Macromolecules

High Anionic Polymerizability of Benzofulvene: New Exo-Methylene Hydrocarbon Monomer

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Supporting Information



ABSTRACT: The anionic polymerization of benzofulvene (BF) quantitatively proceeded with various initiators, such as sec-BuLi, diphenylmethyllithium, diphenylmethylpotassium, triphenylmethyllithium, and triphenylmethylpotassium, in THF at -78°C to give polymers having predicted molecular weights based on the molar ratios between BF and the initiators and narrow molecular weight distributions (MWD, $M_w/M_n < 1.1$). Although the initiation efficiencies were not quantitative, BF could also be polymerized with benzylmagnesium chloride, potassium tert-butoxide, and the anionic living poly(tert-butyl methacrylate), indicating the high anionic polymerizability. The planar conformation and the polarized electron density of BF obtained by the density functional theory (DFT) calculation supported the observed anionic polymerizability higher than that of 2-phenyl-1,3butadiene, the acyclic analogue of BF. A series of new block copolymers, polystyrene-b-poly(BF), poly(2-vinylpyridine)-bpoly(BF), and poly(tert-butyl methacrylate)-b-poly(BF), were synthesized by the sequential anionic copolymerization of BF and the comonomers. On the other hand, no polymerization of styrene and 2-vinylpyridine took place with the living poly(BF), indicating the low nucleophilicity of the propagating indenyl anion formed from BF. BF readily underwent the free-radical polymerization with α, α' -azobis(isobutyronitrile), while the observed cationic polymerizability of BF was quite low. ¹H and ¹³C NMR analyses revealed that the repeating units of poly(BF) consisted of a 1,2-addition unit and a 1,4-addition unit without a 3,4addition unit regardless of the polymerization conditions. The exo-methylene moiety $(CH_2=)$ of BF always participated in the addition polymerization. The addition modes were dependent on the polymerization temperature and not on the solvent or the countercation of the anionic initiator. For instance, polymer obtained with sec-BuLi in THF at 40 °C contained 72% of the 1,4addition unit and 28% of the 1,2-addition unit. Therefore, BF acted as a polymerizable 1,3-diene possessing a fixed transoid framework.

■ INTRODUCTION

It has been established that conventional hydrocarbon vinyl monomers, such as styrene, α -methylstyrene, 1,3-butadiene, and isoprene, undergo the anionic polymerization to provide stable living polymers with well-defined chain structures including predicted molecular weights and narrow molecular weight distributions (MWD, $M_w/M_n < 1.1$).¹ These living polymerization systems also allow the syntheses of tailored block copolymers by the sequential copolymerization and end-functionalized polymers by the suitable termination reactions. Although the propagating carbanions derived from the hydrocarbon monomers show extremely high nucleophilicities, the anionic polymerizability of hydrocarbon monomers is significantly lower than those of polar monomers including vinylpyridines, (meth)acrylates, and *N*,*N*-dialkylacrylamides.^{1,2} Typical strong anionic initiators, such as *sec*-butyllithium (*sec*-

BuLi) and potassium naphthalenide (K-Naph), are necessary to quantitatively initiate the polymerization of hydrocarbon monomers. It is noteworthy that the range of the hydrocarbon monomers capable of the living anionic polymerization is still limited regardless of the recent progress of this research field.

In our recent communication,³ we proposed a novel hydrocarbon monomer, benzofulvene (BF, α -methyleneindene). We have succeeded in the living anionic polymerization of BF initiated with *sec*-BuLi in THF at -78 °C, as illustrated in Scheme 1.³ The resultant poly(BF)s had predictable molecular weights from the molar ratios between BF and initiators and narrow MWDs ($M_w/M_n = 1.1$). Similarly, we recently found

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Scheme 1. Anionic Polymerization of BF with sec-BuLi in THF or in Benzene



that BF underwent the living anionic polymerization with *sec*-BuLi in a nonpolar hydrocarbon, such as benzene, at 0-55 °C.⁴ Based on its chemical structure, BF is a cyclic analogue of 2-phenyl-1,3-butadiene (2PB)^{5,6} and a derivative of fulvene,⁷ 5-methylene-1,3-cyclopentadiene, showing an extremely high reactivity derived from the planar cross-conjugated π -electron system including the exo-methylene group.⁸ BF indeed acted as a 1,3-butadiene derivative during the anionic polymerization, since the resulting polymer possessed 1,4- and 1,2-addition repeating units depending on the polymerization modes (Scheme 1).^{3,4} The exo-methylene carbon in BF always took part in the addition polymerization, and no 3,4-structure was certainly observed in the repeating unit of the resulting poly(BF).

On the other hand, the 3-phenyl-7-methyl-9 and 2ethoxycarbonyl-3-phenyl-substituted BF derivatives¹⁰ were synthesized and polymerized. Interestingly, their polymerizations exclusively proceeded in the 1,2-addition mode on the exo-methylene groups. Thus, their polymerizabilities were significantly different from that of the nonsubstituted BF, since the 3,4-carbons in these BF derivatives were substituted with the bulky groups.^{9,10} The intriguing polymerizability of the novel hydrocarbon monomer, BF, has just been discovered regardless of its simple and attractive fulvene framework. We herein report the polymerization behavior of BF in more detail. The various anionic initiators, including a series of anionic living polymers, are newly employed in order to clarify the relative reactivity of BF. We also compare the anionic polymerizability of BF with 2PB in order to discuss the relative reactivity of the exo-methylene BF monomer with the acyclic counterpart. The stable conformations and the electron densities of BF and 2PB are estimated by the density functional theory (DFT) calculations¹¹⁻¹⁵ to compare the relative polymerizabilities. The free-radical and cationic polymerizations of BF are also examined to clarify the reactivity. The microstructure and the property of the new polymers are of great interest.

RESULTS AND DISCUSSION

Monomer Synthesis. BF could be synthesized by the dehydration of hydroxymethylindenes (HMIs) including 1-hydroxymethylindene (1HMI) and 3-hydroxymethylindene (3HMI) using potassium *tert*-butoxide (tBuOK), as shown in Scheme 2. In our previous studies, the HMIs were obtained from the reaction of indenylmagnesium bromide or indenyllithium with paraformaldehyde.^{3,4} In fact, the latter route was superior to the former one from the viewpoints of yield of the HMIs and reproducibility. Chong and co-workers reported the synthesis of 9-hydroxymethylfluorene by the reaction of paraformaldehyde and fluorenyllithium.¹⁶ They used an equivalent quantity of *n*-BuLi to fluorene and used 1.1-fold of

Scheme 2. Synthesis of BF from Indene



paraformaldehyde, since this reaction was very sensitive to the molar ratios of the starting compounds. We followed their experimental procedure to abstract the acidic CH_2 proton of indene with *n*-BuLi in a mixed solvent of hexane and THF at 0 °C. HMIs were obtained in 60% yield in a high reproducibility, and the following dehydration produced the BF monomer.

Herein, the difficulty of isolation of BF should be noted. The resultant BF was a yellow solid and spontaneously polymerized in the solid state. When we checked the melting point of BF using a differential scanning calorimetry (DSC) measurement, we observed only an exothermic peak starting from 70 °C presumably due to the thermal polymerization of BF. In fact, an attempt at the vacuum distillation of BF using a rotary pump with heating (~0.5 mmHg/80 °C) produced an insoluble polymeric product. Therefore, we have purified BF by a flash column silica gel chromatography and completely removed the solvents in order to form the solid BF. We then degassed the solidified BF using a rotary pump for 5 min and immediately diluted it with dry THF. Although this purification was sufficient to prepare a poly(BF) with controlled molecular weight by the anionic polymerization, it was preferable to distill BF from CaH₂ under high-vacuum conditions using an oil diffusion pump ($\sim 10^{-6}$ mmHg) on a vacuum line. The distilled BF was frozen with liquid nitrogen during the course of the distillation. After the distillation, the isolated BF was immediately diluted with dry THF, and the resultant yellow solution was stored at -30 °C. The BF monomer in solution was rather stable and could be stored in a sealed glass ampule for several weeks.

Anionic Polymerization of BF and Microstructure of Poly(BF). The anionic polymerization of BF in THF was carried out with *sec*-BuLi under various conditions as shown in Table 1. Upon the addition of the yellow THF solution of BF to *sec*-BuLi in *n*-heptane, the color of the system immediately changed to the characteristic orange. The orange color was maintained during the polymerization and instantaneously disappeared to afford a colorless solution by quenching with methanol. This suggests the presence of propagating chain ends

					$M_{\rm n}~({\rm kg/mol})$			(%)	
run	BF (mmol)	initiator (mmol)	temp (°C)	time (h)	calcd ^b	obsd ^c	$M_{\rm w}/{M_{\rm n}}^d$	1,2-	1,4-
1	6.35	sec-BuLi, 0.0921	-78	15	8.9	8.9	1.11		
2	4.69	sec-BuLi, 0.0473	-78	10 min	12	13	1.09		
3	8.21	sec-BuLi, 0.0645	-78	20	16	18	1.03	41	59
4	8.04	sec-BuLi, 0.0380	-78	1	27	28	1.11		
5	5.45	sec-BuLi, 0.0588/TMEDA, ^e 0.242	-78	1	12	15	1.11	43	57
6	3.96	sec-BuLi, 0.0499	-95	30 min	10	12	1.11	41	59
7	3.24	sec-BuLi, 0.0423	-40	2.5	8.6	10	1.17	36	64
8	3.38	sec-BuLi, 0.0402	40	15 min	10	8.3	2.10	28	72
9	6.65	K-Naph, 0.195	-78	1	8.8	8.2	1.08	38	62
10	5.91	Ph ₂ CHLi, 0.0808	-78	1	9.3	12	1.09	41	59
11	5.16	Ph ₂ CHNa, 0.0452	-78	1	15	15	1.10	41	59
12	6.35	Ph ₂ CHK, 0.0921	-78	1	11	13	1.05	40	60
13	5.58	Ph ₂ CHK, 0.0616/18-crown-6 ^{,f} 0.282	-78	1	12	9.5	1.18	36	64
14	5.02	Ph ₂ CHCs, 0.0465	-78	1	11	14	1.07	44	56
15	4.49	Ph ₃ CLi, 0.0843	-78	2	13	17	1.11		
16	6.59	Ph ₃ CK, 0.0884	-78	2	9.2	9.9	1.14		
17	5.09	BzMgCl, 0.163	-78	17	3.6	193	3.21	43	57
18	6.00	tBuOK, 0.496	-78	1	1.6	13	1.35		

Table 1. Anionic Polymerization of BF in THF^a

^{*a*}Conversion ~100%. ^{*b*} M_n (calcd) = (MW of monomer) × [M]/[I] + MW of initiator residue. ^{*c*} M_n (obsd) was determined by SEC-RALLS equipped with triple detectors, such as refractive index (RI), light scattering (LS), and viscometer detectors. ^{*d*} M_w/M_n was determined by SEC calibration using polystyrene standards in THF. ^{*e*} N_nN_n'/N' -Tetramethylethylenediamine. ^{*f*}1,4,7,10,13,16-Hexaoxacyclooctadecane.



Figure 1. SEC curves of poly(BF)s obtained with *sec*-BuLi in THF at -78 °C after 15 h (A) and at 40 °C after 15 min (B). Peak (A): $M_{n,calcd} = 8900$, $M_{n,RALLS} = 8900$, $M_w/M_n = 1.11$. Peak (B): $M_{n,calcd} = 10\ 000$, $M_{n,RALLS} = 8300$, $M_w/M_n = 2.10$.

and also supports the complete consumption of the yellow BF monomer. In fact, the polymerization of BF rapidly proceeded and was completed within 10 min at -78 °C to quantitatively give a polymer. The poly(BF)s produced at -78 °C (runs 1-4) possessed molecular weights predictable from the molar ratios between BF and sec-BuLi and narrow MWDs $(M_w/M_n < 1.11)$. The SEC curve of poly(BF) maintained a unimodal and narrow shape even after 15 h, indicating the absence of cross-linking and chain degradation at -78 °C in THF. The controlled polymerization of BF also occurred with sec-BuLi in the presence of 4.1-fold N,N,N',N'-tetramethylethylenediamine (TMEDA) as a strong chelating reagent (run 5). Tailored poly(BF)s were similarly formed with sec-BuLi at -95 and -40 °C in THF (runs 6 and 7). On the other hand, the MWD of the polymer obtained at 40 °C significantly broadened, and the polydispersity index, M_w/M_n , increased to 2.10 (run 8). A temperature lower than -40° C was preferable to control the

polymerization of BF. At -78 °C for 1 h, potassium naphthalenide (K-Naph), a radical anion, produced a well-defined poly(BF) in 100% yield (run 9).

We then employed a series of diphenylmethyl carbanions, diphenylmethyllithium (Ph₂CHLi), diphenylmethylsodium (Ph₂CHNa), diphenylmethylpotassium (Ph₂CHK), and diphenylmethylcesium (Ph₂CHCs), to examine the effect of the countercation of the initiators (runs 10–12 and 14). In each case, the polymerization of BF quantitatively proceeded within 1 h at -78 °C, and the produced poly(BF) had a controlled M_n and narrow MWD ($M_w/M_n = 1.05-1.10$). Ph₂CHK could initiate the polymerization of BF in the presence of 4.6-fold crown ether, 18-crown-6, while the MWD of the resulting poly(BF) slightly broadened (run 13, $M_w/M_n = 1.18$). Thus, BF smoothly underwent the controlled anionic polymerization with these diphenylmethyl carbanions regardless of the counter cations.

Next, the anionic polymerizations using the bulkier triphenylmethyl carbanions, such as triphenylmethyllithium (Ph₃CLi) and triphenylmethylpotassium (Ph₃CK), were examined in THF at -78 °C for 2 h. Ph₃CLi and Ph₃CK also induced the polymerization of BF to provide a polymer having narrow MWDs and predicted molecular weights in quantitative yields (runs 15 and 16). These results clearly indicate that the bulky π -conjugated triphenylmethyl carbanions can initiate the polymerization of BF in quantitative efficiencies similar to strong anionic initiators, such as sec-BuLi and K-Naph. The control of the chain length of the poly(BF)s was successfully attained using these bulky nucleophiles. This observed polymerizability of BF is remarkably higher than those of other hydrocarbon monomers, such as styrene and isoprene, since the bulky π -conjugated carbanions are often intact or show low efficiencies to initiate the conventional hydrocarbon monomers.

Surprisingly, BF could be initiated with benzylmagnesium chloride (BzMgCl) and tBuOK at -78 °C in THF (runs 17 and 18), although both nucleophiles cannot effectively initiate the hydrocarbon monomers, such as styrene and 1,3-diene, under similar polymerization conditions. In each case, the polymer yield was quantitative, though the polymerization behavior was far from a controlled fashion. In fact, the MWDs were broad and the molecular weights were much higher than the calculated values. The initiation efficiency of BzMgCl and tBuOK was roughly estimated to be 2 and 12%, respectively. Nevertheless, it should be emphasized again that even the low nucleophilic Grignard reagent and alkoxide anion could initiate the polymerization of this particular hydrocarbon monomer, BF. This strongly supports the fact that BF is categorized as a new class of hydrocarbon monomers from the viewpoint of anionic polymerizability.^{1,7}

Finally, we discuss the microstructures of the obtained polymers as also shown in Table 1. The microstructures can be determined by the integral ratio in the ¹³C NMR spectra of the methylene signal of poly(BF), as previously reported (Figure S1).^{3,4} The exo-methylene (CH₂=) group in BF was always consumed during the propagation, and no 3,4-addition mode was observed in the resulting polymers (Scheme 1). In other words, the repeating unit of poly(BF) contained only the 1,2and 1,4-addition modes regardless of the polymerization conditions. As can also be seen in Table 1, the 1,4-addition mode was always a major unit and varied from 56 to 72%. The effects of the countercation of the initiator and the additive effect of the chelating reagents, such as TMEDA and crown ether, were not significant but negligible. In fact, the 1,4contents of poly(BF) obtained with sec-BuLi, sec-BuLi/ TMEDA, K-Naph, Ph₂CHLi, Ph₂CHNa, Ph₂CHK, Ph₂CHCs, Ph₂CHK/18-crown-6, and BzMgCl at -78 °C ranged from 56 to 64%. On the other hand, the 1,4-addition mode tended to slightly increase from 59 to 72% by increasing the polymerization temperature from -95 to 40 °C. Thus, BF acted as a 1,3-diene during the addition polymerization, since not only the exo-methylene group but also the C=C linkage in the cyclopentadiene part of BF participated in the polymerization (Scheme 1). It is noted that the polymerization temperature certainly affects the addition mode of the repeating units of poly(BF).

Anionic Polymerization of 2PB. Next, the anionic polymerization of 2PB, an acyclic analogue of BF, was investigated with various initiators employed in Table 1 to compare their polymerization behaviors. Fujimoto and co-

workers reported that 2PB can be initiated by highly reactive anionic initiators, such as *sec*-BuLi, *n*-BuLi, and cumylpotassium, to afford well-defined poly(2PB)s having narrow MWDs $(M_w/M_n < 1.1)$ and predicted molecular weights.⁶ Similarly, the tailored poly(2PB)s were obtained by the quantitative initiation of K-Naph, Ph₂CHLi, and Ph₂CHK in THF at -78 °C, as shown in Table 2 (runs 20–22). On the other hand, the

Table 2. Anionic Polymerization of 2PB in THF at -78 °C for 24 h

				$M_{\rm n}$:		
run	2PB (mmol)	initiator (mmol)	yield ^a (%)	calcd ^b	RALLS ^c	$M_{ m w}/M_{ m n}^{\ d}$
19	3.12	sec-BuLi, 0.0403	92	10	13	1.04
20	4.12	K-Naph, 0.0960	100	11	12	1.08
21	5.66	Ph ₂ CHLi, 0.0881	100	8.5	11	1.05
22	4.16	Ph ₂ CHK, 0.0323	100	17	18	1.03
23	5.96	Ph ₃ CLi, 0.0852	39	3.6	93	1.23
24	3.24	Ph ₃ CK, 0.0577	31	2.3	82	1.19
25	6.49	BzMgCl, 0.121	0		no polym	er
26	6.94	tBuOK, 0.626	0		no polym	er

^{*a*}Methanol-insoluble part. ^{*b*} M_n (calcd) = (MW of monomer) × [M]/ [I] × (yield of polymer) + MW of initiator residue. ^{*c*} M_n (obsd) was determined by SEC-RALLS equipped with triple detectors, such as refractive index (RI), light scattering (LS), and viscometer detectors. ^{*d*} M_w/M_n was determined by SEC calibration using polystyrene standards in THF.

poly(2PB)s obtained with Ph₃CLi and Ph₃CK had rather broad MWDs with long tailings and molecular weights higher than the calculated values (runs 23 and 24). In fact, the initiation efficiencies of Ph₃CLi and Ph₃CK for 2PB were estimated to be 9.6% and 8.7%, respectively. Furthermore, low nucleophilic initiators, such as a Grignard reagent (BzMgCl) and alkoxide (tBuOK), could not initiate 2PB at all in THF at -78 °C, resulting in the quantitative recovery of the monomer (runs 25 and 26). It is again noteworthy that BF can be readily polymerized with BzMgCl or tBuOK under similar conditions, while the initiation efficiency was far from quantitative (Table 1, runs 17 and 18). These results indicate that the anionic polymerizability of 2PB, the acyclic counterpart of BF, is certainly lower than that of BF. Nevertheless, 2PB showed an anionic polymerizability higher than 1,3-butadiene or isoprene due to the phenyl substituent conjugated with the 1,3-diene framework. For example, no polymeric product was obtained by the reaction of isoprene with Ph₃CK under similar conditions, while 2PB underwent the polymerization.¹⁷

To theoretically understand such a distinct anionic polymerizability between 2PB and BF, we optimized the equilibrium structures of BF and 2PB in the ground state *in vacuo* by the DFT calculation and focused on four factors including the dihedral angle, bond angle of the sp² carbon of the exomethylene (vinyl) group, atomic charge on the β -carbon of the vinyl group, and LUMO value, as shown in Table 3. As can be seen in Figure 2, both monomers showed quite different geometries. We evaluated two kinds of dihedral angles: one was a twist angle between the vinyl and phenyl groups ($\angle C1-C2-C3-C4$), and the other was a twist angle in the 1,3-diene framework ($\angle C1-C2-C3'-C4'$). In fact, both angle values

monomer	∠C1-C2-C3-C4	∠C1-C2-C3′-C4′	∠C3-C2-C3′	atomic charge on C1 ^b	LUMO (eV)				
BF	0.0	0.0	105.4	-0.301	-0.162				
2PB	57.3	8.7	119.5	-0.346	+0.706				
All structures were optimized by ω B97X-D/6-311G(d,p). ^b Natural charges were obtained by NBO analysis.									



Figure 2. Molecular frameworks and most stable structures of BF and 2PB determined by the DFT calculation.

 (0°) of BF clearly indicated its complete planar structure and the effective conjugation between the exo-methylene group and phenyl ring. On the other hand, the resonance effect between the vinyl moiety and the phenyl group in 2PB might be negligible due to the highly twisted conformation (57°) , while the transoid 1,3-diene framework in 2PB maintained an effective conjugation (8.7°). The bond angles ($\angle C3-C2-$ C3'), which might reflect the distortion at the sp²-conjugated C2 carbon of BF and 2PB, were 105.4° and 119.5°, respectively. The former value of BF was apparently smaller than the ideal value of 120° for the typical sp²-conjugated carbon. It is thus suggested that the C2 carbon of BF is more strained and reactive compared to that of 2PB. The strained sp²-conjugated C2 carbon changes to the less strained sp³ carbon by releasing the stress, if the polymerization of BF proceeds in the 1,2addition mode. The calculated atomic charges on the β carbons (C1) of the exo-methylene (vinyl) groups in BF and 2PB were -0.301 and -0.346, respectively. This means that the β carbon of BF can be more easily attacked by the nucleophiles than 2PB

due to the lower atomic charge. The same tendency was observed in the calculated LUMO values. The LUMO values of BF and 2PB were -0.162 and +0.706 eV, respectively. BF is considered to be more reactive to the nucleophiles because the energy level of the unoccupied molecular orbital of BF is much lower than that of 2PB. All these calculated results supported the experimental observations that the exo-methylene-type BF had a higher anionic polymerizability than the corresponding vinyl-type 2PB.

Article

Block Copolymerization of BF. In this section, we performed the sequential copolymerization of BF with comonomers possessing different anionic polymerizabilities, such as styrene, isoprene, 2-vinylpyridine (2VP), 4-cyanostyrene (4CNSt),¹⁸ MMA, and tert-butyl methacrylate (tBMA) for the synthesis of various block copolymers (Table 4). In addition, the results of the sequential copolymerization (crossover reaction) will provide the relative reactivity of the monomers including BF. All the employed comonomers undergo the living anionic polymerizations to provide polymers with well-defined chain structures.¹⁹ At first, a series of anionic living polymers of styrene, isoprene, 2VP, 4CNSt, MMA, and tBMA were synthesized for the macroinitiators for BF in THF. All the living polymers could initiate the polymerization of BF, and the copolymers were obtained in quantitative yields (runs 27-32). The $M_{\rm p}$ values of the block copolymers possessing poly(BF) segments were estimated from either the RALLS-SEC or ¹H NMR measurement. In fact, the resulting novel block copolymers possessed relatively narrow MWDs (M_w/M_p) = 1.09 - 1.22) along with predicted molecular weights. Since the SEC curves of the block copolymers were almost unimodal, the efficiencies of the crossover reactions from the various living polymers to BF were estimated to be quantitative.

As a typical example, the polymerization of BF was performed with a living poly(tBMA), prepared with Ph_2CHK in THF at -78 °C for 2 h (run 32). When BF was added to the living poly(tBMA) to reinitiate the copolymerization, the color

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Lable 4. Block	Copolymerization	of BF with Styrene	. Isoprene. 2VP.	4UNSE MIMA.	and this an	THE at -78 °C
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				block copolymer (homopolymer ^b)		
				M _n (kg/mol)		
run	initiator	1st monomer	2nd monomer	calcd	obsd ^c	$M_{ m w}/M_{ m n}^{\ d}$
27	sec-BuLi	styrene	BF	19 (5.0)	14 (4.5)	1.12 (1.10)
28	K-Naph	isoprene	BF	23 (11)	26 (11)	1.14 (1.19)
29	Ph ₂ CHLi	2VP	BF	19 (5.5)	19 (3.2)	1.22 (1.10)
30	Ph ₂ CHK	4CNSt	BF	12 (5.2)	11 (3.3)	1.11 (1.11)
31 ^e	sec-BuLi/DPE/LiCl	MMA	BF	18 (4.7)	22 (4.4)	1.09 (1.05)
32	Ph ₂ CHK	tBMA	BF	30 (6.7)	29 (5.5)	1.11 (1.10)
33 ^e	sec-BuLi/LiCl	BF	MMA	15 (6.0)	18 (6.7)	1.18 (1.16)
34	Ph ₂ CHLi	BF	tBMA	14 (9.6)	10 (8.0)	$1.50^{f}(1.22)$

"Yield of copolymer was quantitative in each case. ^bHomopolymer was obtained at the first-stage polymerization. ${}^{c}M_{n}$ (obsd) was determined by SEC-RALLS equipped with triple detectors, such as refractive index (RI), light scattering (LS), and viscometer detectors. ${}^{d}M_{w}/M_{n}$ was determined by SEC calibration using polystyrene standards in THF. ^cReference 3. ^fBimodal SEC curve.

of the polymerization system rapidly changed from colorless to orange upon the addition of BF, indicating the occurrence of a rapid crossover reaction (Scheme 3). A copolymer was

Scheme 3. Crossover Reaction of BF with Living Polymethacrylate



Figure 3. SEC curves of poly(tBMA) (A, dotted line) and poly(tBMA)-*b*-poly(BF) (B, solid line). Peak (A): $M_{n,calcd} = 6500$, $M_{n,RALLS} = 5500$, $M_w/M_n = 1.10$. Peak (B): $M_{n,calcd} = 28\ 000$, $M_{u,RALLS} = 29\ 000$, $M_w/M_n = 1.11$ (run 32). SEC curves of poly(BF) (C, dotted line) and poly(BF)-*b*-poly(tBMA) (D, solid line). Peak (C): $M_{n,calcd} = 9500$, $M_{n,RALLS} = 8000$, $M_w/M_n = 1.22$. Peak (D): $M_{n,calcd} = 14\ 000$, $M_{n,RALLS} = 10\ 000$, $M_w/M_n = 1.50$ (run 34).

quantitatively obtained after 1 h. Figures 3A and 3B show the SEC curves of the poly(tBMA) and a poly(tBMA)-*b*-poly(BF). The SEC curve of the copolymer shifts toward the higher molecular weight region from the SEC curve of poly(tBMA) maintaining a unimodal and narrow MWD. This clearly indicates the formation of the tailored AB diblock copolymer of tBMA and BF, poly(tBMA)-*b*-poly(BF). In other words, a hydrocarbon monomer, BF, can be polymerized with a low nucleophilic enolate anion of poly(tBMA) similar to the previous results using the living poly(MMA).³ This high electrophilicity of BF is in good accordance with the polymerization results observed in the former section.

Next, we used BF as the first monomer to prepare block copolymers in the reversed sequences. However, a living poly(BF) could not initiate at all the polymerization of

Tab	le 5.	Po	lymerization	of BF	with	AIBN	and	BF ₃ OEt ₂
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comonomers, such as styrene, isoprene, 2VP, and 4CNSt, when these monomers were added to the living poly(BF). The homopolymers of BF, formed during the first stage polymerization, were recovered from the reaction systems along with the comonomers. This is due to the low nucleophilicity of the propagating indenyl anion formed from BF (Scheme 3). Since the BF monomer shows an extremely high anionic polymerizability, the resulting propagating carbanion has a very low nucleophilicity. In contrast, the living poly(BF) could initiate the polymerization of MMA, an α_{β} -unsaturated carbonyl compound showing a high electron affinity, with a quantitative efficiency to give a well-defined poly(BF)-b-poly(MMA) as previously reported (run 33).³ On the other hand, the initiation efficiency of the copolymerization of tBMA was not quantitative and less than 50% to give a mixture of a block copolymer and a homopoly(BF), as shown in Figures 3C and 3D (run 34). The relative polymerizability of tBMA might be lower than that of MMA probably due to the steric effect of the bulky tert-butyl group.

Thus, these results strongly indicate the comparable anionic polymerizability of BF and methacrylates, since the reversible sequential copolymerization of BF and methacrylates is possible to produce the block copolymers. In particular, the quantitative crossover reaction of polymethacrylates to BF is of great interest from a synthetic viewpoint. This high anionic polymerizability can be explained by the relative acidity of the conjugated acids for indene ($pK_a = 20.1$) and ethyl acetate ($pK_a = 24.4$).²⁰ The less basic π -stabilized indenyl anion of BF forms via the initiation with the more basic propagating ester enolate of the polymethacrylates, as shown in Scheme 3. In summary, the relative anionic polymerizability of BF is estimated from the results of the homopolymerization and block copolymerization as follows.¹⁹

relative anionic polymerizability:

MMA ~ BF > 4CNSt > 2VP > styrene ~ isoprene

Radical and Cationic Polymerization of BF. We then attempted to polymerize BF with radical and cationic initiators as summarized in Table 5. At first, stirring of BF and α,α' -azobis(isobutyronitrile) (AIBN) in benzene at 70 °C for 15 h led to the quantitative formation of an insoluble gel-like product (run 35). We then shortened the polymerization time to 6 h (runs 36 and 37). The conversion of BF was monitored by ¹H NMR measurements. In each case, the radical polymerization of BF with AIBN was completed within 6 h to afford a soluble polymer as a powder in a good to quantitative yield. The SEC curves of the obtained polymers were unimodal and the observed molecular weights were 14 000–33 000 by the SEC-RALLS analysis. As shown in Figure 4, the ¹H NMR spectrum of the radically obtained polymer, poly(BF-r), is significantly different from that of the

run	initiator, mol %	solvent	time (h)	temp (°C)	yield ^{a} (%)	$M_{\rm n}~({\rm kg/mol})~{\rm obsd}^b$	$M_{ m w}/{M_{ m n}}^b$
35	AIBN, 1.1	benzene	15	70	100	insoluble	
36	AIBN, 1.1	benzene	6	70	80	14	2.46
37	AIBN, 0.87	benzene	6	70	96	33	4.63
38	BF ₃ OEt ₂ , 8.0	CH_2Cl_2	48	0	0		
39	BF ₃ OEt ₂ , 37	CH_2Cl_2	4	0	46	3.9	24.3
40	BF ₃ OEt ₂ , 43	CH_2Cl_2	24	0	98	15	3.18 ^c

^aMethanol-insoluble part. ${}^{b}M_{n}(obsd)$ and M_{w}/M_{n} were determined by SEC calibration using polystyrene standards in THF. ^cMultimodal.

(A)

(B)

(C)

aromatic

b,c,e



Solubility and Thermal Property of Poly(BF). Poly(BFa) and poly(BF-r) were off-white powders and showed similar solubilities in various solvents. In fact, they were insoluble in *n*hexane, cyclohexane, dimethyl sulfoxide, methanol, and water but soluble in benzene, toluene, chloroform, and THF at room temperature. It is noted that the microstructure of poly(BF) does not considerably affect their solubilities.

The thermal stabilities of poly(BF-a) and poly(BF-r) were measured by a thermogravimetric analysis (TG/DTA) under nitrogen (Figure 5). When we heated the samples from room



Figure 5. TGA curves of poly(BF)s: (A) poly(BF-a), 10% weight loss temperature $(T_{10}) = 326 \ ^{\circ}C_{i}$ (B) poly(BF-r), $T_{10} = 311 \ ^{\circ}C_{i}$

temperature to a higher temperature, the thermal degradations of the poly(BF)s occurred around 270 °C with decreasing the weight of the polymer samples. At 600 °C, the residual weights of the ashes derived from poly(BF-a) and poly(BF-r) were observed to be 32 and 23 wt %. The 10% weight loss temperatures, T_{10} , of poly(BF-a) and poly(BF-r) were observed at 326 and 311 °C, respectively. These observations suggest that no significant relationship is present between the thermal stability and the microstructure of the poly(BF) samples.

The glass transition temperature (T_{σ}) of a series of poly(BF) was analyzed by DSC measurements as shown in Figure 6. In addition to poly(BF-a) and poly(BF-r), the poly(BF-a-Bz) samples, obtained with sec-BuLi in benzene at 0 $^{\circ}C$,⁴ were added in Figure 6. The microstructure of poly(BF-a-Bz) (1,4content ~76%, 1,2-content ~24%) rather resembled that of poly(BF-r), while the samples were produced with the anionic



Figure 6. Relationship between $T_{\rm g}$ and $M_{\rm n}$: (A) poly(BF-a), (B) poly(BF-a-Bz), and (C) poly(BF-r).



1,2-unit

a,d

d

1,4-unit

anionically obtained polymer, poly(BF-a), produced with sec-BuLi in THF. We could assign several signals of poly(BF-r) with using 2D NMR (HMQC), since its spectrum was much simpler than that of poly(BF-a). However, it is also difficult from the ¹H NMR spectrum to estimate the contents of the addition modes in the radical polymerization. The ¹³C NMR measurements then revealed that the contents of the 1,2- and 1,4-units of poly(BF-r) were 9 and 91%, respectively. Similar to the anionic polymerization, BF acted as a polymerizable 1,3diene derivative during the course of the radical polymerization.

We next attempted to polymerize BF with boron trifluoride etherate (BF₃OEt₂) (8.0 mol %) at 0 °C in CH₂Cl₂ for 48 h (Table 5, run 38). The reaction mixture showed a black color during the reaction and was quenched with degassed methanol. However, no polymeric product was obtained and only BF was recovered from the reaction system. We then increased the amount of BF₃OEt₂ to 37 mol % and reacted BF at 0 °C in CH₂Cl₂ for 4 h (run 39). In this case, the polymerization of BF managed to proceed, and the conversion of BF reached 46%. After 24 h, BF was completely consumed, and a quantitative yield of a polymeric product was obtained (run 40). Thus, the cationic polymerization of BF with BF₃OEt₂ at 0 °C slowly proceeded, while the anionic polymerization was completed within 10 min even at -78 °C in THF. This cationically obtained polymer, poly(BF-c), possessed a molecular weight around 15 000 and a broad MWD ($M_w/M_n = 3.18$). More interestingly, the poly(BF-c) showed a ¹H NMR spectrum significantly different from those of poly(BF-a) and poly(BF-r), as can be seen in Figure 4C. In fact, it was very difficult to estimate the microstructure of the poly(BF-c) based on the ¹³C NMR spectrum due to the broadness of the spectra, as shown in Figure S1. However, it was obvious that the microstructure of poly(BF-c) differed from those of poly(BF-a) and poly(BFr). Under the cationic conditions, some possible side reactions related to the aromatic ring might occur along with the normal propagation of the exo-methylene group of BF. Thus, the observed polymerizability of BF toward the cationic initiator was remarkably low, although the propagation barely occurred to form a polymer. This observation is reasonable, since BF presents a very high anionic polymerizability as discussed above.

initiator, sec-BuLi. The T_g value of poly(BF-a) increased with the increasing molecular weight and reached 164 °C ($M_{\rm n}$ = 31 000). The T_{σ} value of poly(BF-a-Bz) similarly increased to 150 °C in the sample with the highest molecular weight. In the case of the poly(BF-r)s, the T_{σ} values were observed at around 145 °C, slightly lower than those of poly(BF-a-Bz). The T_{σ} values of poly(BF-a-Bz) and poly(BF-r) were always lower than that of poly(BF-a), even if the former ones possessed molecular weights higher than poly(BF-a). Thus, the order of the T_g values of poly(BF) was estimated as follows: poly(BF-a) > poly(BF-a-Bz) > poly(BF-r). Therefore, the T_g values tend to increase with the contents of the 1,2-structure, indicating the effect of the rigid indene ring perpendicular to the polymer main chain. This observation suggests that the movement of the polymer main chain in the 1,2-addition mode is more restricted compared to the repeating units consisting of the 1,4-addition mode.

CONCLUSIONS

We have succeeded in the anionic, free-radical, and cationic polymerizations of a hydrocarbon monomer, BF, possessing a fixed transoid 1,3-diene framework in the molecule. In particular, BF readily undergoes the living anionic polymerizations in the 1,2- and 1,4-addition modes to afford polymers with tailored chain lengths. Based on the results of the homopolymerization and sequential block copolymerization, the high anionic polymerizability of BF, comparable to those of the methacrylates, is clearly demonstrated. BF can be polymerized with various anionic initiators showing a low nucleophilicity, including the bulky π -conjugated diphenylmethyl and triphenylmethyl anions, Grignard reagents, alkoxides, and ester enolates derived from methacrylates. On the other hand, a propagating indenyl anion showing a low nucleophilicity was formed from BF during the course of the polymerization. The observed high anionic polymerizability of the exo-methylene-type BF can be explained by the conformation, the bond angle, and the electron density determined by the DFT calculation by comparing these values of 2PB and clearly breaks the conventional image of hydrocarbon monomers showing low anionic polymerizabilities. The polarized planar fulvene framework in BF might induce the remarkable anionic polymerizability as a new class of hydrocarbon monomers.

EXPERIMENTAL SECTION

Materials. All reagents were purchased from Tokyo Chemical Industry (TCI) Co., Ltd., unless otherwise stated. Indene, tBuOK, and n-BuLi (2.6 M in hexane, Kanto Chemical Co., Inc.) were used without purification. Paraformaldehyde was dried under vacuum condition over P2O5 overnight. THF was refluxed over sodium for 3 h and distilled from LiAlH4 under nitrogen. THF used as a polymerization solvent was further purified by the distillation from sodium naphthalenide solution on a vacuum line. LiCl was dried in vacuo for 2 days and used as a THF solution. 2PB^{5a} and 4CNSt¹⁸ were synthesized and purified according to the previous report. DPE was distilled from CaH₂ under reduced pressure and then distilled in the presence of 1,1-diphenylhexyllithium on a vacuum line. Styrene was distilled over CaH2 under reduced pressure and finally distilled over dibutylmagnesium on the vacuum line. 2VP was distilled over CaH₂ under reduced pressure and finally distilled over CaH2 on the vacuum line. MMA and tBMA were distilled over CaH2 under reduced pressure and finally distilled over $(C_8H_{17})_3Al$ on the vacuum line. TMEDA and 18-crown-6 were distilled over CaH₂ under reduced pressure and diluted with THF.

Initiators. Commercially available sec-BuLi (1.0 M in cyclohexane, Kanto Chemical Co., Inc.) was used without purification and diluted with dry *n*-heptane. K-Naph was prepared by the reaction of a small excess molar quantity of naphthalene with potassium in THF. Ph2CHLi, Ph2CHNa, Ph2CHK, and Ph2CHCs were synthesized by the reaction of corresponding metal naphthalenides and 1.5-fold diphenylmethane in dry THF under argon at room temperature for 48 h. Ph₃CLi and Ph₃CK were synthesized by the reaction of corresponding alkali metal and triphenylmethane in dry THF under argon at room temperature for 48 h. These initiators were sealed off under high-vacuum conditions in ampules equipped with break-seals and stored at -30 °C. The concentration of initiator was determined by colorimetric titration using standardized 1-octanol in THF in a sealed reactor under vacuum, as previously reported.²¹ BzMgCl was prepared by the reaction of benzyl chloride and magnesium in THF. AIBN for radical polymerization was purified by recrystallization from ethanol. BF₃OEt₂ was distilled in the presence of CaH₂ on a vacuum line and then diluted with CH₂Cl₂.

Synthesis of BF. A solution of n-BuLi (2.60 M, 66.0 mL, 172 mmol) was added dropwise to a solution of indene (19.9 g, 171 mmol) in dry THF (400 mL) at 0 °C under nitrogen. The reaction mixture was stirred at 0 °C for 5 min. Then, paraformaldehyde (5.61 g, 187 mmol) was added to the mixture in one portion at 0 °C. The reaction mixture was stirred at 0 °C for 3 min and at rt for 5 min. The reaction mixture was quenched with aqueous solution of NaHCO₃. The layers were separated, and the aqueous layer was extracted with diethyl ether three times. Then, the combined organic layer was washed with aqueous solution of NaCl twice and water once and then dried over anhydrous MgSO4. MgSO4 was removed by filtration, and the filtrate was concentrated in vacuo. The residual liquid was purified by flash column chromatography (silica gel, hexane/ethyl acetate) to give a mixture of hydroxymethylindenes (16.0 g, 109 mmol, 64%), including 15% of 1-hydroxymethylindene (1HMI) and 85% of isomeric 3-hydroxymethylindene (3HMI). The resulting mixture of 1HMI and 3HMI was used for the following dehydration without further purification.

The mixture of 1HMI and 3HMI (16.0 g, 109 mmol) in dry methanol (150 mL) was added to a solution of tBuOK (13.4 g, 120 mmol) in dry methanol (200 mL) at 0 $^\circ\text{C}.$ The reaction mixture was stirred at 40 °C for 30 min. The mixture was then cooled to room temperature and was added to ice water to quench the reaction. Then, the mixture was extracted with hexane three times. The combined organic phase was washed with water twice and dried over anhydrous MgSO₄. MgSO₄ was removed by filtration, and the filtrate was concentrated in vacuo. The residual liquid was purified by flash column chromatography (silica gel, hexane) to give BF as yellow solid (5.53 g, 43.2 mmol, 40%, mp ~80 °C (polymerized)). ¹H NMR (CDCl₃): δ = 5.73 and 6.07 (2s, 2H, CH₂=), 6.50 (d, J = 5.46 Hz, 1H, H_b), 6.87 (d, J = 5.46 Hz, 1H, H_c), 7.16–7.28 (m, 3H, H_e, H_f, H_g), 7.58 (d, 1H, H_h, J = 7.16 Hz). ¹³C NMR (CDCl₃): $\delta = 114.1$ (CH₂=), 119.8 (C_h), 120.9, 125.3, 128.1 (C_e , C_f , C_g), 129.8 (C_b), 133.4 (C_c), 135.9 (C_i), 143.5 (C_d), 147.6 (C_a).



Purification of BF. After flash column chromatography (silica gel, hexane), solidified BF was degassed and sealed off in an all-glass apparatus equipped with a break-seal in the presence of CaH₂. The sealed BF was immediately dissolved in dry THF. The monomer solution in THF was distilled from CaH₂ on the vacuum line into an ampule fitted with a break-seal and immediately diluted with dry THF. The resulting yellow monomer solution (0.3–0.7 M) was stored at -30 °C until ready to use for the anionic polymerization.

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Anionic Polymerization. All anionic polymerizations were carried out in dry THF at -78 °C in an all-glass apparatus equipped with break-seals under high-vacuum conditions (10^{-6} mmHg) .²¹ The polymerization was terminated with degassed methanol. The polymer was precipitated by pouring the reaction mixture in methanol, and the precipitated polymer was recovered by filtration. The resulting polymer was purified by freeze-drying from benzene and characterized by ¹H and ¹³C NMR spectroscopies.

Block Copolymerization of BF and MMA. The anionic copolymerization of MMA and BF was carried out in an all glassapparatus equipped with break-seals under high-vacuum conditions similar to the homopolymerization. Typical procedure of sequential copolymerization was as follows: MMA (0.544 g, 5.44 mmol) in THF (5.20 mL) was added to a mixture of sec-BuLi (0.115 mmol) in nheptane (3.05 mL) and DPE (0.210 mmol) in THF (4.75 mL) at -78 °C and reacted for 10 min. The color of initiator system changed immediately from red to colorless, indicating the rapid initiation of MMA. Then, LiCl (0.0800 M, 0.400 mmol) in THF (5.00 mL) was successively added to the resulting living poly(MMA) at -78 °C. After 10 min, a THF solution (12.7 mL) of BF (1.08 g, 8.45 mmol) was finally added to the living poly(MMA) at -78 °C. The color of polymerization system instantaneously changed from colorless to orange, indicating the formation of indenyl anion derived from BF. The polymerization of BF was continued for 1 h at -78 °C and quenched with degassed methanol. The reaction mixture was poured into methanol to precipitate a polymer. The yield of poly(MMA)-bpoly(BF) was almost quantitative (1.60 g, 100%, $M_{\rm n}$ = 22 000, $M_{\rm w}/M_{\rm n}$ = 1.09. Table 4. run 31).

Radical Polymerization. BF (3.71 g, 28.9 mmol) and AIBN (40.0 mg, 0.244 mmol) were dissolved in benzene (20 mL) in a two-neck flask. After three freeze—thaw cycles under vacuum, the solution was heated at 70 °C for 6 h under nitrogen. After cooling to room temperature, the reaction mixture was poured into methanol to precipitate a poly(BF-r) (3.58 g, 96% yield, $M_{n,RALLS} = 33\ 000$, $M_w/M_n = 4.63$).

Cationic Polymerization. BF (0.56 g, 4.38 mmol) in dichloromethane (10 mL) was added to BF₃OEt₂ (0.266 g, 1.87 mmol) in CH₂Cl₂ in an all-glass apparatus at 0 °C. The solution was stirred at 0 °C for 24 h and quenched with degassed methanol. The reaction mixture was poured into methanol to precipitate a poly(BF-c). The yield of polymer was almost quantitative (0.55 g, 98%, $M_{\rm n}$ = 15 000, $M_{\rm w}/M_{\rm n}$ = 3.18).

Measurements. ¹H and ¹³C NMR spectra were measured on a Bruker DPX300 in CDCl₃. Chemical shifts were recorded in ppm downfield relative to CHCl₃ (δ 7.26) and CDCl₃ (δ 77.1) for ¹H and ¹³C NMR as standard, respectively. Size exclusion chromatogram (SEC) curves for determination of $M_{\rm w}/M_{\rm p}$ were obtained in THF at 40 °C at flow rate of 1.0 mL min⁻¹ with a Viscotek TDA302 equipped with three polystyrene gel columns (TSKgelG5000H_{HR} + G4000H_{HR} + $G3000H_{HR}$). The combination of viscometer, right angle laser light scattering detection (RALLS), and refractive index (RI) detection was applied for the online SEC system in order to determine the absolute molecular weights of homopolymer and block copolymer. The T_{gs} of the polymers were measured by DSC using a Seiko Instruments DSC6220 apparatus under nitrogen flow. The polymer sample was first heated to 120 °C, cooled to 30 °C, and then scanned at a rate of 10 °C min⁻¹. The ground state geometries were fully optimized by using density functional theory (DFT) calculations, long-range and dispersion corrected ω B97X-D¹¹ functional with the polarized splitvalence triple zeta 6-311G(d,p) basis set,^{12,13} denoted as $\omega B97X-D/6$ -311G(d,p). Then, the vibrational frequencies were computed at the same level to check each optimized structure as an equilibrium structure. All calculations were carried out using the Gaussian 09 program.¹⁴ Natural charges were obtained by using the NBO 6.0 program.¹⁵

ASSOCIATED CONTENT

S Supporting Information

Figure S1; Tables S1 and S2. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b00944.

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Notes

The authors declare no competing financial interest.

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