	41.5	4940	9 310	1.22	1.88
2	7	79.4	7410	17 800	1.19	2.40
3	12	99.8	10400	22 400	1.14	2.15
4[e]	6	63	6280	14 100	1.36	2.25
5[e]	17	82	7630	18 400	1.31	2.41
6[f]	6.5	87.2	6590	20 600	1.19	3.13

[a] $[MCBE]_0 = 7.99$ mol/L, $[MCBE]_0/[MBP]_0/[CuBr]_0/[dNbpy]_0 = 200{:}1{:}1.5{:}3$; MBP = methyl bromopropionate. [b] Entry number. [c] $M_{n(th)} = ([MCBE]_0/[MBP]_0) \times MW_{MCBE} \times$ conversion. [d] $f = M_{n(th)}/M_{n(GPC)}$. [e] The catalyst was CuCl instead of CuBr. [f] The initiator was methyl 1-bromocyclobutanecarboxylate instead of MBP, at 85 °C.

ATRP of Methyl 1-Cyclobutenecarboxylate (MCBE). We investigated the ATRP of MCBE initiated by the methyl 2-bromopropionate (MBP)/CuBr/dNbpy initiation system, and the results are summarized in Table 1. The rate of polymerization was found to be low at 85 °C, so the homogeneous ATRP of MCBE was carried out in bulk at 100 °C using $[MCBE]_0/[MBP]_0/[CuBr]_0/[dNbpy]_0 = 200{:}1{:}1.5{:}3$. The molecular weights of the polymers linearly increased in the conversion range from about 40 to 100% ($M_n = 4940-10\,400$) with rather narrow polydispersities, $M_w/M_n = 1.14-1.22$ (entries 1, 2, and 3 in Table 1). However, the molecular weights of the obtained polymers were not well controlled, generally about half of the designed values, i.e., $M_{n(GPC)} \sim {}^1/_2 M_{n(th)}$. As can be seen from entries 4 or 5 in Table 1, when CuCl was used as a catalyst instead of CuBr, similar results were observed, but with larger polydispersities (1.31−1.36). The polymerizations catalyzed by CuBr were thus better controlled than those using CuCl. When methyl 1-bromocyclobutanecarboxylate was used as the initiator instead of MBP, the molecular weight was even lower, $M_{n(GPC)} \sim {}^1/_3 M_{n(th)}$, though with a narrow polydispersity (1.19) (entry 6 in Table 1). The initiator efficiency values *f*, computed from $f = M_{n(th)}/M_{n(GPC)}$, were high, usually >2 (Table 1). This indicates that more active species were produced in this particular MCBE polymerization, probably from the facile auto thermal polymerization of monomer MCBE at this high temperature (100 °C).[13a]

RATRP of MCBE. In response to the rather unsatisfactory ATRP results, we decided to investigate other initiation systems. We found that RATRP can be performed effectively at the lower temperature, i.e., 85 °C. The following RATRP initiation system was selected: 2,2′-azobis(isobutyronitrile) (AIBN)/$CuBr_2$/dNbpy, in which AIBN was used as an initiator and $CuBr_2$ as catalyst. The polymerization system, with $[MCBE]_0{:}[AIBN]_0{:}[CuBr_2]_0{:}[dNbpy]_0 \sim 200{:}1{:}2{:}4$, was heterogeneous at room temperature but instantly (<20 s) became homogeneous after the polymerization tubes were placed in a 85 °C oil bath for polymerization. The results show that the number-average molecular weight linearly increased with monomer conversion as shown in Figure 1. $M_{n(GPC)}$, measured by GPC, was almost equal to $M_{n(th)}$ (from 2620 to 9270), while the polydispersity was very

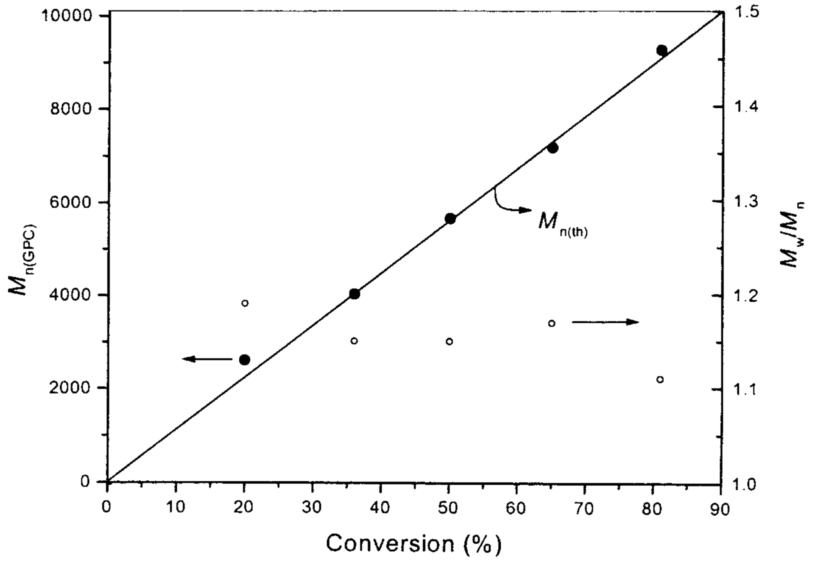


Figure 1. Dependence of molecular weight and polydispersity on conversion in bulk polymerization of MCBE at 85 °C with $[MCBE]_0 = 7.96$ mol/L, $[AIBN]_0 = 0.04$ mol/L, $[CuBr_2]_0 = 0.08$ mol/L, and $[dNbpy]_0 = 0.16$ mol/L.

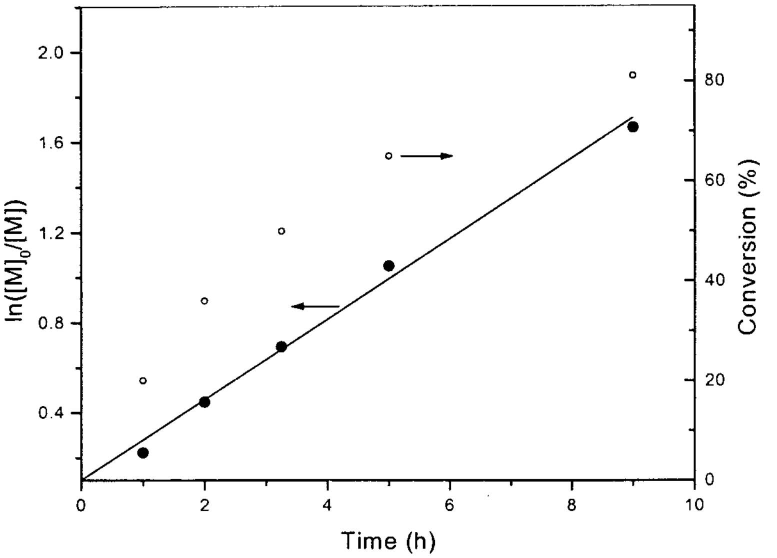


Figure 2. Correlation of $\ln([M]_0/[M])$ and conversion vs time in bulk polymerization of MCBE at 85 °C with $[MCBE]_0 = 7.96$ mol/L and $[AIBN]_0:[CuBr_2]_0:[dNbpy]_0 = 1:2:4$.

Table 2. RATRP of Methyl 1-Cyclobutenecarboxylate (MCBE) Initiated by AIBN/CuBr$_2$/DNbpy

no.[a]	C[b]	temp (°C)	time	conv (%)	$M_{n(GPC)}$	$M_{n(th)}$[c]	M_w/M_n	f[d]
1	200/0.61/1.22/2.44	85	7 h	91	15 500	16 700	1.15	1.08
2	200/1/2/4	100	2.3 h	62.4	7 100	7 000	1.17	0.99
3	200/1/0/0	85	10 min	89	86 600		3.09	

[a] Entry number. [b] $C = [MCBE]_0/[AIBN]_0/[CuBr_2]_0/[dNbpy]_0$. [c] $M_{n(th)} = ([MCBE]_0/2[AIBN]_0) \times MW_{MCBE} \times$ conversion. [d] $f = M_{n(th)}/M_{n(GPC)}$.

narrow, $M_w/M_n = 1.11-1.19$, and the monomer conversion increased from 20% to 81% over a 9 h time period. $M_{n(th)}$ is the theoretical number-average molecular weight, computed from $M_{n(th)} = ([MCBE]_0/2[AIBN]_0) \times MW_{MCBE} \times$ conversion. The initiator efficiencies f were about 1.0 in all cases. These results suggest that the polymerization is well controlled. A plot of $\ln([MCBE]_0/[MCBE])$ vs time displayed first-order kinetics, as seen in Figure 2, indicating that the concentration of propagating radicals was almost constant and that the rate of polymerization was first order in monomer. Therefore, the polymerization of MCBE was a "living" polymerization process without any significant irreversible termination.

Using the AIBN/CuBr$_2$/dNbpy initiation system at 85 °C, but with a higher ratio of $[MCBE]_0$ to $[AIBN]_0$ (200: 0.61 vs 200:1 above), a polymer with higher molecular weight ($M_n = 15\,500$) and still very narrow polydispersity ($M_w/M_n = 1.15$) was produced (entry 1 in Table 2). Even at higher temperature, 100 °C, a well-controlled polymerization of MCBE was still possible. In contrast, the conventional radical polymerization was not at all controlled, with broad molecular weight polydispersities, i.e., $M_w/M_n = 3.09$ (entry 3 in Table 2).

Polymer Structure and Polymerization Mechanism. The structure of the polymer PMCBE synthesized by either AIBN or AIBN/CuBr$_2$/dNbpy is identical, as shown by ^{1}H NMR spectroscopy (Figure 3). The signals

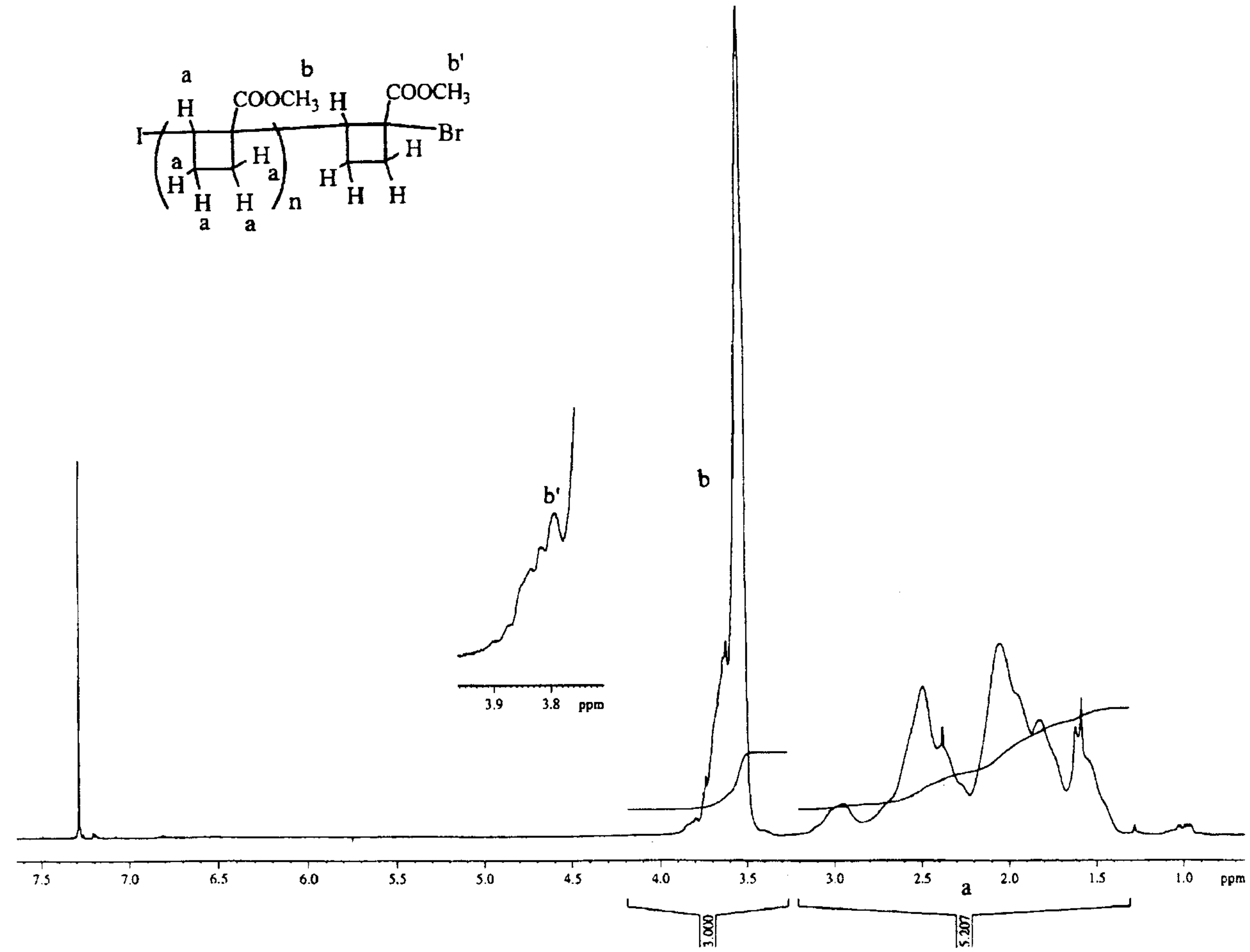


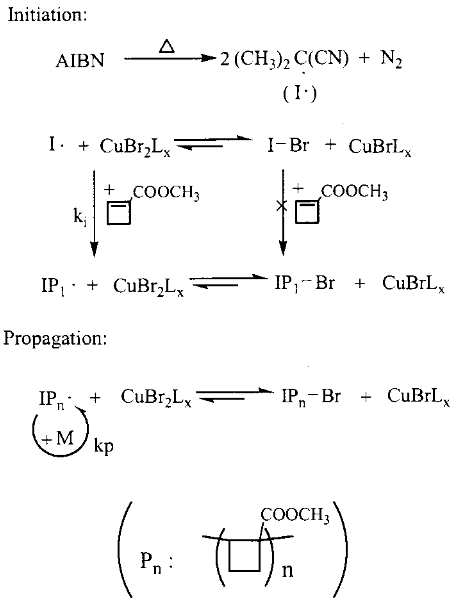
Figure 3. ^{1}H NMR of PMCBE (M_n = 7180, M_w/M_n = 1.17) synthesized by AIBN/CuBr$_2$/dNbpy initiation system at 85 °C.

at chemical shift 1.52−2.92 ppm are due to the five protons of the cyclobutane ring in the polymer backbone and those at 3.52−3.71 ppm to the ester methyl group. This indicates that the polymerization initiated by AIBN/CuBr$_2$/dNbpy proceeded via addition polymerization just like a conventional radical polymerization initiated by AIBN. The signals at 3.79 ppm (b′) are due to the protons of the methoxy groups of the terminal MCBE unit capped with an ω-bromine end group, somewhat similar to those reported by Ando et al.[19]

The presence of an ω-Br end group demonstrates that the polymerization proceeds via an ATRP process. The mechanism of the RATRP of MCBE by the controlled/“living” addition polymerization of cyclobutene ester is depicted in Scheme 2.

The concentration of Cu^{2+} is higher at the beginning of the polymerization in the RATRP system than in ATRP system.[4,9] Our results showed that the radical polymerization was better controlled with the AIBN/CuBr$_2$/dNbpy initiation system than with the MBP/CuBr/dNbpy initiation system. This is probably due to the fact that Cu^{2+} is a strong and efficient inhibitor or retarder for radical polymerization under normal conditions.[20] The spontaneous thermal polymerization and side reactions through conventional radical polymerization were effectively eliminated in the AIBN/CuBr$_2$-catalyzed RATRP system due to several factors: RATRP proceeds at about double the rate of the ATRP polymerization, the concentration of Cu^{2+} is high at the beginning of the polymerization when monomer concentration is high, and the spontaneous thermal polymerization of styrene is very dependent on monomer concentration because it is second order and therefore will slow down considerably as monomer is used up.

Scheme 2



Chain Extension Reaction. A chain extension of PMCBE synthesized with AIBN/CuBr$_2$/dNbpy to another monomer such as St was carried out in diphenyl ether at 100 °C. When $[\mathrm{St}]_0$ = 2.88 mol/L, $[\mathrm{PMCBE}]_0$ = 3.68×10^{-2} mol/L, $[\mathrm{PMBCE}]_0$:$[\mathrm{CuBr}]_0$:$[\mathrm{dNbpy}]_0$ = 1:1:

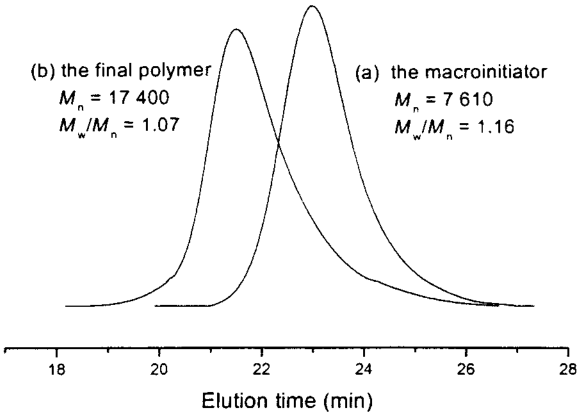


Figure 4. GPC curves of polymers before (a) and after (b) chain extension of PMCBE synthesized by AIBN/$CuBr_2$/dNbpy.

2, M_n of PMCBE = 7610, $M_w/M_n = 1.16$, the conversion of St was 52.2% after 45 h, M_n of the obtained polymer increased to 17 400, and M_w/M_n decreased to 1.07. The increasing molecular weight of the resultant polymer was observed from the GPC curves as shown in Figure 4. The GPC curve (a) for the macroinitiator almost disappeared in the monomodal GPC curve (b) of the final polymer. This result indicates that the PMCBE was used as a macroinitiator to further polymerize the second monomer, St, thereby forming a polymer with larger molecular weight in a conventional ATRP system. It further suggests that the PMCBE synthesized by the AIBN/$CuBr_2$/dNbpy initiation system has an ω-halogen (bromine) end group, and the mechanism of polymerization was through RATRP.

Conclusions

In conclusion, ATRP of the first monocyclic olefin, namely methyl 1-cyclobutenecarboxylate, was successfully carried out by addition polymerization with an RATRP initiation system, AIBN/$CuBr_2$/dNbpy at 85 °C, in a well-controlled/"living" manner. The rate of polymerization was first order in monomer, and the molecular weights of polymer were almost equal to the theoretical ones with very narrow polydispersities ($M_w/M_n = \sim1.15$). The obtained polymer PMCBE is used as a macroinitiator to polymerize a second monomer St in an ATRP system due to the presence of an ω-bromine end group in the polymer molecules. The polymerization of MBCE initiated by a conventional ATRP system, MBP/CuBr/dNbpy, at 100 °C was not well controlled.

Acknowledgment. The authors gratefully acknowledge funding provided by the Petroleum Research Fund, administered by the American Chemical Society. Additional funding was obtained from the National Science Foundation, Division of Material Research.

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MA012104F