

Synthesis and polymerization of a self-condensable macromonomer

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Summary

A novel self-condensable macromonomer that has a polymerizable group at one terminal and an initiator at the other was synthesized by the combination of the conventional macromonomer technique and the SmI_2 -induced transformation. Namely, living poly(tetrahydrofuran) [poly(THF)] carrying α -methacryloyl group was prepared by using methacryloyl chloride and silver trifluoromethanesulfonate. The living chain end was capped with sodium 2-bromoisobutyrate, and the sequential reduction of the terminal C-Br bond with SmI_2 gave a terminating samarium enolate. The resulting samarium enolate copolymerized the α -methacryloyl group with methyl methacrylate, giving a hyperbranched block copolymer whose dendritic part consists of two kinds of polymer segments.

Introduction

Polymers with geometrically complex but well-defined structure such as globular shape dendritic polymers (dendrimers or hyperbranched polymers) have under intensive research due to their unique structure and large potential utility as advanced functional materials.^[1] Especially, hyperbranched polymers are attractive because they are quite readily accessible compared with dendrimers.^[2]

Unfortunately, for most of the previously prepared hyperbranched polymers, their dendritic parts themselves consist of only one kind of polymer segment.^[3] Hence, the properties of hyperbranched polymers usually originate from only their geometrically unorthodox structure (Figure 1a). A limited example was only recently reported by Hawker et al. who demonstrated the synthesis of dendrigraft macromolecules (hyperbranched block copolymer, Figure 1b) having plural kinds of polymer segments in the dendritic part.^[4] Their approach is based on the synthesis of a polymer carrying reactive sites such as chloromethyl or TEMPO (TEMPO = 2,2,6,6-tetramethylpiperidine-*N*-oxide) groups and sequential living radical polymerization of vinyl monomers (Figure 2a). This tandem approach, however, requires several polymerization steps as well as the isolation process of the individual polymeric precursors.

Herein, we wish to report a novel and simple approach to a hyperbranched block copolymer. Our strategy involves two recent developments in polymer chemistry. One is our recent discovery that a cationic growing center can be readily transformed into an anionic one by samarium iodide (the SmI_2 -induced transformation).^[5a] The other is the self-condensing vinyl polymerization technique which affords dendritic macromolecules with high degree of branching.^[6] Namely, the approach includes 1) the preparation of a macromonomer having α -vinyl group (**A**) by the cationic polymerization, 2) the transformation of the cationic growing center into an terminating nucleophile which is active for the polymerization of the α -vinyl group and 3) the copolymerization of the

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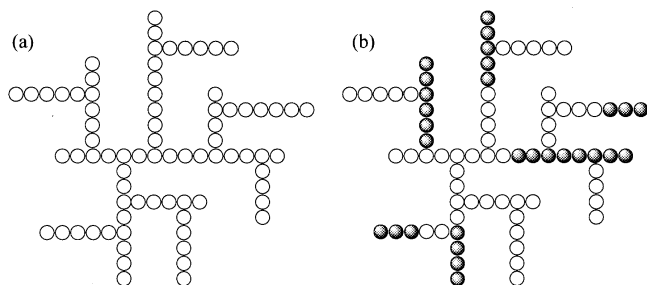


Figure 1. Schematic illustration of a traditional hyperbranched polymer (a) and a hyperbranched block copolymer (b).

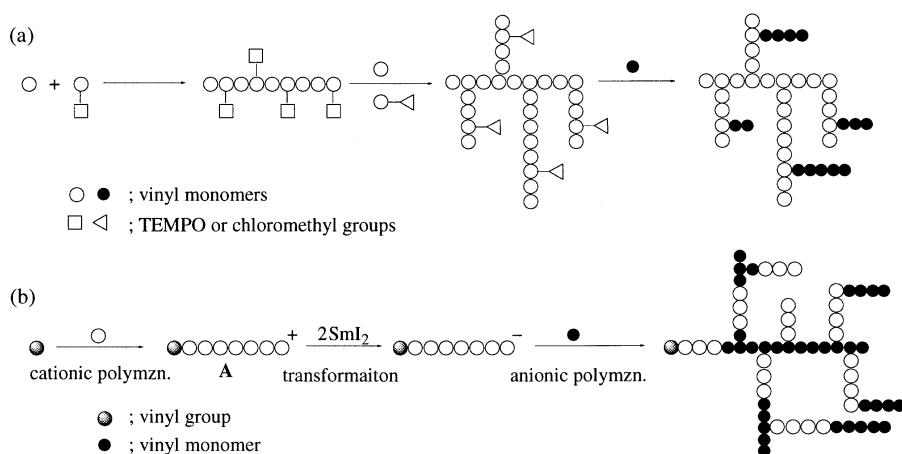


Figure 2. Strategies to the hyperbranched block copolymers; (a) tandem approach and (b) the present method.

corresponding vinyl monomers with the α -vinyl group by the generated nucleophile (Figure 2b).

Results and Discussion

In order to investigate our design for the preparation of hyperbranched block copolymers, the macromonomer **1** was chosen as a starting material because of following reasons; 1) **1** can be readily prepared by the conventional macromonomer technique,^[7] 2) SmI_2 is possible to reduce 2-bromoisobutyl ester moiety into a samarium enolate whereas methacryloyl group does not undergo the reduction, and 3) the samarium enolate is active for the living polymerization of various methacrylates (Scheme 1).^[5b]

1 was prepared by the polymerization of THF with methacryloyl chloride and silver trifluoromethanesulfonate (AgOTf) followed by the end-capping with sodium 2-bromoisobutyrate. Figure 3a, illustrating the ^1H NMR spectrum of **1**, clearly shows the quantitative functionality of the end groups: the signals attributed to the double bond (a), dimethyl protons (e), methyl protons of methacrylate group (b) (these two signals were overlapped) were observed, and the integrated intensities of the signals (a), (c), and (d) ($a+c+d = 2.0 : 3.9$) were in good agreement with the theoretical value. Comparison of the NMR spectra for **1** with **1a** which was formed by the treatment of **1** with 2 equiv of SmI_2

Scheme 1

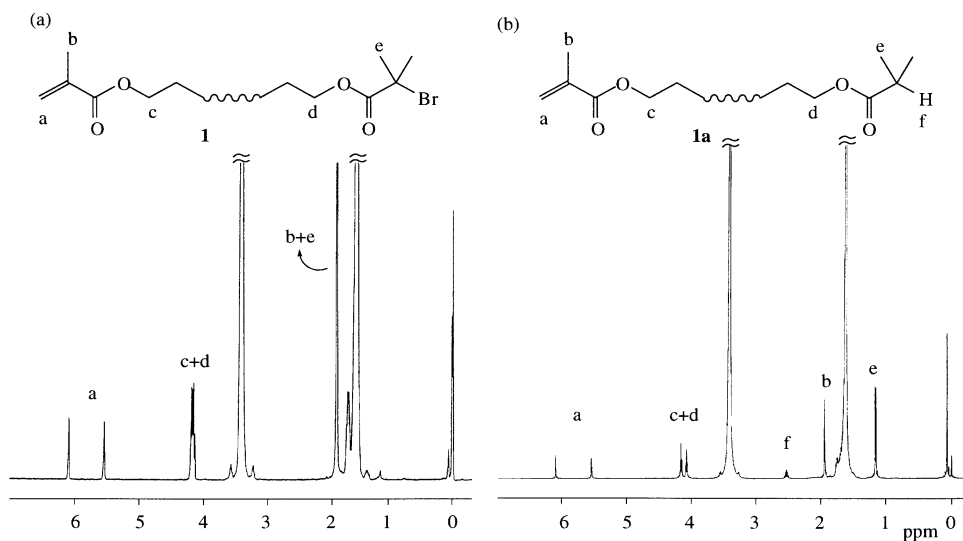
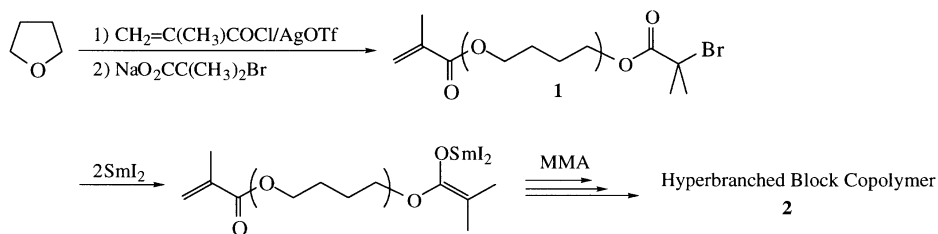


Figure 3. ^1H NMR spectra of **1** and **1a** (400 MHz, CDCl_3).

in the presence of methanol indicates that the C-Br bond was selectively reduced by SmI_2 (Figure 3b). The intensity of the resonance around 2 ppm (b and e in Figure 3a) decreased, and the doublet signal (e) and multiplet one (f) due to the isobutyl group were formed. The integrated intensities of the peaks (a), (c), and (d) ($a : c+d = 2.0 : 4.0$) reveal that the reduction of the C-Br bond proceeded quantitatively and that the double bond remained intact during the reduction. ^{13}C NMR spectrum of **1a** also indicated the absence of the C-Br bond and the formation of isobutyl ester group.

The ability of the present method to selectively reduce the 2-bromoisobutyl ester moiety into a samarium enolate offers an opportunity for the synthesis of hyperbranched block copolymer (**2**) consisting of both poly(MMA) and poly(THF) segments. The copolymerization was performed by the addition of a 0.1 N SmI_2 -solution in THF into the solution of **1** in THF containing MMA at -78°C . As shown in Figure 4, both poly(MMA) and poly(THF) segments were observed in the ^1H NMR spectrum of **2**. The comparison of the ^1H NMR spectrum of **1** with **2** exhibits the significant decrease in the intensity of vinyl protons. This means that the vinyl group of **1** participated in the copolymerization. The kinetic of the polymerization presented in Figure 5 reveals that the increase in the M_n was time-dependence: a slow propagation was observed at the early stage of the polymerization, which was followed by the rapid increase of the molecular

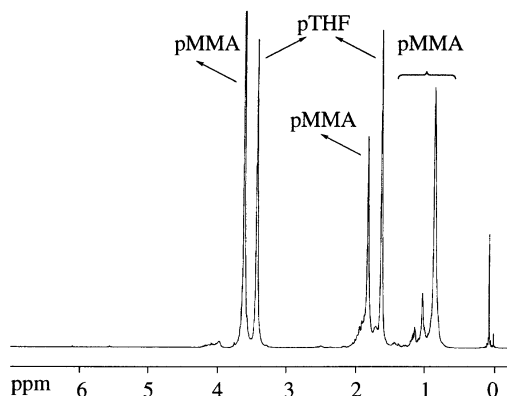


Figure 4. ^1H NMR spectrum of the hyperbranched block copolymer of THF with MMA (**2**) (400 MHz, CDCl_3).

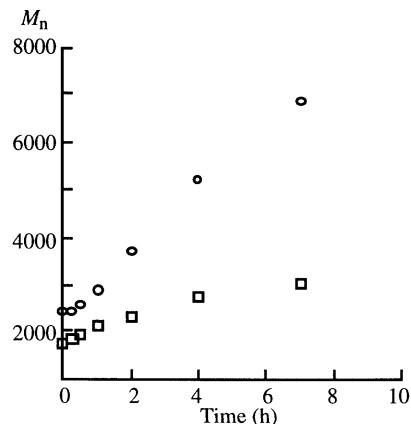


Figure 5. Dependence of M_n of the polymers for hyperbranched block copolymerization (O) and linear block copolymerization (□) on the polymerization time.

Table 1. Hyperbranched block copolymerization of THF with MMA

Run	THF-Polymerization Time (min)	MMA ^[a] (eq)	M_n (M_w/M_n) ^[b]	Unit ratio ^[c] (THF:MMA)
1	5	20	8,200 (2.39)	30:70
2	5	10	5,400 (1.89)	43:57
3	5	5	5,100 (2.57)	61:39
4	2	20	6,100 (2.32)	18:82
5	10	20	10,200 (2.72)	43:57
6 ^[d]	5	20	2,400 (1.48)	19:81

^[a] Equivalent to **1**. ^[b] Estimated by GPC (THF, PSt. Std.). ^[c] Calculated by $^1\text{H-NMR}$. ^[d] Linear block copolymerization.

weight. For example, the copolymerization of **1** ($M_n = 2100$, $M_w/M_n = 1.44$) with MMA (20 eq. to **1**) by SmI_2 gave the copolymer with M_n and polydispersity of 8200 and 2.39, respectively. These results resemble that of a typical polycondensation. On the other hand, in the linear block copolymerization by using poly(THF) having methoxy group at one terminal and 2-bromoisobutyl ester group at the other, the increase in the molecular weight was relatively small compared with that in the hyperbranched block copolymerization, similarly to the conventional chain polymerization behavior. These results support that the present polymerization exhibits a typical AB-monomer polymerization behavior giving the hyperbranched block copolymer with both poly(THF) and poly(MMA) segments.^[8] Table 1 lists the examples of the hyperbranched block copolymerization varying the reaction conditions. No proofs of cross-linking were observed in all cases, and block copolymers with high solubility in common organic solvents were obtained. The ratio of each polymer segment was controlled by the polymerization time of THF and the amount of MMA.

The combination of the self-condensable monomer method and our recent finding of the SmI_2 -induced transformation provided a novel hyperbranched block copolymer

consisting of plural types of polymer segments in the dendritic part. The simplicity of the present polymerization technique would allow the formation of a variety of new hyperbranched polymers that can not be prepared by the conventional techniques.

Experimental

Materials. AgOTf was purchased and used without purification. Methacryloyl chloride was dried over P₂O₅ and distilled under reduced pressure. THF was distilled prior to use from sodium/benzophenone under nitrogen. A 0.1M THF solution of SmI₂ was prepared according to the reported manner.[9] MMA was distilled from CaH₂ under reduced pressure. Methyl trifluoromethanesulfonate was distilled from P₂O₅ under a nitrogen atmosphere. Sodium 2-bromoisobutyrate was prepared by the treatment of 2-bromoisobutyric acid with NaH in ether and washed with dry THF.

Measurements. NMR spectra were recorded with JEOL JNM-EX-400 spectrometers. Molecular weight and its distribution (M_w/M_n) were determined by gel permeation chromatography on a Toyo Soda HLC-8020 (TSK gel G4000HXL, THF) after calibration with standard poly(methyl methacrylate). HPLC analysis was carried out on a Nihon Bunseki Kogyo Model LC80.

Preparation of 1. A typical procedure is as follows; to a solution of AgOTf (69.9 mg, 0.27 mmol) in dry THF (5 mL) was added methacryloyl chloride (25.7 mg, 0.25 mmol) at room temperature, and the reaction mixture was stirred at room temperature for 5 min under nitrogen. Sodium 2-bromoisobutyrate (122 mg, 0.65 mmol) was then added in one portion under nitrogen, and the reaction mixture was kept stirring at room temperature for 30 min. Filtration of the mixture by G4-glass filter under a nitrogen atmosphere followed by the removal of the solvent to dryness gave **1** as colorless oil. Further purification was carried out by HPLC to give **1** (75.4 mg).

Hyperbranched Block Copolymerization. Into a solution of **1** (0.21 mmol) and methyl methacrylate (400 mg, 4.00 mmol) in THF (5 mL) was added a THF-solution of SmI₂ dropwise over 1 min at -78 °C, and the solution was allowed to be stirred at -78 °C for 20 h. After the addition of a few drops of aqueous HCl solution (3 %), the reaction mixture was partitioned between toluene (ca. 30 mL) and water (ca. 20 mL). The aqueous layer was extracted with toluene (2 X 10 mL), and the combined organic layers were washed with brine, dried with MgSO₄, filtered and evaporated to dryness to give the hyperbranched block copolymer (606 mg).

References and Notes

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