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Block copolymerization of tetrahydrofuran with δ-valerolactone by the samarium iodide-induced transformation

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Summary

Polymerization behavior of δ-valerolactone (VL) with alkylsamarium ($RSmI_2$) was studied, and its application to the block copolymerization of tetrahydrofuran (THF) with VL was examined. Polymerization of VL by butylsamarium gave the corresponding poly(VL) in good yield. The yield increased with increasing the concentration of VL and decreasing the polymerization temperature, resulting from the equilibrium between VL and poly(VL). The decrease in the molecular weight of poly(VL) by prolonging the polymerization time indicated the existence of back-biting reaction to form cyclic oligomers. The polymerization of VL with poly(THF)-macroanion obtained by the two-electron reduction of the propagation center of living poly(THF) with SmI_2 led to the block copolymer of THF with VL. The initiation efficiency of VL-polymerization was almost quantitative, and the unit ratio of THF and VL-segments could be controlled by both the polymerization time of THF and the amounts of VL.

Introduction

Transformation of growing centers enables it to supply block copolymers consisting of plural monomers with different polymerization mechanisms [1]. We have recently reported a novel transformation reaction from a cationic polymerization into an anionic one by utilizing samarium iodide (SmI_2) as a reducing agent [2]. The characteristic points of this transformation compared with the traditional ones are as follows; (1) both the two-electron reduction of the growing center of living poly(THF) and the initiation efficiency of second monomer-polymerization are quantitative. (2) The corresponding block copolymers can be obtained selectively in one-pot without the formation of any homopolymer under mild reaction conditions (Scheme 1). As the part of our recent investigation of this SmI_2-induced transformation, we report in this article the polymerization of VL with poly(THF) macroanion to produce block copolymer of VL with THF with the objective of expanding the attainable electrophilic monomers (Scheme 2) [3].

Results and Discussion

The polymerization behavior of VL was first examined by using butylsamarium which mimics the chain end of poly(THF)-macroanion to optimize the reaction conditions. The polymerization of VL was carried out by the addition of VL into the reaction mixture of butylsamarium obtained by the reduction of butyl iodide with two-equivalent of SmI_2 [4]. The results are summarized in Table 1.

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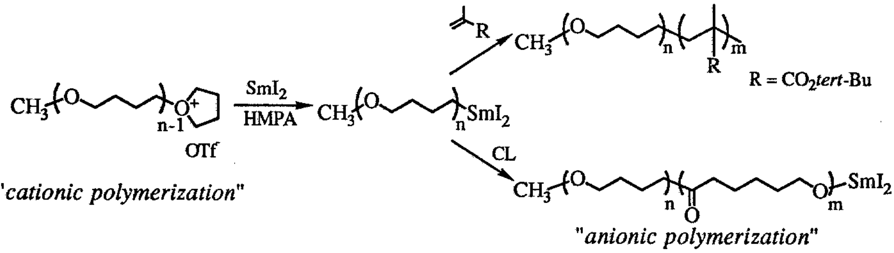
Scheme 1



Scheme 2

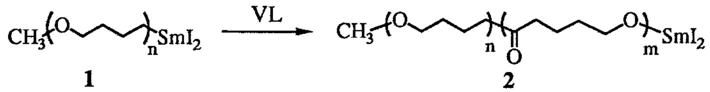


Table 1. Polymerization of VL initiated by *n*-BuSmI$_2$[a]

run	VL (mmol)	time (min)	temp. (°C)	yield (%)	$\overline{M}_n$[b]	MWD[b]
1	4.61	10	rt	53	1800	1.30
2	4.75	15	rt	57	2400	1.30
3	4.86	40	rt	68	2400	1.32
4	4.77	60	rt	68	3000	1.32
5[c]	4.71	60	rt	79	3500	1.47
6[d]	8.19	60	rt	82	6300	1.42
7	4.62	12h	rt	78	3400	1.64
8	4.84	48h	rt	77	700	2.93
9	5.44	48h	-20	79	5200	2.86

[a] [VL] = 0.5 mol/L. [b] Estimated by GPC (THF, PSt standard). [c] [VL] = 1.14 mol/L.
[d] [VL] = 1.98 mol/L

When the polymerization was conducted at room temperature for more than 40 min, poly(VL) was obtained in moderate yield (runs 1-4). Molecular weight distribution of the polymer was relatively broad whereas the polymerization of ε-caprolactone by alkylsamarium exhibited highly living nature [2e], which is probably due to the equilibrium between VL and the polymer.[5] The increasing in the yield of poly(VL) at a high concentration of VL is explained by the equilibrium between the monomer and polymer (runs 5 and 6). The equilibrium was also suggested by the increase of the yield with the decrease of the polymerization temperature (run 9). No serious decrease of molecular weight was observed in cases the polymerization time was within 1h, which indicates the formation of cyclic oligomer is negligible under the reaction conditions. Prolonging the polymerization time resulted in broadening the molecular weight distribution of the polymer (run 7). Furthermore, only low molecular weight products were obtained by the polymerization for 48h (run 8). This is a consequence of the back-biting reaction to give cyclic oligomers. According to these results, VL-polymerization by the poly(THF)-macroanion was carried out under the similar conditions to run 4.

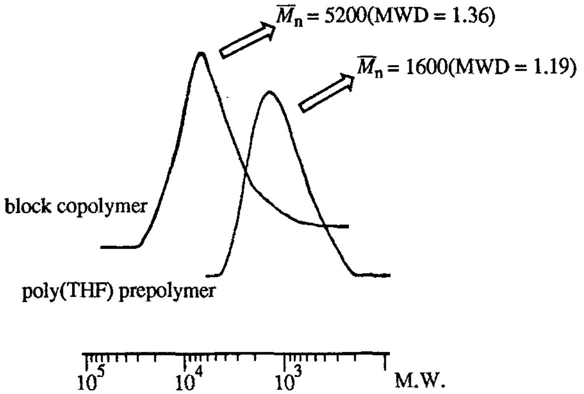
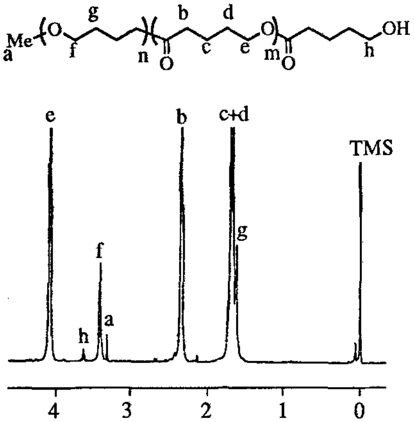


Figure 1. GPC curves of the poly(THF)-macroanion and the block copolymer.



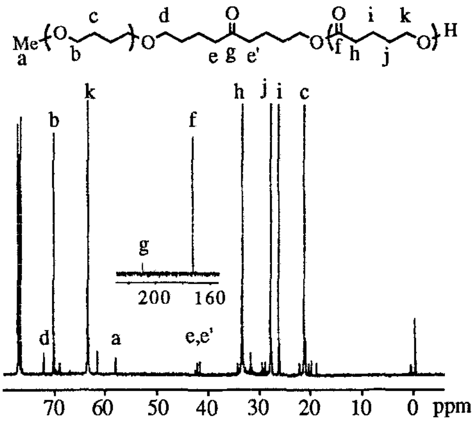


Figure 2. ^1H NMR spectrum of the block copolymer (in $CDCl_3$, 27°C).

Figure 3. ^{13}C NMR spectrum of the block copolymer (in $CDCl_3$, 27°C).

Block copolymerization of THF with VL by the SmI_2-induced transformation technique was next examined. The preparation of poly(THF)-macroanion (**1**) was performed according to our previous reports [2]. The GPC curves of poly(THF)-macroanion and resulting block copolymer are illustrated in Figure 1. The increase in molecular weight was observed after charging VL into the reaction mixture, which means the formation of block copolymer of THF with VL. The molecular weight distribution of the block copolymer was broader than that of the prepolymer, which is due to the equilibrium between VL and poly(VL). The formation of unimodal copolymer suggests the absence of homopolymer of THF or VL. The signals due to both poly(THF) and poly(VL) segments observed in the ^1H NMR spectrum of the produced polymer gives a proof of the formation of the block copolymer (**2**) (Figure 2). The absence of the triplet signal at 0.9 ppm attributed to the terminal methyl protons of water-quenched **1** indicates that the initiation efficiency of VL polymerization was almost quantitative. In ^{13}C NMR spectrum of the block copolymer, one can observe a signal attributed to the joint unit (g) at 210 ppm, which also confirms the formation of **2**.

Table 2. One-Pot Block Copolymerization of THF with VL

run	THF-polymerization[a]		block copolymerization[b]					
	MeOTf (mmol)	time (min)	VL (mg)	polymer (mg)	conv. of VL (%)	$\overline{M}_n$[c]	MWD[c]	m:n[d]
1	0.17	5	715	602	76	5200	1.36	87:13
2	0.17	5	474	404	72	4600	1.42	79:21
3	0.18	5	344	347	72	3500	1.43	75:25
4	0.16	5	231	211	57	3000	1.35	57:43
5	0.19	2.5	467	386	74	2900	1.39	86:14
6	0.17	10	487	442	75	4000	1.33	61:39

[a] Polymerization conditions: THF 5mL, rt. [b] Polymerization conditions: [VL] = 0.5 mol/L, rt, 1h.
[c] Estimated by GPC (THF, PSt standard). [d] Determined by ^{1}H NMR spectra.

Table 2 gives the results of the block copolymerization varying the polymerization time of THF and the amounts of VL. Unimodal block copolymer was obtained, and the formation of homopolymer was not detected in the GPC profile in each case. The conversion of VL increased with increasing the amounts of VL, and it was close to the value calculated from the equilibrium constant of VL-polymerization. The unit ratio of THF to VL increased with the increase in the polymerization time of THF. In the similar way, the ratio of VL to THF-segment increased with increasing the amount of VL. In other words, the unit ratio could be controlled by both the polymerization time of THF and the amount of VL.

In summary, we have demonstrated the block copolymerization of THF with VL by the SmI_2-induced transformation in order to expand the availability of electrophilic monomers. A novel block copolymer of THF with VL was facilely obtained under mild reaction conditions by the polymerization of VL with the poly(THF)-macroanion. Their segment ratios could be controlled by the polymerization time of THF and the amounts of VL. The applications of this transformation would make it possible to provide a wide variety of functional materials such as degradable materials, compatibilizers, polymer surfactants, and so on.

Experimental Section

Materials and Instruments. A 0.1N THF solution of SmI_2 was prepared according to the reported manner [6]. THF was distilled prior to use from sodium/benzophenone under nitrogen. VL and HMPA were distilled from CaH_2 under reduced pressure. Methyl trifluoromethanesulfonate was distilled from P_2O_5 under a nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra were recorded with JEOL JNM-EX-400 spectrometer. Gel permeation chromatographic analysis was carried out on a Toyo Soda (CCP&8000, TSK gel G3000, THF) after calibration with standard polystyrenes.

Polymerization of VL by butylsamarium. A typical procedure is as follows: A 0.1N THF solution of SmI_2 (3.6 mL, 0.36 mmol) was added into the solution of butyl iodide (33 mg, 0.18 mmol) in THF (5 mL), and the mixture was kept stirring for 30 min (until the complete change of the mixture into yellow-brown). After charging VL (477 mg, 4.76 mmol) at rt, the reaction mixture was stirred at rt for 1h. After addition of 3% HCl aq. (ca. 5 mL), the organic layer was extracted with toluene, washed with brine several times, dried over $MgSO_4$, and concentrated to give poly(VL).

Block copolymerization of THF with VL. A typical procedure is as follows: MeOTf (27.5 mg, 0.17 mmol) was added to THF (5 mL), and the solution was stirred at room temperature for 5 min. After addition of HMPA (250 µL) and a THF-solution of SmI_2 (3.4 mL, 0.34 mmol), the reaction mixture was stirred at rt for 30 min (until the color was changed into yellow-brown). VL (474 mg, 4.74 mmol) was then added at rt, and the reaction mixture was stirred at rt for 1 h. After addition of 3% HCl aq. (ca. 5 mL), the organic layer was extracted with toluene, washed with brine several times, dried over $MgSO_4$, and concentrated to give 2.

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