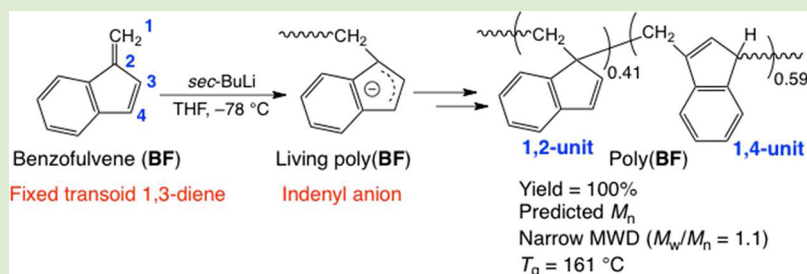


Living Anionic Polymerization of Benzofulvene: Highly Reactive Fixed Transoid 1,3-Diene

Yuki Kosaka, Keita Kitazawa, Sotaro Inomata, and Takashi Ishizone*

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1-S1-13 Ohokayama, Meguro-ku, Tokyo 152-8552, Japan

S Supporting Information



ABSTRACT: Anionic polymerization of benzofulvene (BF, α -methyleneindene), an exomethylene monomer having a fixed transoid 1,3-diene moiety, quantitatively proceeded with *sec*-BuLi or diphenylmethylpotassium in THF at $-78\text{ }^{\circ}\text{C}$ for 1 h. The resulting poly(BF)s possessed the predicted molecular weights based on the molar ratios between monomer and initiators and narrow molecular weight distributions ($M_w/M_n = 1.1$). High anionic polymerizability of BF was realized by the fact that a well-defined diblock copolymer, poly(methyl methacrylate)-*block*-poly(BF), was obtained by the sequential copolymerization of BF with a low nucleophilic enolate anion of living poly(methyl methacrylate) in quantitative efficiency. NMR analyses indicated that the repeating units of poly(BF) consisted of a 1,2-addition unit (41%) and a 1,4-addition unit (59%) without a 3,4-addition unit, suggesting that the exomethylene group of BF always participated in the polymerization. Thus, BF acted as a novel polymerizable transoid 1,3-diene in the anionic polymerization.

Fulvene (FV), C_6H_6 , is known to be a unique cross-conjugated hydrocarbon and one of the isomers of benzene (Figure 1).^{1–4} Contrary to benzene, six π -electrons

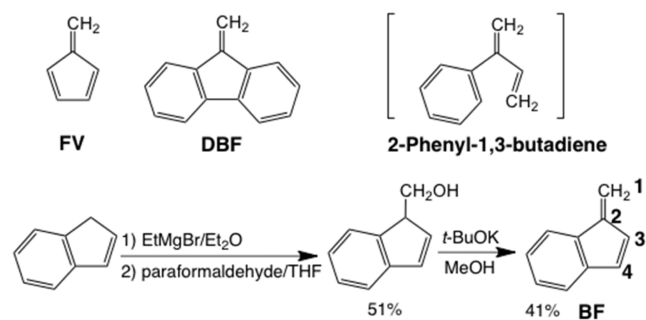


Figure 1. Chemical structures of fulvene derivatives and synthetic scheme of BF.

in FV do not satisfy the Hückel rule due to a cross-conjugated exomethylene group in the molecule. The exomethylene groups in FV and the derivatives show high reactivity toward various chemical reagents derived from the strongly polarized structures.^{1–4}

From the viewpoints of polymer chemists, the exomethylene group in FV can be considered as an attractive polymerizable group, because the polymerizations of various exomethylene

monomers have been realized.^{5–8} In fact, there are several examples of polymers derived from FV derivatives, such as benzofulvenes (BF)^{9,10} and dibenzofulvene (DBF).¹¹ Nakano and his co-workers reported that DBF allowed radical, cationic, and anionic polymerizations exclusively on the exomethylene group to form a vinyl polymer possessing a ring structure vertical to the main chain.¹¹ In contrast to DBF, the polymerization behavior of BF has not been clarified, regardless of the simple structure.¹² From the chemical structure, BF is a planar cyclic analogue of 2-phenyl-1,3-butadiene showing polymerizability as a conjugated 1,3-diene.¹³ Therefore, the reactivity of the fixed transoid 1,3-diene structure in BF is anticipated to be polymerizable. Only the polymerizations of 3-phenyl-7-methyl- and 2-ethoxycarbonyl-3-phenyl-BF derivatives have been reported.^{9,10} In these cases, the polymerizations selectively occurred in a 1,2-addition mode, because the 3,4-carbons on transoid 1,3-diene frameworks in these monomers were substituted with bulky substituents. This is the first report to demonstrate the polymerization behavior of a simple BF monomer without substituents. In fact, BF can be readily polymerized with anionic and radical initiators to form

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polymers. The anionic polymerization of **BF** provided a polymer with well-defined chain structures in quantitative yield, and the high anionic polymerizability of **BF** was demonstrated. The simple structure of **BF** may play a very important role in clarifying its polymerizability as a 1,3-diene.

BF was synthesized from indene in 20% yield via a two-step reaction, as shown in Figure 1 (see Supporting Information). Crude **BF** was purified by column chromatography and subsequent vacuum distillation over calcium hydride. Isolated **BF** was a yellow solid and was diluted with organic solvents such as THF or benzene just after the vacuum distillation.

The result of anionic polymerization of **BF** is summarized in Table 1. The complete conversion of **BF** was always achieved

Table 1. Anionic Polymerization of BF in THF at $-78\text{ }^{\circ}\text{C}$ for 1 h^a

run	initiator	M_n (kg/mol)		M_w/M_n^d
		calcd ^b	obsd ^c	
1 ^e	<i>sec</i> -BuLi	8.9	8.9	1.11
2 ^f	<i>sec</i> -BuLi	16	18	1.03
3	<i>sec</i> -BuLi	27	28	1.11
4	Ph ₂ CHK	11	13	1.05

^aYield $\sim 100\%$. ^b $M_n(\text{calcd}) = (\text{MW of monomer}) \times [M]/[I] + \text{MW of initiator}$. ^c $M_n(\text{obsd})$ was determined by SEC-RALLS equipped with refractive index (RI), light scattering (LS), and viscometer detectors. ^d M_w/M_n was determined by SEC calibration using polystyrene standards in THF. ^eFor 15 h. ^fFor 20 h.

by initiation with *sec*-BuLi or diphenylmethylpotassium (Ph₂CHK) in THF at $-78\text{ }^{\circ}\text{C}$ within 1 h. The polymerization system always showed a characteristic orange color during the course of polymerization of **BF**. The coloration disappeared immediately on addition of methanol to terminate the polymerization. A white powder of poly(**BF-a**)¹⁴ was quantitatively obtained by precipitation of the reaction mixture into methanol. Size exclusion chromatograms (SEC)s showed that the resulting poly(**BF-a**)s possessed unimodal molecular weight distributions. The polydispersity index, M_w/M_n , was always around 1.1, indicating the narrow molecular weight distribution (MWD). Furthermore, the observed molecular weights of the poly(**BF-a**)s agreed well with the calculated values based on the molar ratios of **BF** and the initiators, indicating quantitative initiation efficiency. It was noted that **BF** shows high anionic polymerizability, because even bulky π -stabilized Ph₂CHK can initiate the polymerization of **BF** in quantitative efficiency.¹⁵

Surprisingly, the anionic polymerization of a hydrocarbon monomer, **BF**, could also be initiated with a low nucleophilic enolate anion derived from methyl methacrylate (MMA) in quantitative efficiency.¹⁶ When **BF** was added to the anionic living poly(MMA) in THF at $-78\text{ }^{\circ}\text{C}$, the polymerization system immediately changed from colorless to orange, indicating that rapid initiation took place. In fact, a well-defined diblock copolymer, poly(MMA)-*block*-poly(**BF**), was successfully obtained by sequential anionic copolymerization of MMA and **BF**. As can be seen in Figure 2A,B, the SEC trace of poly(MMA)-*block*-poly(**BF**) shifts from that of homopoly(MMA) toward a higher molecular weight region by maintaining a narrow MWD. This clearly substantiates the extremely high anionic polymerizability of **BF**, which can be explained by the formation of the highly π -stabilized indenyl anion of **BF** via initiation with the ester enolate of poly(MMA),

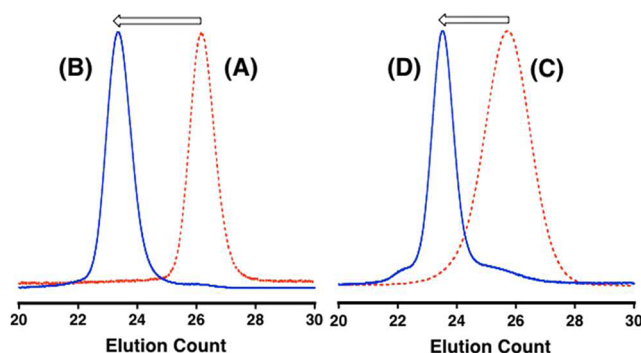
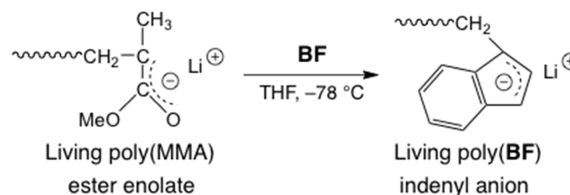


Figure 2. SEC curves of block copolymerization of MMA (first monomer) and **BF** (second monomer): (A) Poly(MMA), $M_n(\text{calcd}) = 4700$, $M_n(\text{obsd}) = 4400$, $M_w/M_n = 1.05$; (B) Poly(MMA)-*block*-poly(**BF**), $M_n(\text{calcd}) = 18000$, $M_n(\text{obsd}) = 22000$, $M_w/M_n = 1.09$. SEC curves of block copolymerization of **BF** (first monomer) and MMA (second monomer): (C) Poly(**BF**), $M_n(\text{calcd}) = 6000$, $M_n(\text{obsd}) = 6700$, $M_w/M_n = 1.16$; (D) Poly(**BF**)-*block*-poly(MMA), $M_n(\text{calcd}) = 15000$, $M_n(\text{obsd}) = 18000$, $M_w/M_n = 1.18$.

as shown in Scheme 1. This can be explained by the fact that the relative acidity of conjugated acid for indene ($\text{p}K_a = 20.1$) is significantly higher than that of ethyl acetate ($\text{p}K_a = 24.4$).¹⁷

Scheme 1. Block Copolymerization of BF with Living Poly(MMA)



Next, the stability of the propagating indenyl anion derived from **BF** was confirmed by sequential copolymerization of **BF** (first monomer) and MMA (second monomer) by changing the additional order of comonomers, as shown in Figure 2C,D. After a 1 h polymerization of **BF** with *sec*-BuLi in THF at $-78\text{ }^{\circ}\text{C}$, MMA was added to the polymerization system of **BF**. A rapid color change from orange to colorless indicated that a crossover initiation from the poly(**BF**) anion to MMA occurred immediately. After termination, a tailored poly(**BF**)-*block*-poly(MMA) possessing the predicted molecular weight and composition was quantitatively obtained. This strongly supports the living character of the polymerization system of **BF** under anionic conditions. The results of sequential copolymerizations using **BF** and MMA indicate that the anionic polymerizability of **BF** was remarkably high and comparable to that of MMA. To the best of our knowledge, **BF** is the first example of a 1,3-diene hydrocarbon showing such high anionic polymerizability.

On the other hand, free radical polymerization of **BF** with α,α' -azobisisobutyronitrile (AIBN) in benzene at $70\text{ }^{\circ}\text{C}$ for 6 h yielded poly(**BF-r**)¹⁸ (96% yield, $M_n = 33000$, $M_w/M_n = 4.63$). The resulting poly(**BF-a**) and poly(**BF-r**) were white powder and were soluble in various organic solvents such as benzene, chloroform, and THF, but insoluble in hexane, methanol, and water. The glass transition temperatures (T_g)s of poly(**BF-a**) and poly(**BF-r**) were observed at 161 and $145\text{ }^{\circ}\text{C}$, respectively.

We then analyzed ¹H and ¹³C NMR spectra to estimate the microstructure of the resulting polymers. Three polymerization

modes, 1,2-, 1,4-, and 3,4-addition modes, can be considered if BF acts as a conjugated 1,3-diene in the polymerizations. Figure 3 shows the ^{13}C NMR spectra of poly(BF-a) obtained with *sec*-

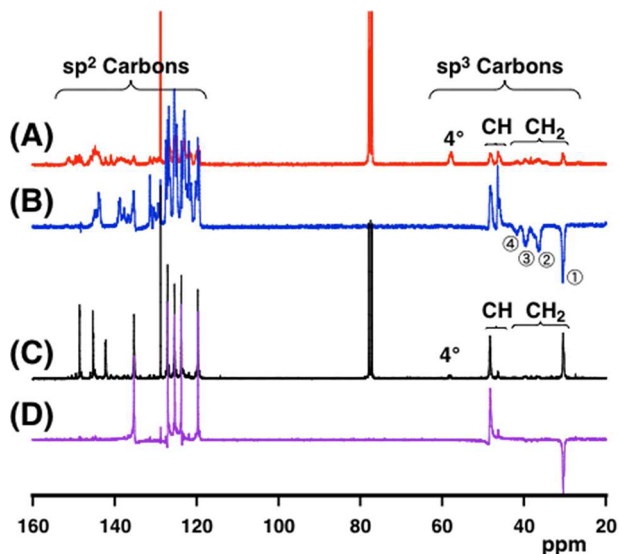


Figure 3. ^{13}C NMR spectra of poly(BF) measured in CDCl_3 . Poly(BF-a) obtained with *sec*-BuLi in THF: (A) complete decoupling, (B) DEPT135. Poly(BF-r) obtained with AIBN in benzene: (C) complete decoupling, (D) DEPT135.

BuLi in THF and poly(BF-r) obtained with AIBN in benzene. Most importantly, no signals attributable to exomethylene groups are observed around 103 ppm in either ^{13}C NMR spectrum.¹⁹ This means that the exomethylene group in BF always participates in anionic and radical polymerizations via the 1,2- and/or 1,4-addition mode, as shown in Figure 4. In other words, 3,4-addition units can be ruled out in the poly(BF-a) and poly(BF-r) samples.

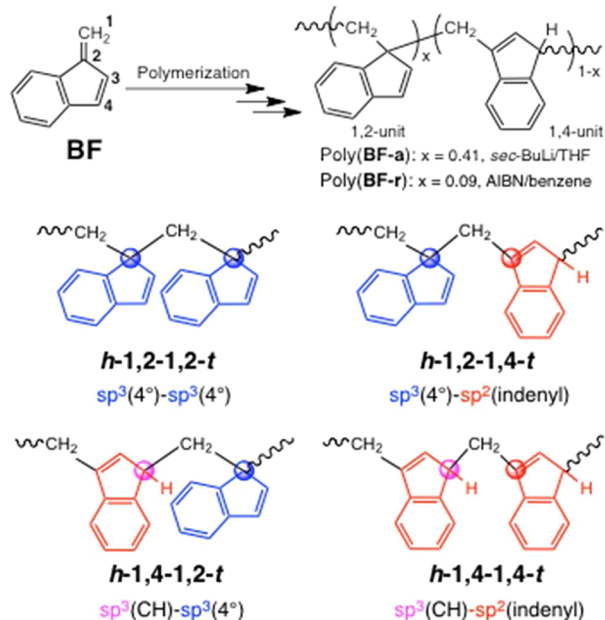


Figure 4. Polymerization modes of BF and four possible diad units in poly(BF).

As the next significant feature, anionically synthesized poly(BF-a) shows a number of complicated ^{13}C NMR signals between 30 and 57 ppm in contrast to the simple signals of poly(BF-r) produced with AIBN. Distortionless enhancement by polarization transfer (DEPT) measurement revealed that the signal at around 57 ppm corresponded to the aliphatic quaternary carbons specific to the 1,2-repeating unit. The intensity of this quaternary carbon signal in poly(BF-a) is apparently stronger than that of poly(BF-r) when comparing it with other signal intensities. On the other hand, poly(BF-r) showed negligible intensity of the quaternary carbon, and alternatively a strong aliphatic methine carbon specific to the 1,4-repeating unit was detected at around 48 ppm. This indicates that the major structure for poly(BF-r) is a 1,4-addition mode, because the 1,2-repeating unit does not involve the methine carbon in the aliphatic region.

Figure 4 illustrates the chemical structures of four possible diad repeating units in poly(BF). If we ignore the effect of stereoregularity of the diad sequence, we can draw these four possible sequences for BF dimers: *h*-1,2-1,2-*t*; *h*-1,2-1,4-*t*; *h*-1,4-1,2-*t*; and *h*-1,4-1,4-*t* (*h* and *t* mean head and tail in the structures). Apparently, the environments of the methylene groups in the four sequences should differ from each other from the viewpoints of hybridization states (sp^3 or sp^2) and features (quaternary, tertiary, or indenyl) of the two adjacent carbons in the main chain. As can be seen in Figure 3A,B, poly(BF-a) shows four methylene signals at 30, 36, 39, and 41 ppm, indicating the large differences in their electronic environment. On the other hand, one methylene signal at 30 ppm is predominantly observed in poly(BF-r). From the relative intensity of the methylene carbons, we tentatively estimated that the poly(BF-a) obtained with *sec*-BuLi in THF possessed 59% of the 1,4-structure and 41% of the 1,2-structure,²⁰ while 91% of the 1,4- and 9% of the 1,2-structures were observed for the poly(BF-r) formed with AIBN at 70 °C. Compared to the ^{13}C NMR spectra, the ^1H NMR spectra could not provide useful information for evaluation of the polymerization modes because of the broadness of the spectra. It is, however, noteworthy that the ^1H NMR spectrum of poly(BF-a) significantly differed from that of poly(BF-r), supporting the differences in polymerization modes again.

In conclusion, we have succeeded in the living anionic polymerization of a novel exomethylene monomer, BF, to afford polymers with predicted molecular weights and narrow MWDs. The extremely high anionic polymerizability of this hydrocarbon is newly demonstrated. The NMR analyses reveal that BF acts as a conjugated 1,3-diene to give polymers containing the 1,2- and 1,4-addition modes. A detailed study on the polymerization behavior of BF and on controlling of the microstructures is in progress and will be reported in a forthcoming paper.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: tishizon@polymer.titech.ac.jp.

Notes

The authors declare no competing financial interest.

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- (12) Ref 7. Radical and anionic polymerizations of α -methyleneindane were reported. The polymerizability of α -methyleneindane was much lower than that of **BF** because of the difference in the π -conjugated system.
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- (14) Poly(**BF-a**): anionically synthesized poly(**BF**).
- (15) Although Ph₂CHK could initiate the anionic polymerization of styrene in THF at -78 °C, the resulting polystyrene possessed a broad molecular weight distribution and a molecular weight higher than the calculated value. The initiation efficiency was less than 50% due to the low nucleophilicity.
- (16) No polymerization of styrene or isoprene occurred with the enolate anion of living poly(MMA) under similar conditions.
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- (18) Poly(**BF-r**): radically synthesized poly(**BF**).
- (19) As a reference signal of the 3,4-addition mode, the ¹³C NMR signal of the exomethylene group (CH₂=) of α -methyleneindane was observed at 102.5 ppm.
- (20) The microstructure of polyisoprene obtained with *sec*-BuLi in THF at -30 °C contained the 3,4- (80%) and 1,2-(20%) modes, but the 1,4-mode was negligible.