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Atom Transfer Radical Polymerization of Methyl Bicyclobutane-1-carboxylate

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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),[1−3] nitroxyl-mediated polymerization,[4] and reversible addition−fragmentation chain transfer (RAFT)[5] techniques.

To date, the monomers subjected to these techniques have been conventional vinyl monomers, including styrene, (meth)acrylates, vinylpyridines, etc. More recently, the "living" free radical ring-opening polymerization of 5,6-benzo-2-methylene-1,3-dioxepane by ATRP has been reported.[6] Bicyclobutanes carrying electronegative substituents at one or both bridgehead atoms are another family of monomers that undergoes free radical homopolymerization, and copolymerization with vinyl monomers occurs readily.[7] Here the strained 1,3-bond is π-like in character and readily undergoes S_H2 propagation reaction (Scheme 1).[8,9] Polymers containing only cyclic repeat units in the backbone often show desirable physical properties, e.g., improved thermal, mechanical, optical, and piezoelectric properties.[7−9] These enhanced properties may qualify them for specialty, high-tech applications.

We now demonstrate the power and beauty of ATRP by extending it to the class of ester-containing bicyclic monomers, namely methyl bicyclobutane-1-carboxylate (MBC), which was successfully carried out by radical ring-opening polymerization in a controlled/"living" manner.

The homogeneous ATRP[10] of MBC in diphenyl ether led to controlled polymers having all rings in the backbone, with predetermined molecular weights and relatively narrow polydispersities, $M_w/M_n \approx 1.3$. The initiation system was methyl 2-bromopropionate (MBP)/CuBr/4,4′-dinonyl-2,2′-bipyridyl (dNbpy). Using $[MBC]_0$:$[MBP]_0$:$[CuBr]_0$:$[dNbpy]_0 \approx 200:1:1.5:3$ at 70 °C, the number-average molecular weight increases linearly with monomer conversion as shown in Figure 1. $M_{n(GPC)}$ was very close to $M_{n(th)}$, in the range 2980−18 200, while the polydispersity was fairly low, $M_w/M_n = 1.23−1.33$, as the monomer conversion increased from 13.6% to 83.2% within 14 h. $M_{n(th)}$ is the theoretical number-average molecular weight, calculated from $M_{n(th)} = ([MBC]_0/[MBP]_0) \times MW_{MBC} \times$ conversion. The initiator efficiencies f ($f = M_{n(th)}/M_{n(GPC)}$) were about 1.0. These results suggest that the polymerization is well-controlled. A straight line was obtained from a plot of ln($[MBC]_0/[MBC]$) vs time, as seen in Figure 2, indicating that the concentration of propagating radicals was constant and the rate of polymerization was a first-order reaction in monomer. Therefore, the polymerization was "living", without significant irreversible termination. However, there was an inhibition period resulting from the excess of CuBr at the beginning of the polymerization. The conventional radical polymerization was uncontrolled, with broad molecular weight polydispersity of polymer, i.e., $M_w/M_n = 4.3$ (entry 6 in Table 1).

The initial ratio of initiator to catalyst and the polymerization temperature were critical to obtain controlled polymerization. We investigated the ATRP of MBC with a $[MBP]_0$:$[CuBr]_0$ ratio of 1:1 (Table 1). Using these fixed conditions, the polydispersities were not well-controlled ($M_w/M_n \approx 1.5$) at 75 or 60 °C after 2 h (entries 1 and 2). At a lower temperature, namely 50 °C (entry 3), a polymer with relatively low polydispersity, $M_w/M_n = 1.34$, was obtained after 2 h; however, the lower f (0.60) suggested the rate of decomposition of the C−Br bond was too slow at 50 °C. When the concentration of CuBr was increased, i.e., the ratio of $[MBP]_0$:$[CuBr]_0$ was 1:1.5 (entry 5), the polymerization became well controlled at 70 °C, with a narrower polydispersity ($M_w/M_n = 1.27$) and designed molecular weight, with 13.6% of conversion after 2 h. This demonstrated that a higher concentration of catalyst could efficiently deactivate the active species in the polymerization system. However, when the temperature was lowered to 60 °C (entry 4), only a trace of polymer and a lower rate of polymerization were observed.

On the basis of previous reports,[8,9] the cyclobutane rings present in the polymer backbone can be either in a cis or in a trans configuration; i.e., there are two types of methoxy groups for the esters in the chains of PMBC, i.e., trans or cis CH_3 ester, which have chemical shifts at 3.65 or 3.68 ppm, respectively. The signals at 3.79 or 3.82 ppm are due to the protons of the trans or cis methoxy groups, respectively, of the terminal MBC unit capped with an ω-end bromine, somewhat similar to those reported by Ando et al.[11] The presence of an ω-Br end group demonstrates that the polymerization proceeds via an ATRP process. The chemical shifts at 1.03 and 1.04 ppm are assigned to the protons of α-C$\boldsymbol{H}_3$CH(COOCH$_3$) group from the initiator MBP. Moreover, the $M_{n(NMR)}$ (8600) is close to $M_{n(GPC)}$ (8700), indicating that almost every polymer chain has a bromine end group. In other words, MBP as initiator effectively initiates the polymerization and CuBr as catalyst effectively deactivates the active species during the polymerization; thus, we conclude that the radical polymerization was carried out in a controlled manner through ATRP mechanism. Also, the polymers from this non-olefinic monomer are well-defined, not only with narrow polydispersity and predetermined number-average molecular weight but also with precise α-$CH_3CH(COOCH_3)$ and ω-bromine atom end groups. The ^{13}C spectrum of PMBC synthesized by ATRP is similar to that of polymers obtained from other methods such as thermal, photochemical, or redox processes. The proportion of cis to trans rings in the polymer chains by ATRP is the same as that from other methods; i.e., 66% of the rings are trans fused.[9,12] This indicates that ATRP has no special effect on the chain structures of the PMBC.

On the basis of our results and the accepted mechanism for conventional radical polymerization of MBC,

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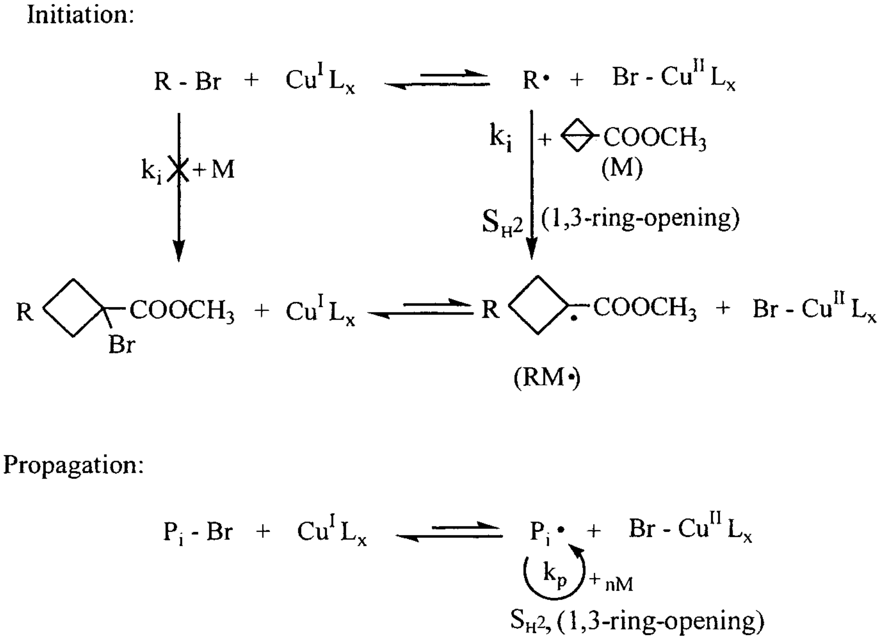
Scheme 1. Atom Transfer Radical Polymerization of Methyl Bicyclobutane-1-carboxylate



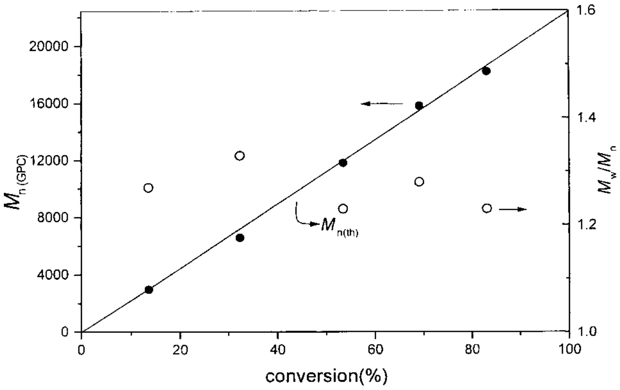


Figure 1. Dependence of molecular weights and polydispersities on conversion in solution polymerization of MBC in diphenyl ether at 70 °C with $[\mathrm{MBP}]_0 = 0.02$ mol/L, $[\mathrm{CuBr}]_0 = 0.03$ mol/L, and $[\mathrm{dNbpy}]_0 = 0.06$ mol/L.

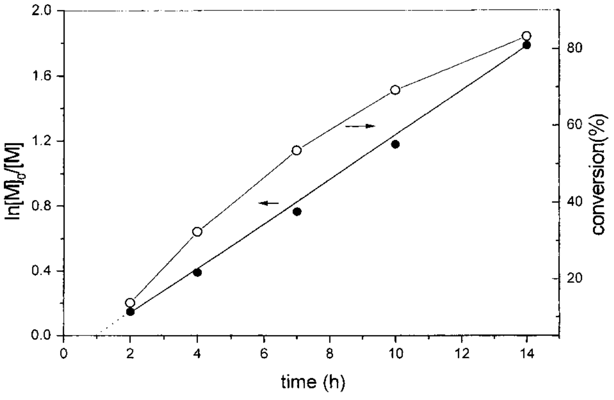


Figure 2. Correlation of $\ln([M]_0/[M])$ and conversion vs time in the solution polymerization of MBC in diphenyl ether at 70 °C with $[\mathrm{MBP}]_0{:}[\mathrm{CuBr}]_0{:}[\mathrm{dNbpy}]_0 = 1{:}1.5{:}3$.

Table 1. Polymerization of Methyl 1-Bicyclobutanecarboxylate (MBC) in Diphenyl Ether[a]

no.[b]	C[c]	T (°C)	conv (%)	$M_{\mathrm{n(GPC)}}$	$M_{\mathrm{n(th)}}$[d]	PDI	f[e]
1	1:1	75	63	6790	14100	1.46	2.08
2	1:1	60	49.4	7360	11100	1.57	1.51
3	1:1	50	7.4	2750	1660	1.34	0.60
4	1:1.5	60		trace			
5	1:1.5	70	13.6	2980	3050	1.27	1.02
6[f]		70	82	11300		4.3	

[a] $[\mathrm{MBC}]_0{:}[\mathrm{MBP}]_0 = 200{:}1$, $[\mathrm{CuBr}]_0{:}[\mathrm{dNbpy}]_0 = 1{:}2$; time = 2 h; MBP = methyl 2-bromopropionate, dNbpy = 4,4′-dinonyl-2,2′-bipyridyl. [b] Entry number. [c] $C = [\mathrm{MBP}]_0{:}[\mathrm{CuBr}]_0$. [d] $M_{\mathrm{n(th)}} = ([\mathrm{MBC}]_0/[\mathrm{MBP}]_0) \times \mathrm{MW_{MBC}} \times$ conversion. [e] $f = M_{\mathrm{n(th)}}/M_{\mathrm{n(GPC)}}$. [f] Control experiment of a conventional radical polymerization in diphenyl ether: $[\mathrm{MBC}]_0 = 2.2316$ mol/L, $[\mathrm{AIBN}]_0 = 0.2736$ mol/L, 5 h.

the mechanism for ATRP of MBC by radical ring-opening is proposed as depicted in Scheme 1. The primary radicals R$^\bullet$ initiate monomers to form monomer radicals RM$^\bullet$, and these active radicals combine with monomers to form the polymer chains by 1,3-ring-opening of the monomers. The controlled polymerization proceeds via a number of atom transfer radical addition equilibria, in which growing radicals P_i are deactivated by the transition-metal catalyst at higher oxidization state $\mathrm{Cu^{II}L}_x$, and the dormant species P_i−Br and the transition-metal catalyst at lower oxidization state $\mathrm{Cu^{I}L}_x$ are reversibly produced.

Since PMBC synthesized by the ATRP initiation system has an ω-bromine end group, it can be used as a macroinitiator for ATRP. For example, for a solution process at 75 °C, using PMBC with $M_n = 17\,300$ and $M_w/M_n = 1.30$, $[\mathrm{PMBC}]_0 = 6.02 \times 10^{-3}$ mol/L, $[\mathrm{MMA}]_0 = 5.71$ mol/L, $[\mathrm{CuBr}]_0 = 6.02 \times 10^{-3}$ mol/L, and $[2{,}2\text{-bipyridine}]_0 = 1.81 \times 10^{-2}$ mol/L; a conversion of 96.5% was achieved after 22 h, with M_n of the resultant polymer = 260 800 and $M_w/M_n = 1.20$.

In conclusion, ATRP has been successfully extended to a non-olefinic monomer, methyl 1-bicyclobutanecarboxylate, in a well controlled/"living" manner. A well-defined polymer with all cyclobutane ring units in the chains was synthesized by the controlled/"living" radical ring-opening polymerization, not only with narrow polydispersity and designed number-average molecular weight but also with precise end groups.

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(10) A typical polymerization was carried out at 70 °C by heating a reddish brown MBC solution in phenyl ether of MBP (0.005 molar equiv relative to monomer), CuBr (1.5 molar equiv relative to initiator MBP), and dNbpy (2 molar equiv relative to CuBr) in a glass tube sealed under vacuum after three freeze−pump−thaw cycles. The tube was then placed in an oil bath held at the desired temperature by a thermostat. At a specific time, the polymerization was stopped by cooling the tube in an ice−water bath. 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, calibrated with polystyrene standards, 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. The conversion of polymerization was determined gravimetrically.

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(12) ^{1}H NMR (in $CDCl_3$ on a Bruker DRX-500 MHz spectrometer): δ (ppm): 3.68 and 3.65 (3H, cis and trans CH_3 ester), 3.82 and 3.79 (protons of Br-end capped cis and trans CH_3 ester), 2.71, 2.57 and 2.47 (1H, CH of cyclobutane), 2.27 (2H, CH_2 exo of cyclobutane), 2.01 and 1.92 (2H, CH_2 endo of cyclobutane), 1.03 and 1.04 (3H, α-CH_3). ^{13}C spectrum ($CDCl_3$): δ (ppm): 177.06 and 176.44 (carbonyl cis and trans), 52.01 and 51.75 (CH_3 ester cis and trans), 46.19 and 44.06 (C cyclobutane), 35.11, 33.48 and 33.01 (CH cyclobutane, cis and trans), 29.30 and 28.56 (CH_2 cyclobutane).

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