5372 *Macromolecules* **1995,** *28,* 5372−5374

Synthesis of Poly(ϵ-caprolactone-*b*-tetrahydrofuran-*b*-ϵ-caprolactone) through the Samarium Iodide-Induced Transformation

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Received March 14, 1995

Revised Manuscript Received April 25, 1995

Introduction

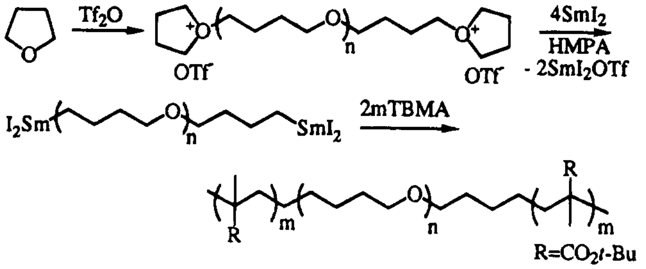
Triblock copolymers have attracted much attention because of their unique physical properties and have been applied to a lot of functional materials, particularly to thermoplastic elastomers.[1] One of the most convenient methods for the preparation of triblock copolymers is the sequential polymerization of second monomers with bifunctional polymers which have living growing centers at both polymer ends. Recent developments in bifunctional polymerization initiators such as metal-based bis initiators[2] especially have facilitated the production of triblock copolymers. However, almost all of the synthetic effort has been focused on chain polymerization by a single propagating mechanism. Therefore, there are serious limitations of the number of attainable monomers which can be copolymerized. These restrictions can be decreased by the transformation of the growing centers.[3] The transformation of growing centers can be theoretically achieved by one- or two-electron transfer to or from growing centers (Scheme 1). However, the traditional transformations have required complicated multistep paths and often resulted in the formation of multimodal block copolymers due to the low initiation efficiency of the second monomer polymerization.[4]

We have recently succeeded in the quantitative one-pot transformation of the cationic growing centers of telechelic poly(tetrahydrofuran) [poly(THF)] into anionic ones by using samarium(II) iodide (SmI$_2$) in the presence of hexamethylphosphoramide (HMPA).[5a] The transformed poly(THF) macrodianion could initiate the polymerization of *tert*-butyl methacrylate (TBMA) with quantitative initiation efficiency, leading to a unimodal triblock copolymer of TBMA with THF (Scheme 2). We have also reported that the transformed poly(THF) macroanion was active for the living polymerization of ϵ-caprolactone (CL) to produce diblock copolymers of THF with CL (Scheme 3).[5b] As part of our recent investigation of this SmI$_2$-induced transformation, we report in this paper the polymerization of CL with poly(THF) macrodianion to produce an ABA-type triblock copolymer of CL with THF (Scheme 4). The produced living triblock copolymer is expected as a building block for the controlled synthesis of a new type of functional gel.

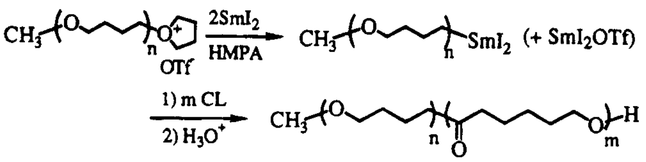
Results and Discussion

Scheme 1

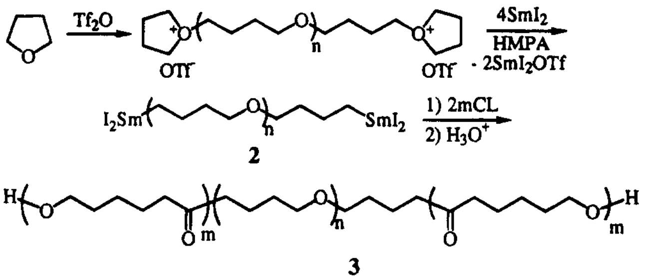
Scheme 2



Scheme 3



Scheme 4



Telechelic living poly(THF) (**1**) was synthesized by using trifluoromethanesulfonic anhydride (Tf$_2$O) as an initiator at room temperature according to the reported manner.[6] The two-electron reduction of the growing centers at both polymer ends was carried out by the addition of HMPA and 4 equiv of SmI$_2$ to the initiator at room temperature. The reduction was complete within 30 min, which could be monitored by the color change of the reaction mixture from purple to yellow.[7] ^{1}H NMR measurements showed the quantitative two-electron reduction of both growing centers. Thus, the peak due to the terminal methylene protons adjacent to the hydroxyl group (a) completely disappeared (Figure 1a), whereas a newly formed triplet signal attributed to the terminal methyl protons (b) could be observed in the ^{1}H NMR spectra of **2a** (Figure 1b).

Triblock copolymerization of THF with CL was performed by the addition of CL into the reaction mixture of **2** at 0 °C for 3 h. GPC traces of **2** and the resulting polymer (**3**) are illustrated in Figure 2. The GPC curve of **2** showed the formation of living poly(THF) with a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.21), which was consistent with the previous result of ring-opening polymerization of THF initiated by Tf$_2$O.[6] After charging CL to the reaction mixture of **2**, the GPC curve shifted to the high molecular weight region while maintaining the narrow molecular weight distribution. It should be noted that the GPC trace attributed to the prepolymer **2** could not be detected in the GPC curve of **3**. Moreover, the triplet signal at 0.8 ppm (the terminal methyl group of **2a**) almost completely disappeared, and the signals attributed to both THF and CL units were observed in the ^{1}H NMR spectrum of **3** (Figure 3a). Similarly, the terminal methyl signal of **2a** (12.5 ppm) could not be detected in the ^{13}C NMR of **3**, whereas the

0024-9297/95/2228-5372$09.00/0

Table 1. One-Pot Triblock Copolymerization of THF with CL

	polymerization of THF[a]		block copolymerization[b]					
run	amt of Tf_2O (mmol)	time (min)	amt of CL (mg)	amt of polym (mg)	conv of CL (%)	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]	CL:THF[d]
1	0.055	2.5	337	355	94	16 000	1.21	84:16
2	0.053	2.5	250	307	100	11 000	1.23	75:25
3	0.054	2.5	149	205	96	6 600	1.29	59:41
4	0.050	2.5	75	171	100	5 500	1.24	40:60
5	0.059	5	267	344	94	12 000	1.19	63:37
6	0.059	10	255	475	100	15 000	1.13	43:57

[a] Polymerization conditions: THF 5 mL, room temperature. [b] Carried out for 2.5 h at 0 °C. [c] Estimated by GPC (THF, PSt standards). [d] Determined by ^1H NMR spectra.

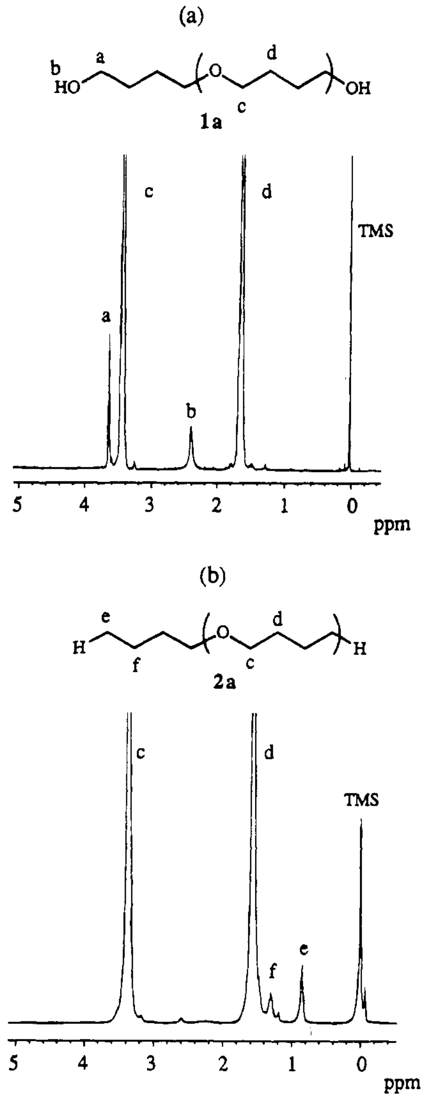


Figure 1. ^1H NMR spectra of (a) hydroxy-terminated poly(THF) (**1a**) and (b) reduced poly(THF) (**2a**).

signal due to the carbonyl group of the joint unit could be observed at 211 ppm (Figure 3b). The triplet signal at 3.8 ppm in the ^1H NMR spectrum of **3** was assignable as the methylene protons adjacent to the terminal hydroxyl group. The methylene protons of the joint unit (j or j′) were also observed at 2.4 ppm. From these results, it can be concluded that the transformed macroanion initiated the anionic polymerization of CL with quantitative initiation efficiency by cleaving the acyl–oxygen bond.

The results of the triblock copolymerization of THF with CL under various conditions are summarized in Table 1. In all runs, no trace based on the prepolymer **1** was observed in the GPC measurements. The GPC analyses also showed that molecular weight distribution of the copolymers was unimodal and relatively narrow in each experiment. Additionally, the peaks attributed to both poly(THF) and poly(CL) were observed in the ^1H NMR spectra of the resulting copolymers in all cases. These results mean that the triblock copolymerization successively occurred without serious side reactions such as termination and chain transfer reaction. The unit ratio (*m*:*n*) was calculated by the integrated ratio of signals of each unit in their ^1H NMR spectra. The molecular weights, yields of the copolymers, and unit ratio of CL and THF could be facilely controlled by both the polymerization time of THF and the amount of CL resulting from the living nature of both the THF- and CL-polymerization.

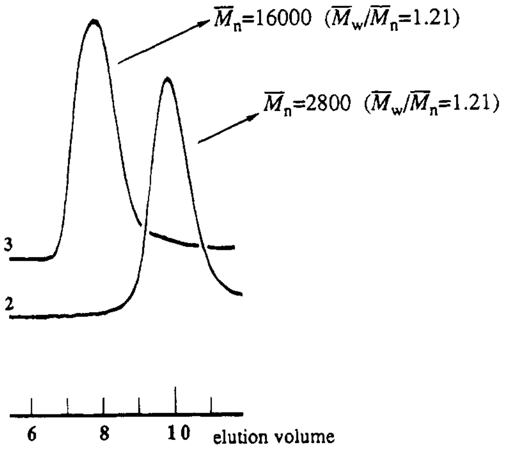
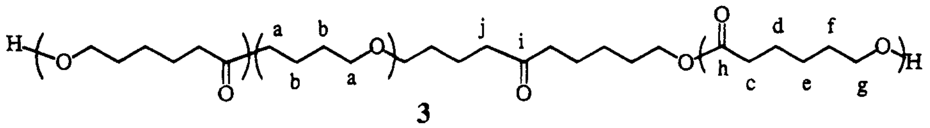


Figure 2. GPC curves of **2** and **3**.

Table 2 summarizes the solubility of the resulting triblock copolymers as well as that of AB-type diblock copolymers. The triblock copolymers are soluble in THF, toluene, chloroform, and dioxane but insoluble in methanol, hexane, and DMF. It is interesting that **3** is soluble in hot methanol in spite of the insolubility of poly(CL) in hot methanol, probably due to the high solubility of the poly(THF) unit in the triblock copolymers. The unit ratio of THF and CL in this range did not contribute to the clear difference in solubility of both **3** and the diblock copolymer. It is interesting that **3** was insoluble in DMF whereas the diblock copolymer exhibited high solubility.

In conclusion, we have demonstrated the quantitative two-electron reduction of the growing centers of living telechelic poly(THF) into anionic ones and subsequent polymerization of CL, affording triblock copolymers of THF with CL. Polymerization of CL proceeded with quantitative initiation efficiency without the formation of a homopolymer of THF or CL. The triblock copolymers with well-defined structure could be obtained by this procedure. We believe that this method is one of the most convenient methods for the preparation of



3

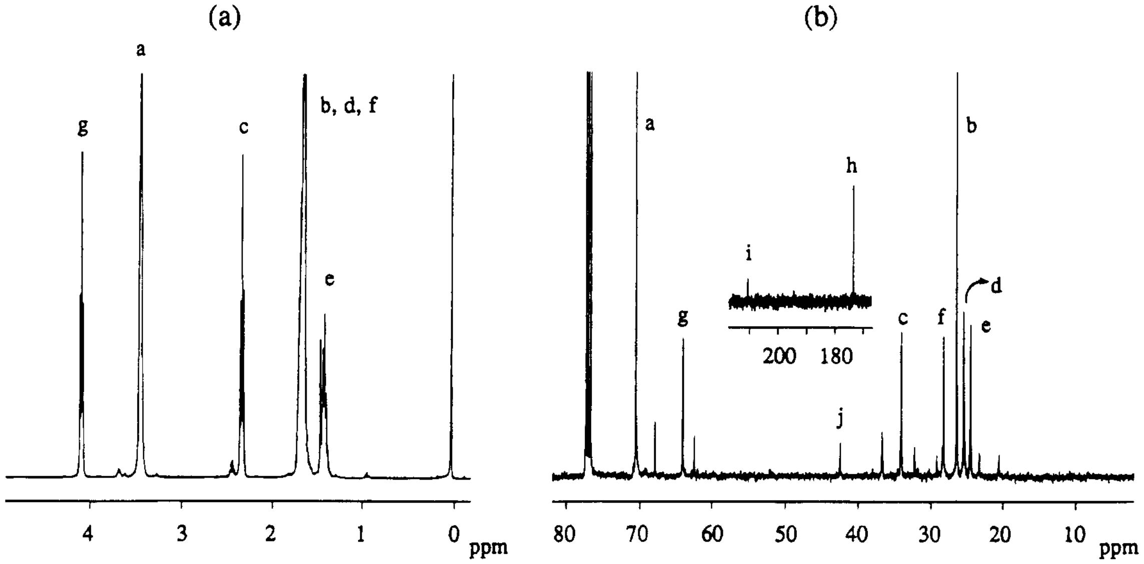


Figure 3. (a) ^{1}H NMR spectra of **3** and (b) ^{13}C NMR of **3** (in $CDCl_3$, 28 °C).

Table 2. Solubility of Poly(CL-*b*-THF-*b*-CL) and Poly(THF-*b*-CL)[a]

	poly(CL-*b*-THF-*b*-CL) CL:THF		poly(THF-*b*-CL) CL:THF	
solvent	75:25	43:57	67:33	35:65
THF	yes	yes	yes	yes
toluene	yes	yes	yes	yes
chloroform	yes	yes	yes	yes
dioxane	yes	yes	yes	yes
hexane	no	no	no	no
methanol	no	no	no	no
DMF	no	no	yes	yes
hot methanol	yes	yes	yes	yes
hot DMF	yes	yes	yes	yes

[a] As observed with the naked eye.

triblock copolymers consisting of different types of monomers in the polymerization mechanism.

Experimental Section

Materials and Instruments. A THF solution of SmI_2 was prepared according to the reported manner.[8] THF was distilled prior to use from sodium/benzophenone under nitrogen. CL and HMPA were distilled from CaH_2 under reduced pressure. Trifluoromethanesulfonic anhydride was distilled from P_2O_5 under a nitrogen atmosphere.

^{1}H and ^{13}C NMR spectra were recorded with JEOL JNM-EX-90 and JNM-EX-400 spectrometers. Gel permeation chromatographic analysis was carried out on a Toyo Soda (CCP&8000, TSK gel G3000, THF) after calibration with standard polystyrenes.

Triblock Copolymerization of THF with CL. A typical procedure is as follows: Tf_2O (15.4 mg, 0.055 mmol) was added to THF (5 mL), and the solution was stirred at room temperature for 5 min. After addition of HMPA (165 μL) and a THF solution of SmI_2 (2.2 mL, 0.22 mmol), the reaction mixture was stirred at room temperature for 30 min (until the color was changed to yellow-brown). CL (336.5 mg, 2.95 mmol) was then added at 0 °C, and the reaction mixture was stirred at 0 °C for 3 h. After addition of 3% aqueous HCl (ca. 5 mL), the organic layer was extracted with toluene, washed with brine several times, dried over $MgSO_4$, and concentrated to give **3**.

References and Notes

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