Synthesis of New Telechelic Polymers Containing Two OH Groups at the Same Chain End Using 8-Boraindane/Oxygen Controlled Radical Initiator

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Telechelic polymers,[1] possessing two terminal functional groups, are an important class of polymeric materials. They find applications as prepolymers for inclusion in final products (linear polymers, networks, or surfaces)[2] with well-specified properties.[3] A well-known example is polyol, such as telechelic poly(ethylene oxide) and poly(propylene oxide) having two terminal OH groups (one on each chain end), which becomes part of polyurethane[4] after coupling with diisocyanates or/and triisocyanates. They can be used along or mixed with other diols or triols to control the final polymer architecture. In general, the prepolymers provide flexibility to the polymer design in order to prepare materials with a wide array of physical properties. However, the purity of prepolymer, with a functionality of 2 ($f = 2$) in each polymer chain, is essential for successful construction of the final polymer structure.

In chemistry, the ability to synthesize telechelic polymers containing exactly two terminal functional groups ($f = 2$) is very limited. Most commercial telechelic polymers, such as aliphatic polyesters[5] (with two opposing terminal acid or alcohol groups) and poly(ethylene oxide) and poly(propylene oxide)[6] (with two opposing terminal alcohol groups), are prepared by polycondensation reaction and ring-opening polymerization with suitable initiators, respectively. The preparation of telechelic vinyl polymers ($f = 2$) is very difficult and usually requires the combination of living polymerization, difunctional initiators[7] or functionally substituted initiators,[8] and selective termination (functionalization) chemistry. Although this methodology has been applied to practically all vinyl polymerization techniques, including anionic,[9] cationic,[10] free radical,[11] and metathesis,[12] only a few examples have been demonstrated to achieve a functionality of 2 in each polymer chain. The complete end-capping of the active polymer chain end with a functional group is particularly difficult due to the low concentration of active sites and the limited number of suitable reagents that can achieve 100% functionalization.

It is scientifically interesting to develop a new synthesis route for preparing vinyl-based telechelic polymers as well as new telechelic polymer structures that have two terminal functional groups located at the same chain end. Upon subsequent condensation reaction, this telechelic prepolymers can be incorporated as the long side chains in the final polymer structure (branch, network, supermolecular structures) to provide specific properties.

In this paper, we discuss a novel route for preparing new telechelic polymers, including poly(methyl methacrylate) (PMMA) and poly(trifluoroethyl acrylate) (PTFEA), containing two reactive OH groups at the same polymer chain end. The process is centered on a bicycloborane compound (i.e., 8-boraindane) serving as a functional initiator that not only initiates the controlled radical polymerization but also produces two functional groups at the beginning of the polymer chain, as illustrated in Scheme 1.

Scheme 1 only explains the reaction mechanism; however, oxidation reactions on both 5- and 6-member rings are possible. Ideally, one of the three cyclic C−B bonds in 8-boraindane (**I**) is oxidized under a controlled oxidation condition to form a peroxide compound ($C-O-O-BR_2$) (**II**) that initiates controlled radical polymerization.[13] In the presence of MMA monomers at ambient temperature, the $C-O-O-BR_2$ species is further decomposed to an alkoxyl radical ($C-O^*$) and a borinate radical ($^*O-BR_2$). The alkoxyl radical is active in initiating the polymerization of MMA. On the other hand, the borinate radical is believed to be too stable to initiate polymerization due to the back-donating of electrons to the empty p-orbital of boron. However, this "stable" borinate radical may form a reversible bond with the radical at the growing chain end to form dormant species and prolong the lifetime of the propagating radical. In the whole polymerization process, the monooxidized bicycloborane residue remains bonded to the beginning of the polymer chain (**III**), despite the continuous growth of the polymer chain. After completing the polymerization, the two unreacted C−B bonds in the borane residue can be completely converted to two OH groups[14] by H_2O_2/NaOH reagent. The resulting telechelic PMMA polymer (**IV**) has two OH groups located at the same chain end as well as a controlled molecular weight and relatively narrow molecular weight distribution.

Table 1 summarizes several comparative polymerization sets in the preparation of telechelic PMMA and PTFEA polymers, including both bulk and solution reaction conditions. After mixing 8-boraindane with MMA or TFEA monomers (with or without solvent) a controlled amount of oxygen was slowly introduced into the system to start the polymerization at ambient temperature. The 8-boraindane/O_2 mole ratios were controlled between 3/1 and 3/2 to minimize the potential for multiple-oxidation reaction on each 8-boraindane. Comparing the polymer yield vs reaction time in two bulk polymerization sets (runs 1−5 and 6−9) shows that there was almost double the productivity in the 3/2 case vs the 3/1 case, which indicates the formation of active sites linearly proportional to the oxygen quantity under controlled oxidation conditions. As expected, the polymer molecular weight also showed a significant reduction in the higher active site environment. After a designated reaction time, all polymers were treated with NaOH and H_2O_2 to ensure complete oxidation of the borane moieties. The resulting polymers were characterized by ^{1}H and ^{13}C NMR-DEPT measurements and gel permeation chromatography (GPC) using a standard polystyrene calibration curve.

Figure 1 (top) compares the GPC curves of three telechelic PMMA samples (runs 1, 3, and 5 in Table 1).

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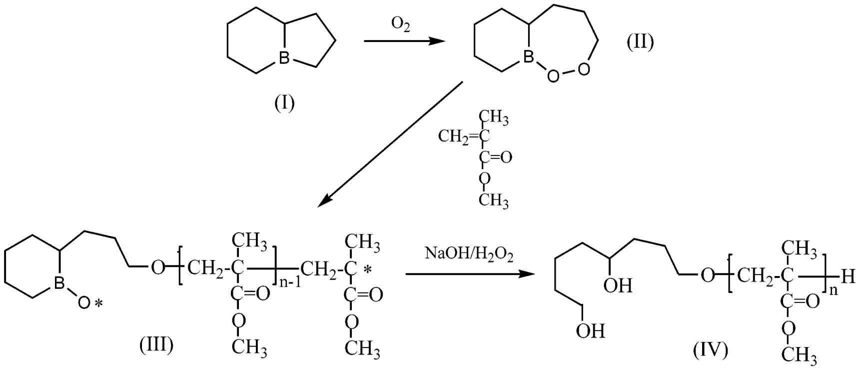
Scheme 1



The molecular weight of obtained polymer continuously increased throughout the polymerization process, from 18 000 g/mol in run 1 to 100 000 g/mol in run 5. The broader molecular weight distribution at the beginning of the polymerization may be attributed to the slow formation of active sites that are prepared in situ by reacting two very dilute reagents, including borane reagent in solution and oxygen in gas phase. Similar results were also observed in the PTFEA polymers (runs 10−14) that were prepared in THF solution. With longer reaction time, the polymer increases its molecular weight and the overall molecular weight distribution gradually reduces. In the second reaction set (runs 6−9), both the polymer molecular weight and the molecular weight distribution increase with reaction time. The broadening in the molecular weight distribution may indicate the diffusion problem in the bulk condition, especially after high monomer conversions (runs 7 and 8).

Figure 1 (bottom) plots polymer molecular weight vs monomer conversion in the first bulk polymerization set (runs 1−5 in Table 1) using a 1/3 [oxygen]/[borane] mole ratio. Compared with a theoretical line based on the [g of monomer consumed]/[mole of initiator], a good match with the straight line through the origin supports the presence of controlled radical polymerization in the reaction. The linear increase of the molecular weight with a relatively narrow molecular weight distribution implies a "stable" propagating chain end without significant termination and chain transfer reactions. Apparently, a constant number of active sites are formed after the oxidation reaction, which maintained reactivity throughout the polymerization process. This controlled radical polymerization was also evidenced in the preparation of diblock copolymers, such as poly(methyl methacrylate-*b*-trifluoroethyl acrylate), by sequential monomer addition (discussed later).

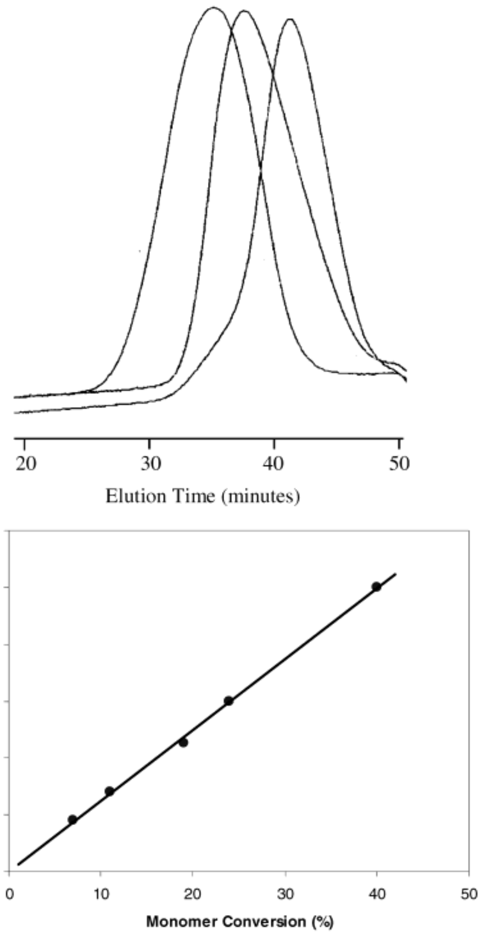


Figure 1. (top) GPC curves of telechelic PMMA samples (runs 1, 3, and 5). (bottom) Plots of polymer molecular weight vs monomer conversion (runs 1−5).

The two terminal OH groups located at the beginning of the polymer chain were examined by a combination of ^{1}H and ^{13}C NMR-DEPT measurements. Figure 2 shows the ^{1}H NMR spectra of a telechelic PMMA ($M_n = 11 \times 10^3$; $M_w/M_n = 1.6$) and its corresponding trimethylsilane derivative. In addition to the expected chemical shifts between 0.9 and 1.9 ppm, corresponding to the $C\mathbf{H}_3$ and $C\mathbf{H}_2$ groups in the PMMA backbone, there is a strong singlet chemical shift at 3.58 ppm ($-O-C\mathbf{H}_3$ group in PMMA) overlapping with several weak peaks that indicate the existence of OH groups. To determine the concentration of the OH groups, the telechelic PMMA polymer was quantitatively converted to the corresponding silane derivative by reacting with $Cl-Si(CH_3)_3$ reagent. In Figure 2b, a new chemical shift at 0.15 ppm corresponding to $-O-Si(C\mathbf{H}_3)_3$ is clearly observed with a reasonable intensity for qualitative analysis. The peak intensity ratio between two peaks (3.58 and 0.15 ppm) and the representing protons indicate about two OH groups per PMMA chain.

To provide direct experimental evidence for the existence of both primary and secondary OH groups in the telechelic polymer (as shown in eq 1), the resulting polymers were also examined by the ^{13}C NMR (DEPT-135) technique. Figure 3 shows the ^{13}C NMR (DEPT-135) spectrum of a relatively low molecular weight telechelic PTFEA polymer ($M_n = 7 \times 10^3$; $M_w/M_n = 2$). In addition to three expected chemical shifts at 25.4−35.6 ppm (negative), 41.1 ppm (positive), and 60.1 ppm (negative), corresponding to the $\mathbf{C}H_2$, $\mathbf{C}H$, and $O-\mathbf{C}H_2$

Table 1. A Summary of Telechelic PMMA and PTFEA Polymers Prepared by 8-Boraindane/O$_2$

	reaction conditions^a				PMMA polymer			
run no.	monomer (mL)	borane/O$_2$ (mmol/mmol)	solvent (mL)	time (min)	yield (%)	M_n (g/mol)	M_w (g/mol)	PDI (M_w/M_n)
1	MMA/10	1.2/0.4	0	10	7	18 000	42 000	2.3
2	MMA/10	1.2/0.4	0	20	11	28 000	60 000	2.1
3	MMA/10	1.2/0.4	0	40	19	45 000	76 000	1.8
4	MMA/10	1.2/0.4	0	60	24	60 000	110 000	1.7
5	MMA/10	1.2/0.4	0	90	40	100 000	160 000	1.6
6	MMA/10	1.2/0.8	0	20	22	15 300	34 400	2.2
7	MMA/10	1.2/0.8	0	40	42	18 600	51 200	2.8
8	MMA/10	1.2/0.8	0	60	63	20 300	68 500	3.4
9	MMA/10	1.2/0.8	0	90	80	*b*	*b*	*b*
10	TFEA/5	0.6/0.4	THF/40	120	12	7000	14 000	2.0
11	TFEA/5	0.6/0.4	THF/40	240	19	12 000	23 500	2.0
12	TFEA/5	0.6/0.4	THF/40	360	40	25 000	49 000	1.9
13	TFEA/5	0.6/0.4	THF/40	480	52	30 500	52 500	1.7
14	TFEA/5	0.6/0.4	THF/40	600	60	33 000	56 000	1.6

[a] Reaction temperature: 25 °C. [b] Double peaks.

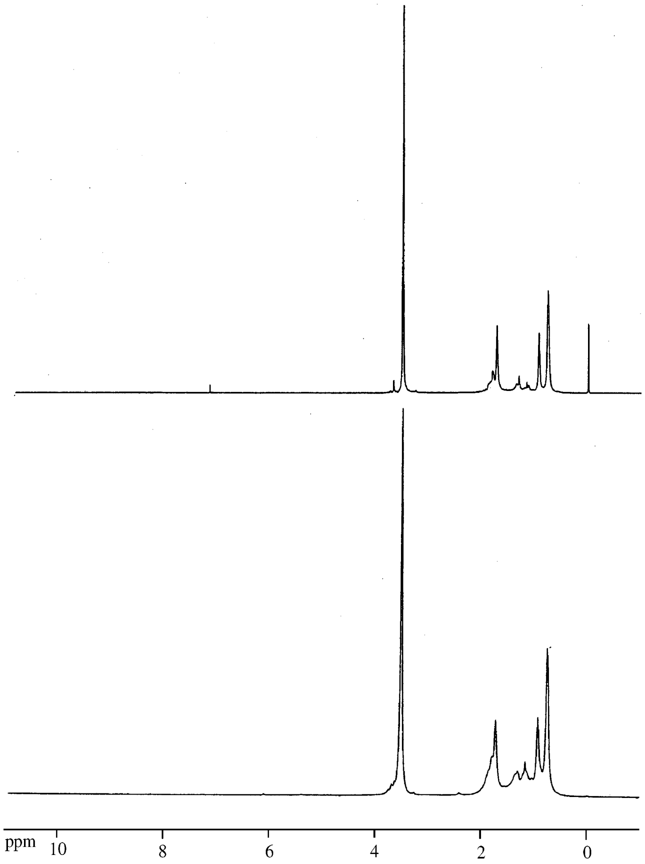


Figure 2. ^{1}H NMR spectra of (bottom) a telechelic PMMA (M_n = 11 × 10^3; M_w/M_n = 1.6) and (top) its corresponding trimethylsilane derivative.

groups, respectively, in the PTFEA backbone, there are two distinctive chemical shifts—one negative peak at 68.2 ppm, corresponding to the primary **C**H$_2$−OH group, and one positive peak at 77.6 ppm, corresponding to the secondary **C**H−OH group.

It is interesting to take advantage of the controlled radical polymerization mechanism to broaden the molecular structure, especially for block copolymers. In addition, the preparation of diblock copolymers, such as poly(methyl methacrylate-*b*-trifluoroethyl acrylate) by sequential monomer addition, provides strong evidence for the controlled radical polymerization. Figure 4 compares the ^{1}H NMR spectra and GPC curves of poly(methyl methacrylate-*b*-butyl methacrylate) diblock copolymer and the corresponding poly(methyl methacrylate) homopolymer. The molecular weight almost doubles from the homopolymer (M_n = 12 400 and M_w = 24 000 g/mol) to the diblock copolymer (M_n = 32 800 and M_w = 58 000 g/mol) without a broadening in the molecular weight distribution. Basically, the copolymer composition is controlled by the monomer feed ratio and reaction time.

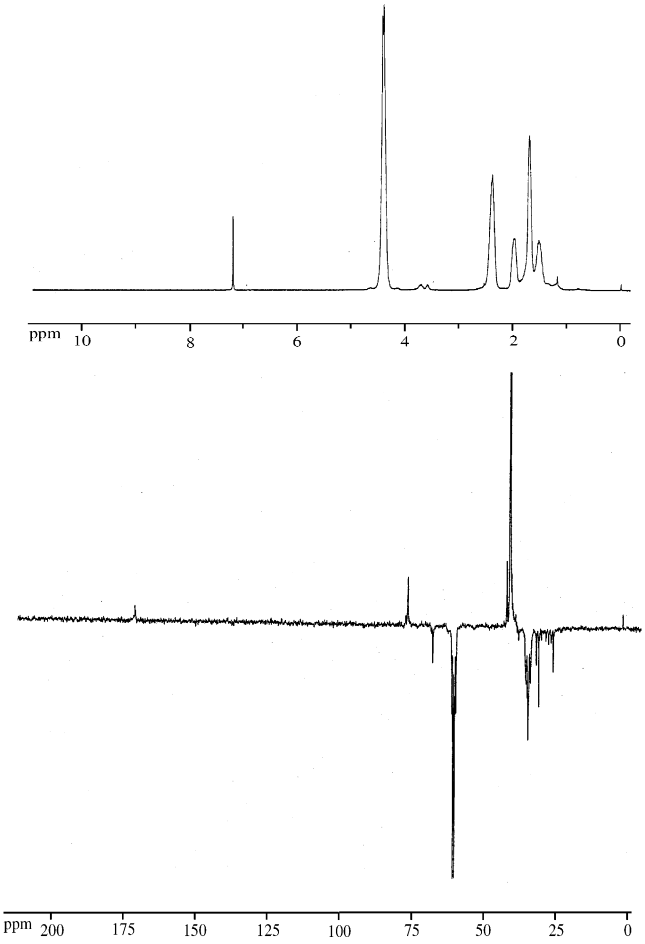


Figure 3. (top) ^{1}H and (bottom) ^{13}C NMR (DEPT-135) spectrum of a telechelic PTFEA polymer (M_n = 7 × 10^3; M_w/M_n = 2).

Overall, the combined experimental results strongly indicate a clean and effective route for preparing telechelic polymers, including PMMA, PTFEA, and PMMA-

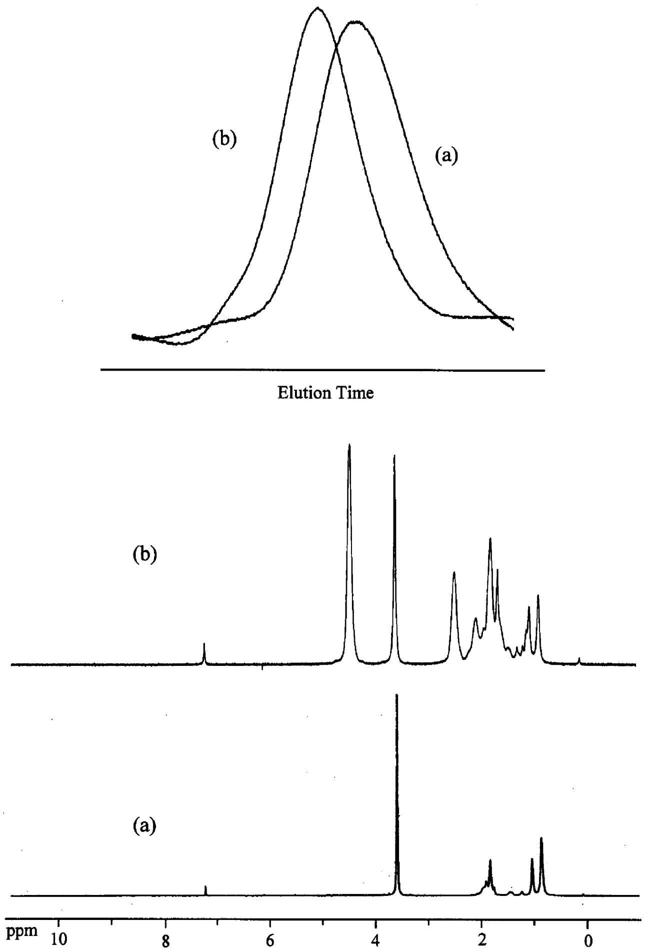


Figure 4. (top) GPC and (bottom) ^{1}H NMR spectra of (a) PMMA and (b) PMMA-*b*-PTFEA diblock copolymer.

b-PTFEA, with two OH groups at the same polymer chain end. The unique dicyclic structure in 8-boraindane allows not only the controlled radical polymerization but also later functionalization of the polymer chain end to form two OH groups.

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Supporting Information Available: Experimental procedures, syntheses details, and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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