Synthesis of Novel Block Copolymers Comprised of Polyisobutylene and Poly(vinylferrocene) Segments

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Received April 17, 2007; Revised Manuscript Received July 16, 2007

ABSTRACT: Well-defined poly(vinylferrocene)s with predictable molecular weights and low polydispersities were prepared by living anionic polymerization of vinylferrocene initiated with ^{n}BuLi in tetrahydrofuran (THF) at −28 °C as well as 0 °C. The living poly(vinylferrocenyl)lithium (PVFcLi) was first employed in coupling reactions with haloallyl chain-end functionalized polyisobutylene (PIB) series. By using bromoallyl chain-end functionalized PIB, the coupling proceeded in THF at 0 °C to afford a new AB diblock copolymer comprised of PIB and PVFc segments with high coupling efficiency (∼85%) limited by undesired lithium-halogen exchange. The synthesis of an ABA triblock copolymer, PVFc-*b*-PIB-*b*-PVFc, was also attempted by coupling of α,ω-bromoallyl difunctionalized PIB and PVFcLi; however, lithium-halogen exchange yielded a significant amount of byproducts. In contrast, PIB-*b*-PVFc and PVFc-*b*-PIB-*b*-PVFc with excellent coupling efficiencies (>94%) could be successfully synthesized by using chlorosilyl chain-end functionalized PIB in coupling reactions with PVFcLi. The polymers were characterized by gel permeation chromatography (GPC)−multiangle laser light scattering (MALLS) and proton nuclear magnetic resonance (^{1}H NMR) analyses. The differential scanning calorimetry (DSC) thermogram of PVFc-*b*-PIB-*b*-PVFc showed two glass transition temperatures at −65 and 198 °C, suggesting microphase-separated morphology. Transmission electron microscopy (TEM) corroborated the typical disordered spherical morphology of a PVFc-*b*-PIB-*b*-PVFc thin film. The stress−strain plot of a solution cast sample of PVFc-*b*-PIB-*b*-PVFc showed typical elastomeric property.

Introduction

Since metal-containing polymers have emerged as an important class of polymers in the past 30 years, a large number of ferrocene and other metal-containing polymers have been prepared and reviewed so far.[1,2] Poly(vinylferrocene) (PVFc) is of special interest among them because of its thermal stability (400 °C), high glass transition temperature (T_g = 190−220 °C), high ultraviolet and γ-radiation absorbability, inertness to air, semiconductivity after doping, and redox activity. Particularly, polymer−ferrocene conjugates exhibit high antiproliferative activity, which may suppress proliferation and migration of cells as inflammatory responses. In addition, these conjugates show low in-vivo toxicity that can possibly be exploited for many biomedical applications.[3]

PVFcs with molecular weights (MWs) ranging from 1000 to 200 000 were first accomplished by radical polymerizations of vinylferrocene (VFc) initiated with azobis(isobutyronitrile).[4−6] Copolymerizations of VFc with styrene,[5] methyl (meth)acrylate,[5] acrylonitrile,[5] and *N*-vinyl-2-pyrrolidone[6] have also been demonstrated; however, higher molecular weight (MW) products possessed broad and multimodal molecular weight distributions. The cationic polymerization of VFc was conducted with a series of boron trifluoride−diethyl etherate, titanium(IV) chloride, tin(IV) chloride, aluminum chloride, ethylaluminum dichloride−*tert*-butyl chloride (1:1), and diethylaluminum chloride−*tert*-butyl chloride (1:1) as initiators to obtain PVFcs with relatively low MWs (<3500) reported by Aso et al.[7] In the early 1990s, the living anionic polymerization of VFc was achieved in tetrahydrofuran (THF) at −70 to 0 °C using *n*- and *sec*-butyllithium where the MWs could be controlled by the feed ratio of monomer to initiator up to around 12 000, keeping the polydispersity indices (PDI = M_w/M_n) less than 1.3.[8] Based on the successful homopolymerization of VFc, an array of PVFc-*b*-polystyrene (PS)-*b*-PVFc, PVFc-*b*-PS, PVFc-*b*-poly(methyl methacrylate) (PMMA), and PVFc-*b*-poly(propylene sulfide) could be synthesized. Durkee et al. reported the synthesis of PVFc-*b*-polyisoprene by sequential anionic polymerization of VFc and isoprene.[9] Recently, Manners and coworkers employed cyclic monomers of ferrocenophanes for the anionic ring-opening polymerization affording poly(ferrocenylsilane)[10] and poly(ferrocenylphosphine)[11] bearing iron in the main chains. A number of morphological studies have been reviewed with a wide variety of block copolymers with those polymer segments.[2] In contrast, there are relatively few examples of block copolymers comprised of PVFc segments despite the commercial availability of VFc. PVFc is structurally different from polyferrocenophanes since PVFc bears pendant Fc molecules arranged in side chains. Additionally, main chains of PVFcs are much stiffer than those of polyferrocenophanes which possess soft silicone or phosphine linkages in main chains.

Block copolymers containing immiscible segments phase separate in the solid state. The resulting self-assembled materials are ordered on the nanometer scale and are of considerable current interest for applications in nanolithography, electronic devices, and drug delivery systems. Particularly ABA triblock copolymers with outer hard (A) and middle soft (B) segments can be employed as thermoplastic elastomers (TPEs) in addition to aforementioned potential applications. In order to obtain strong TPEs, it is necessary to anchor the ends of the middle rubber segment with glassy blocks. Many common TPEs were derived from styrenic block copolymers with polydiene segments based on anionic polymerization. In the past decade, various new ABA triblock TPEs with a saturated and therefore highly stable polyisobutylene (PIB) middle segment have been prepared. Following the successful synthesis of PS-*b*-PIB-*b*-

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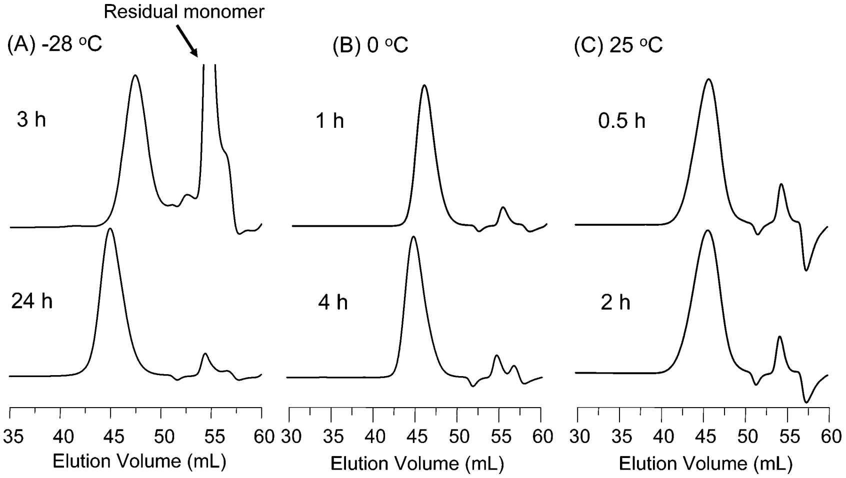


Figure 1. Gel permeation chromatography refractive index traces of poly(vinylferrocene)s obtained in tetrahydrofuran at (A) −28 °C, 3 and 24 h, (B) 0 °C, 1 and 4 h, and (C) 25 °C, 0.5 and 2 h.

Table 1. Anionic Polymerization of Vinylferrocene with *n*-Butyllithium in Tetrahydrofuran

			M_n				
temp (°C)	time (h)	conv (%)[a]	calcd[b]	GPC-MALLS[c]	^{1}H NMR	PDI	fn[d]
−28	3	59	3060	2500		1.15	
−28	24	95	4930	4850		1.10	
0	1	89	4310	4510		1.14	
0	4	98	4750	4830	4810	1.10	1.00
0	4	75	9260	9350		1.22	
0	8	88	10900	12400	12700	1.19	0.98
0	14	90	17500	18600[e]	20600	1.35	0.90
25	0.5	73	3600	4280		1.19	
25	2	69	3420	4000	4960	1.16	0.81

[a] Determined from ^{1}H NMR by comparing the signal intensities at 5.02, 5.35, and 6.48 ppm for the residual VFc and ones at 0.80−2.70 ppm for PVFc prepared. [b] Calculated from the equation $M_n(\text{calcd}) = 57.1\ (C_4H_9) + 212.07\ (\text{VFc}) \times [\text{VFc}]/[^n\text{BuLi}] \times \text{conv} + X\ (X = 1\ (\text{H})\ \text{or}\ 73.09\ (\text{TMS}))$. [c] $dn/dc = 0.248$. [d] TMS chain-end functionality determined by comparing the intensities of the resonances for ferrocene molecules (0.80−2.70 ppm) and those for TMS group (0.20−0.40 ppm), taking into account the degree of polymerization determined by GPC-MALLS. [e] There is a side peak (20%) at very high molecular weight region (>1 m) probably due to the aggregation of multiple PVFc chains. The datum was obtained by excluding that peak.

PS (SIBS) by living cationic sequential block copolymerization,[12] new TPEs where styrene was replaced with other styrenic monomers such as *p*-chlorostyrene,[13] *p*-*tert*-butylstyrene,[14] indene,[15] and *p*-hydroxystyrene[16] were synthesized. Another series of TPEs with *tert*-butyl vinyl ether,[17] poly(cyclohexyl vinyl ether),[18] and poly(cyclohexyl vinyl ether-*stat*-vinyl alcohol) segments[19] was also accomplished on the basis of living cationic copolymerization by our group. In addition, mechanistic transformations combining cationic polymerization with other living polymerization techniques were successfully applied to include poly(L-lactide),[20] poly(pivalolactone),[21] poly(ϵ-caprolactone),[22] and poly(isobornyl acrylate)[23] segments. Since the first report on the synthesis of poly(methyl methacrylate) (PMMA)-*b*-PIB-*b*-PMMA triblock TPEs by the combination of living cationic and anionic polymerizations based on 1,1-diphenylethylene (DPE) chemistry by Müller and co-workers,[24] the synthesis of a series of poly(2-hydroxyethyl methacrylate) (PHEMA)-*b*-PIB-*b*-PHEMA and (PMMA-*co*-PHEMA)-*b*-PIB-*b*-(PMMA-*co*-PHEMA) has been accomplished by our group.[25] We recently have demonstrated a novel concept in which a bromoallyl chain-end functionalized PIB could be coupled with living PMMA anion to prepare the similar block copolymers.[26]

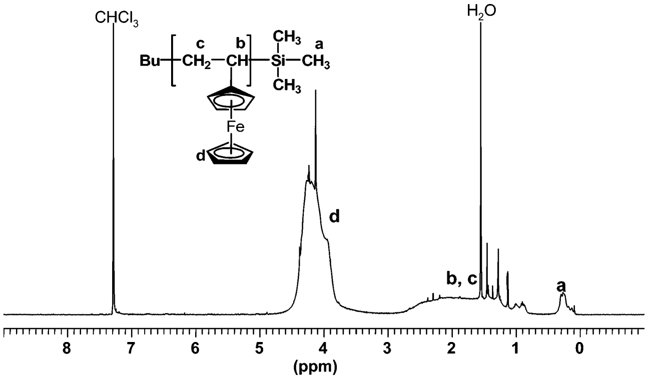


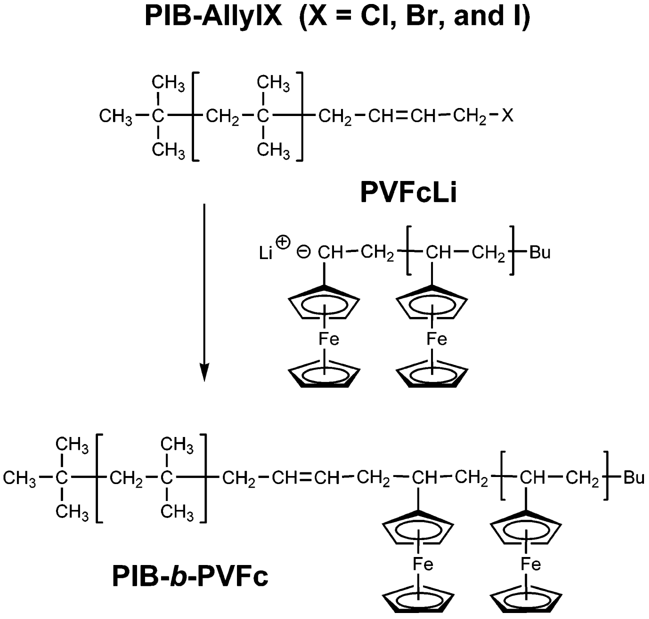
Figure 2. ^{1}H NMR spectrum of poly(vinylferrocene) obtained in tetrahydrofuran at 0 °C for 4 h.

Herein we report on the living anionic polymerization of VFc and the first synthesis of novel AB diblock and ABA triblock copolymers comprised of PVFc (A) and PIB (B) segments by the coupling reaction of living PVFc anion with a haloallyl or chlorosilyl chain-end functionalized PIB following our previously developed concept for the combination of living cationic and anionic polymerizations.

Experimental Section

Materials. All reagents were purchased from Sigma-Aldrich Corp. (>99%) unless otherwise stated. Hexanes (Hex, Doe & Ingals, Technical grade) were refluxed for 48 h with concentrated sulfuric acid. They were washed three times with 10% sodium hydroxide aqueous solution (NaOH(aq)) and then with distilled water several times until neutral. After drying overnight over anhydrous sodium sulfate, they were refluxed under nitrogen overnight with calcium hydride (CaH_2) and distilled. For the anionic polymerization use, they were finally distilled over 1,1-diphenylhexyllithium (DPH-Li) on a vacuum line (10^{-6} Torr). Acetone (Doe & Ingals, Technical grade) and methanol (Doe & Ingals, Technical grade) were purified by the distillation over potassium carbonate and activated magnesium, respectively. Toluene (99%) was sequentially washed with concentrated sulfuric acid twice, 10% NaOH(aq) once, and then with distilled water twice. After drying over calcium chloride and phosphorus pentoxide, it was refluxed over lithium aluminum hydride (LAH) under nitrogen and then distilled. Final distillation over DPH-Li on the vacuum line afforded pure dry toluene. Anhydrous tetrahydrofuran (99.9%) was refluxed over LAH for 24 h under nitrogen and distilled. It was finally dried by the distillation over DPH-Li on the vacuum line. *n*-Butyllithium (^{n}-BuLi, FMC Lithium, 15 wt % solution in hexane) was used as received or after diluting with dry hexanes. The active concentration

Scheme 1. Synthesis of Poly(isobutylene-*b*-vinylferrocene) by the Coupling Reaction of Haloallyl Chain-End Functionalized Polyisobutylene with Poly(vinylferrocenyl)lithium



of a ^{n}BuLi solution was determined by the polymerization of styrene. Vinylferrocene (VFc, 97%) was purified by double sublimation, followed by the azeotropic distillation of a trace amount of water from its dry toluene solution three times. Chlorotrimethylsilane (TMS-Cl, 99+%) and chlorodimethylsilane (DMS-Cl, 98%) were stirred with CaH_2 at 25 °C for 24 h and then distilled under high vacuum. Methyl chloride (MeCl, Airgas Inc., >99.5%) and isobutylene (IB, Matheson Tri Gas, >99%) were dried in the gaseous state by passing them through in-line gas-purifier columns packed with barium oxide/drierite. Titanium(IV) chloride ($TiCl_4$, 99.9%), 2,6-di-*tert*-butylpyridine (DTBP, 97%), 1,3-butadiene (99+%), lithium bromide (LiBr, anhydrous, ≥99%), sodium iodide (NaI, anhydrous, ≥99%), benzene (anhydrous, 99.8%), 2-butanone (≥99%), and Karstedt's catalyst, $Pt_2[CH_2{=}CHSi(CH_3)_2OSi(CH_3)_2{-}CH{=}CH_2]$, 2.1−2.4% in xylene (Gelest) were used as received. 5-*tert*-Butyl-1,3-bis(1-chloro-1-methylethyl)benzene (^{t}BuDicumyl-Cl) was synthesized according to the procedure described elsewhere.[27] Chloroallyl,[28] bromoallyl,[26] and allyl[29] chain-end functionalized PIBs (PIB-AllylCl, PIB-AllylBr, and PIB-Allyl) and α,ω-allyl difunctionalized PIB (Allyl-PIB-Allyl)[29] were synthesized as described elsewhere and purified by the precipitation with hexanes/methanol twice, followed by the azeotropic distillation with dry toluene three times.

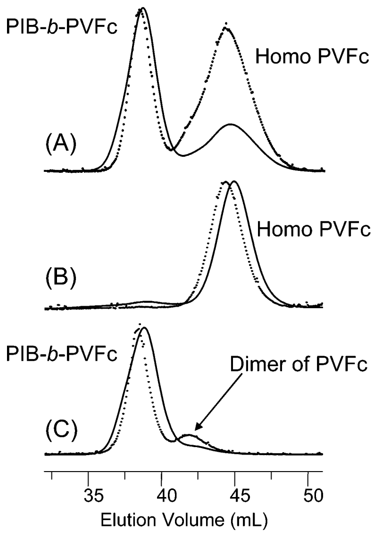


Figure 3. Gel permeation chromatography traces of (A) the product obtained by the coupling reaction of bromoallyl chain-end functionalized polyisobutylene with poly(vinylferrocenyl)lithium at 0 °C for 16 h, (B) the soluble part in tetrahydrofuran/2-butanone (1/4, v/v), and (C) the insoluble part in tetrahydrofuran/2-butanone (1/4, v/v); solid line, refractive index; dotted line, UV.

Table 2. Coupling Reaction of Haloallyl Chain-End Functionalized Polyisobutylene with Poly(vinylferrocenyl)lithium in Tetrahydrofuran[a]

			homo poly(vinylferrocene)		after coupling reaction		
						CE (%)[c]	
halogen	temp (°C)	time (h)	M_n GPC-MALLS	PDI	M_n[b] high M_n/low M_n	UV	^{1}H NMR[d]
Cl	0	16	6220	1.17	17100/6030	25	28
Br	−78	24	3600	1.08	17400/3800	8	10
Br	−20	40	4350	1.09	19900/4200	90	81[e]
Br	0	1	4130	1.11	19200/4030	65	73
Br	0	16	4130	1.11	19600/3920	91	85[e]
I	0	16	4050	1.10	multimodal	12	

[a] The M_ns of PIB-AllylX (X = Cl, Br, and I) are 15 900, 15 600, and 16 000, respectively. [b] Determined from GPC-MALLS. [c] Coupling efficiency. [d] Determined by comparing the signal intensities of the methine protons of the unreacted PIB-AllylX and ones at 4.05−3.80 ppm assignable to the cyclopentadienyl protons of the PVFc main chains, assuming no lithium−halogen exchange. [e] Determined by the weight ratio of the fractions after isolation of PIB-*b*-PVFc and homo PVFc with THF/2-butanone mixture.

Living Anionic Polymerization of Vinylferrocene. Vinylferrocene (VFc) was polymerized in THF at −28, 0, or 25 °C with ^{n}BuLi under a high-vacuum condition ($<10^{-6}$ Torr) in sealed glass reactors with break-seals. The reactors were prewashed with a DPH-Li solution in hexanes after being sealed off from the vacuum line. [^{n}BuLi] and [VFc] were in the range 0.003 90−0.008 90 M and 0.185−0.25 M, respectively. The polymerizations were quenched with degassed methanol or excess TMS-Cl. In a practical experiment, a hexane solution of ^{n}BuLi (0.005 77 M × 1.54 mL = 0.0889 mmol) was placed in an apparatus under high vacuum, and then hexane was completely removed in vacuo. A stock solution of VFc (0.198 M × 10.0 mL = 1.98 mmol, 0.420 g) in THF was next added at 0 °C to start the polymerization. Half of the solution was taken out by heat-sealing and then quenched with TMS-Cl (0.200 mmol) in hexanes (1.25 mL). The remainder was allowed to stand for an additional 3 h and then quenched with TMS-Cl (0.200 mmol) in hexanes (1.25 mL). After quenching, a few drops of pyridine/methanol (50/50, v/v) mixture were immediately added to neutralize the solution. The solutions were filtered to remove the insoluble part (<1 wt %). The polymers were isolated by precipitating from their THF solution into methanol (THF/methanol = 1/4, v/v), followed by freeze-drying with benzene to yield yellow powders. Conversions: 89% (1 h) and 98% (4 h) by ^{1}H NMR. Yields: 0.174 g, 83% (1 h) and 0.193 g, 92% (4 h). M_n (calcd) = 4750, M_n (GPC-MALLS) = 4830 (1 h) and M_n (calcd) = 4310, M_n (GPC-MALLS) = 4510 (4 h). ^{1}H NMR ($CDCl_3$): δ 4.50−3.80 (br, ferrocenyl-H), 2.70−0.80 (br, CH_2 and CH), 0.40−0.19 (br, 9H, $Si(CH_3)_3$).

Synthesis of Iodoallyl Chain-End Functionalized PIB (PIB-AllylI). In a two-necked round-bottomed flask, well-dried PIB-AllylCl (M_n = 15 900, PDI = 1.07, 2.84 g, 0.178 mmol, chloroallyl functionality = 1.00), anhydrous NaI (5.34 g, 35.7 mmol), dry toluene (117 mL), and dry acetone (63 mL) were placed and refluxed with stirring. After 12 h, the solution was cooled to room temperature. Then, the solvent was evaporated under reduced pressure. Excess NaI was removed by reprecipitations using hexanes/methanol three times. The polymer was finally purified by silica gel flash column chromatography using hexanes as an eluent, followed by the azeotropic distillation with dry toluene three times. The conversion was 100% by the fact that the characteristic signal at 4.05 ppm assignable to the two methylene protons of the chloroallyl group completely disappeared, while a new signal at 3.90 ppm assignable to ones of the iodoallyl group appeared in the ^{1}H NMR spectrum. Yield: 2.71 g, 95%. GPC-MALLS: M_n = 16 000, PDI = 1.08, monomodal. ^{1}H NMR ($CDCl_3$): δ 5.80−5.67

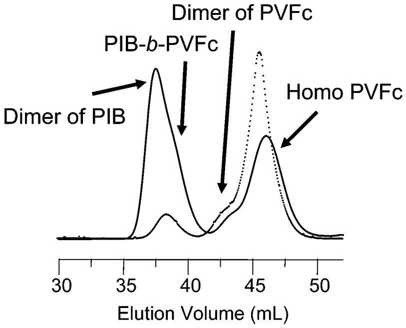


Figure 4. Gel permeation chromatography traces of the product obtained by the coupling reaction of iodoallyl chain-end functionalized polyisobutylene with poly(vinylferrocenyl)lithium at 0 °C for 16 h: solid line, refractive index; dotted line, UV.

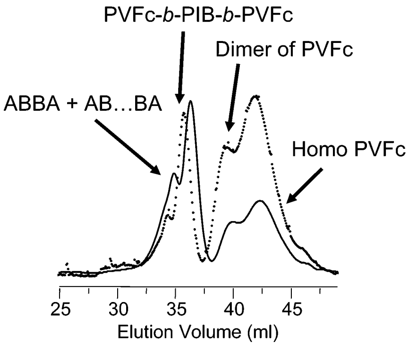


Figure 5. Gel permeation chromatography traces of the product obtained by the coupling reaction of α,ω-bromoallyl difunctionalized polyisobutylene with poly(vinylferrocenyl)lithium at 0 °C for 24 h: solid line, refractive index; dotted line, UV.

(pp, 2H, CH═CH), 3.90 (d, 2H, CH_2I), 2.00 (d, 2H, $C(CH_3)_2CH_2$-CH═), 1.50−1.30 (br, 556H, CH_2), 1.20−0.90 (br, 1677H, CH_3). Iodoallyl functionality = ∼1.0.

Coupling Reaction of Haloallyl Chain-End Functionalized PIB (PIB-AllylX) with Poly(vinylferrocenyl)lithium (PVFcLi). The title reactions were carried out in THF at −78, −20, or 0 °C under a high-vacuum condition in a sealed glass reactor with break-seals. A typical experiment is as follows: An apparatus equipped with the ampules of stock solutions, ^{n}BuLi in hexane, VFc in THF, PIB-AllylBr in THF, and TMS-Cl in hexanes, was washed with DPH-Li in hexanes solution. After the washing solution was discarded, ^{n}BuLi (0.0714 mmol) in hexane was charged in the apparatus. Hexane was completely removed in vacuo, and then a THF stock solution (8.0 mL) of VFc (0.26 g, 1.23 mmol) was added at once with stirring at 0 °C. The solution was allowed to stand at 0 °C for 4 h. After a 20% portion of the solution was taken out by heat-sealing for characterizations, the THF stock solution (5.0 mL) of PIB-AllylBr (M_n = 15 600, PDI = 1.07, 0.37 g, 0.0237 mmol, bromoallyl functionality = 1.00) was added to the rest and divided into two portions by heat-sealing. After 1 or 16 h, the solutions were separately quenched with excess TMS-Cl (0.20 mmol). The concentrations are as follows: [^{n}BuLi] = 0.009 83 M and [VFc] = 0.154 M for the polymerization, [PVFcLi] = 0.004 49 M determined from M_n (GPC-MALLS) and the amount of VFc consumed, and [PIB-AllylBr] = 0.002 08 M for the coupling reaction. A few drops of pyridine/methanol (50/50, v/v) mixture were immediately added, and then the solutions were filtered to remove the insoluble part (<1 wt %). The polymer mixtures in THF were precipitated in methanol (THF/methanol = 1/4, v/v), followed by freeze-drying from their benzene solutions overnight to yield yellow viscous products. Polymer mixture yields: 0.64 g, 94% (1 h) and 0.63 g, 93% (16 h). ^{1}H NMR ($CDCl_3$) for PIB-*b*-PVFc after fractional precipitation: δ 5.70−5.40 (br, 2H, CH_2CH═$CHCH_2CH$), 4.50−3.80 (br, ferrocenyl−H), 2.80−0.80 (br, CH_2 and CH).

Synthesis of α,ω-Bromoallyl Difunctionalized PIB (AllylBr-PIB-AllylBr). The precursor, α,ω-chloroallyl difunctionalized PIB (AllylCl-PIB-AllylCl), was first synthesized under a dry nitrogen atmosphere in an MBraun 150-M glovebox using Hex/MeCl (60/40, v/v) solvent mixture. The concentrations were as follows: [^{t}BuDicumylCl] = 0.001 M, [DTBP] = 0.004 M, [IB] = 0.625 M, [$TiCl_4$] = 0.036 M, and [1,3-butadiene] = 0.02 M. IB (312.5 mmol, 17.5 g), initiated by ^{t}BuDicumylCl (0.5 mmol) in conjunction with $TiCl_4$ (18 mmol), was polymerized at −80 °C for 1.5 h in the presence of DTBP (2 mmol) as a proton trap. Then, 1,3-butadiene (10 mmol) was added and allowed to cap at −80 °C for 5 h. After quenching with prechilled methanol (10 mL), the solution was poured in the ammonium hydroxide/methanol (1/9, v/v) mixture. The polymer was washed with water/2-propanol/sodium chloride (77.5/15/7.5, v/v/w) and precipitated from its hexanes solution into methanol, followed by drying under vacuum to afford AllylCl-PIB-AllylCl. GPC-MALLS: M_n = 35 100, PDI = 1.06, monomodal. ^{1}H NMR ($CDCl_3$): δ 7.20 (s, 3H, Ar), 5.85 (p, 2H, $C(CH_3)_2$-CH_2CH═), 5.62 (p, 2H, ═$CHCH_2Cl$), 4.05 (d, 4H, CH_2Cl), 2.03 (d, 4H, $C(CH_3)_2CH_2CH$═), 1.89 (s, 4H, $ArC(CH_3)_2CH_2$), 1.50−1.30 (br, 1237H, CH_2), 1.20−0.90 (br, 3732H, CH_3). Chloroallyl functionality = 2.00.

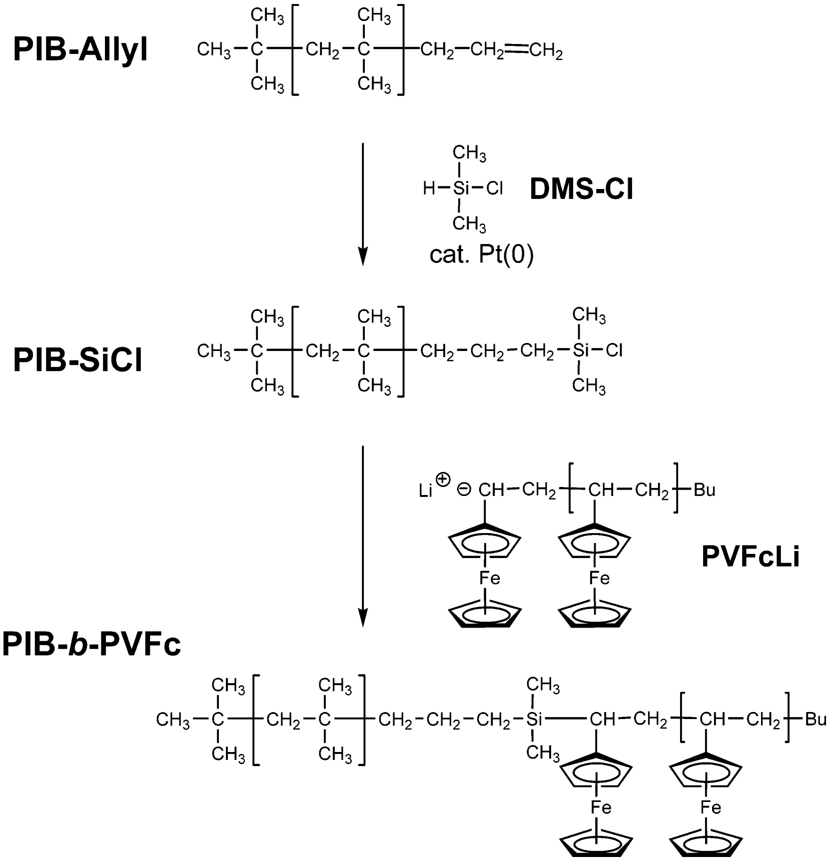
The polymer (0.142 mmol, 5.0 g) was next treated with anhydrous LiBr (114 mmol) in the toluene/acetone (65/35, v/v) mixture under nitrogen at 80 °C for 24 h. The polymer was washed with water three times and then purified by precipitation in methanol followed by silica gel flash column chromatography using hexanes as an eluent to afford AllylBr-PIB-AllylBr. Finally, azeotropic distillation from the absolute toluene solution of the polymer was performed three times to remove traces of water. GPC-MALLS: M_n = 35 200, PDI = 1.07, monomodal. ^{1}H NMR ($CDCl_3$): δ 7.20 (s, 3H, Ar), 5.85 (p, 2H, $C(CH_3)_2CH_2CH$═), 5.72 (p, 2H, ═$CHCH_2$-Br), 3.97 (d, 4H, CH_2Br), 2.05 (d, 4H, $C(CH_3)_2CH_2CH$═), 1.89 (s, 4H, $ArC(CH_3)_2CH_2$), 1.50−1.30 (br, 1225H, CH_2), 1.20−0.90 (br, 3696H, CH_3). Bromoallyl functionality = 1.98.

Coupling Reaction of AllylBr-PIB-AllylBr with PVFcLi. The title reaction was conducted in THF at 0 °C under a high-vacuum condition in a sealed glass reactor with break-seals. The procedure is similar to the coupling reaction of haloallyl monofunctionalized PIB (PIB-AllylX) series. The concentrations are as follows: [^{n}BuLi] = 0.00650 M, [VFc] = 0.267 M for the polymerization, [PVFcLi] = 0.00334 M, and [AllylBr-PIB-AllylBr] = 0.000713 M for the coupling reaction. Polymer mixture yield: 0.85 g, 90%.

Coupling Reaction of Chlorosilyl Chain-End Functionalized PIB (PIB-SiCl) with PVFcLi. In a typical experiment, well-dried allyl chain-end functionalized PIB (PIB-Allyl, M_n = 14 200, PDI = 1.06, 2.0 g, 0.141 mmol, allyl functionality = 1.00) was charged in an apparatus equipped with a break-seal under dry argon and dissolved in dry toluene (30 mL). 10 mL of toluene was removed by distillation together with a trace of moisture. Then, DMS-Cl (0.133 g, 1.41 mmol) was added to the solution followed by injecting Karstedt's catalyst, Pt(0), solution in xylene (100 ppm, ca. 10 μL). The solution was stirred at 95 °C for 3 h under argon. A portion (5%) of the solution was taken out for characterization. Toluene was discarded from the rest of the solution in vacuo, and the azeotropic distillation from dry toluene solution was repeated two times. After drying under high vacuum (10^{-6} Torr) for 24 h, chlorosilyl chain-end functionalized PIB (PIB-SiCl) was afforded. The apparatus was sealed off, and the polymer was subdivided through the break-seal after dissolving in dry hexanes for the later use. Yield: 1.89 g, 99%. GPC-MALLS: M_n = 14 200, PDI = 1.06, monomodal. ^{1}H NMR ($CDCl_3$): δ 3.48 (s, 3H, OCH_3), 1.50−1.30 (br, 502H, CH_2), 1.20−0.90 (br, 1515H, CH_3), 0.60 (t, 2H, −CH_2-Si), 0.13 (s, 6 H, $Si(CH_3)_2$). Chlorosilyl functionality = 1.00.

Subsequent coupling reaction was performed in THF at 0 °C under high vacuum in a sealed glass reactor with the ampules of stock solutions, ^{n}BuLi in hexane, VFc in THF, PIB-SiCl in hexanes, and TMS-Cl in hexanes, which were prewashed with DPH-Li in hexanes. After the washing solution was discarded, ^{n}BuLi (0.105 mmol) in hexane was charged in the apparatus. Hexane was completely removed under high vacuum, and then a THF stock

Scheme 2. Synthesis of Poly(isobutylene-*b*-vinylferrocene) by the Coupling Reaction of Chlorosilyl Chain-End Functionalized Polyisbutylene with Poly(vinylferrocenyl)lithium



solution (8.0 mL) of VFc (0.276 g, 1.30 mmol) was added with stirring at 0 °C. The solution was allowed to stand at 0 °C for 4 h. After 20% of the solution was taken out by heat-sealing for characterizations, the hexanes stock solution (5.0 mL) of PIB-SiCl (0.580 g, 0.0408 mmol) was added to the remaining solution. After 1 h, the system was quenched with degassed methanol (1.0 mL). The concentrations are as follows: [^{n}BuLi] = 0.0131 M and [VFc] = 0.163 M for the polymerization, [PVFcLi] = 0.00645 M, and [PIB-SiCl] = 0.003 58 M for the coupling reaction. The solution was filtered to remove the insoluble part (<1 wt %). The polymer mixtures in THF solution were precipitated in methanol (THF/methanol = 1/4, v/v), followed by freeze-drying from their benzene solution overnight to yield a yellow viscous product. Polymer mixture yield: 0.74 g, 93%. Isolation yield of PIB-*b*-PVFc after fractional precipitation using THF/2-butanone (1/4, v/v): 0.56 g, 80%. GPC-MALLS: M_n = 16 800, PDI = 1.04, monomodal. ^{1}H NMR ($CDCl_3$): δ 4.50−3.80 (br, 127H, ferrocenyl−H), 2.80−0.80 (br, 2059H, CH_2 and CH), 0.40−0.20 (br, 6H, $CH_2Si(CH_3)_2CH$).

Coupling Reaction of α,ω-Chlorosilyl Difunctionalized PIB (SiCl-PIB-SiCl) with PVFcLi. The procedure is similar to the coupling reaction of monofunctionalized PIB-SiCl. The concentrations are as follows: [^{n}BuLi] = 0.0118 M, [VFc] = 0.470 M for the polymerization, [PVFcLi] = 0.002 36 M, and [SiCl-PIB-SiCl] = 0.000 655 M for the coupling reaction. *SiCl-PIB-SiCl after treating with methanol*; yield: 3.0 g, 100%. GPC-MALLS: M_n = 38 600, PDI = 1.04, monomodal. ^{1}H NMR ($CDCl_3$): δ 7.20 (s, 3H, Ar), 3.48 (s, 3H, OCH_3), 1.89 (s, 4H, $ArC(CH_3)_2CH_2$), 1.50−1.30 (br, 1358H, CH_2), 1.20−0.90 (br, 4094H, CH_3), 0.60 (t, 2H, $-CH_2Si$), 0.13 (s, 6 H, $Si(CH_3)_2$). Chlorosilyl functionality = 2.00. *PVFc-b-PIB-b-PVFc after fractional precipitation using THF/2-butanone (1/1, v/v)*; isolation yield: 0.40 g, 73%. ^{1}H NMR ($CDCl_3$): δ 7.20 (s, 3H, Ar), 4.50−3.80 (br, 849H, ferrocenyl−H), 2.80−0.80 (br, 5735H, CH_3), 0.40−0.20 (br, 6H, $CH_2Si(CH_3)_2$-CH).

Measurements. MWs and PDIs were measured with a Waters HPLC system equipped with a model 510 HPLC pump, a model 410 differential refractometer (λ = 930 nm), a model 441 absorbance detector (λ = 254 nm), an online MALLS detector (MiniDawn, Wyatt Technology Inc., 120 V, three angles 45°, 90°, and 135°, λ = 690 nm), a model 712 sample processor, and five Ultrastyragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. THF was used as a carrier solvent at a flow rate of 1.0 mL/min at room temperature. MW and PDI data were calculated on the basis of MALLS and RI with the ASTRA 4.9 software (Wyatt Technology Inc.). The d*n*/d*c* = 0.248 value of PVFc (5 K) was measured by an Optilab DSP refractometer (Wyatt Technology Inc., λ = 690 nm) in THF at 35 °C using a batch mode. NMR spectroscopy was carried out on a Bruker 500 MHz spectrometer using $CDCl_3$ as a solvent. ^{1}H NMR spectra of solutions in $CDCl_3$ were calibrated to tetramethylsilane (TMS) as internal standard (δ_H 0.00). DSC was performed with a DuPont 2910 differential scanning calorimeter. The glass transition temperatures were taken as the onset point of specific heat jumps. The samples were heated at 20 °C/min under nitrogen, and the second thermograms were recorded. Calibrations were made using indium as a standard. TEM images were obtained using a Philips EM400T operated at 100 kV accelerating voltage. The thin film (<500 Å) was prepared by drop-casting onto a carbon-coated TEM copper grid from a chloroform solution (0.01 wt %), drying overnight at room temperature, and thermal annealing at 200 °C for 2 h. The tensile property was measured on a solution-cast film according to ASTMD638-02a (tensile bar dimensions; width: 3.6 mm; gage length: 18 mm) at room temperature. Crosshead speed was set at 0.85 cm/s. The average of four independent experiments was used. All experiments were reproducible within a small error (<5%). The film was prepared by dissolving the polymer in toluene (2.5 wt %), filtering with a Teflon membrane (0.45 μm), and drying very slowly in a Teflon mold for 7 days at room temperature to avoid bubbles in the film, followed by vacuum-drying for 2 days at room temperature. The film thickness was ~0.18 mm.

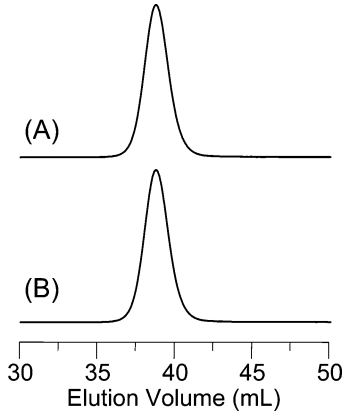


Figure 6. Gel permeation chromatography refractive index traces of (A) allyl chain-end functionalized polyisobutylene and (B) methoxysilyl chain-end functionalized polyisobutylene.

Results and Discussion

Living Anionic Polymerization of VFc. VFc was polymerized with ^{n}BuLi in THF at different temperatures, −28, 0, and 25 °C, under similar conditions reported by Nuyken et al.[6] The solution became slightly turbid at all temperatures probably due to the aggregation of high-MW PVFcs as the polymerization proceeded; however, the insoluble part was only less than 1 wt % in all cases except when high MW (18 K) was targeted, where 5 wt % insoluble part was obtained. To elucidate the active chain end, an excess of chlorotrimethylsilane (TMS-Cl) was added after the polymerization so that the TMS end group could be probed by ^{1}H NMR spectroscopy. Figure 1A−C shows the GPC RI traces of the PVFcs thus obtained. The peaks are sharp and monomodal in all cases. For samples obtained at −28 and 0 °C, the GPC traces shifted to higher MW region with conversion while keeping their shapes and narrow distributions and reached 95% and 98% final conversions, respectively. On the other hand, at 25 °C limiting conversion (70%) was reached in 30 min. The results are summarized in Table 1.

The M_n values measured by GPC-MALLS are in good agreement with those calculated in all runs. The polydispersity indices (PDIs) are low (1.10−1.22), except for the high-MW sample (M_n = 18 600, PDI = 1.35). The M_n values of samples obtained at 0 and 25 °C were also determined from ^{1}H NMR spectroscopy by comparing the signal intensities at 0.2−0.4 ppm assignable to the nine silylmethyl protons in the TMS group at the chain end and the ones at 3.8−4.5 ppm assignable to the cyclopentadienyl protons in the PVFc main chain. Figure 2 shows a representative ^{1}H NMR spectrum of PVFc terminated with TMS group (0 °C, M_n = 4810). The determined M_n values for two samples obtained at 0 °C (4810 and 12 700) agree well with those measured by GPC-MALLS. In addition, the functionalities of the TMS group are close to unity, indicating that all chain ends are active. In the case of high-MW sample, the M_n value (20 600) is somewhat higher than the value from GPC-MALLS (18 600) and the calculated TMS functionality is 0.90. On the other hand, PVFc obtained at 25 °C shows lower TMS-functionality (0.81) even when lower molecular weight was targeted. This might be caused by lithium hydride elimination at chain end or by chain transfer to THF. All of the results are indicative that the anionic polymerization of VFc proceeded in a living manner at −28 and 0 °C when the targeted MW was less than 18 K, resulting in the formation of PVFcs with predictable MWs and narrow PDIs.

Synthesis of PIB-*b*-PVFc by Coupling Reaction of Haloallyl Chain-End Functionalized PIB with Living PVFc. Recently, we have reported a novel coupling of ω-bromoallyl chain-end functionalized PIB (PIB-AllylBr) with living PMMA (PMMALi) in THF at −78 °C with excellent efficiency (>95%) to obtain PIB-*b*-PMMA.[26] Following this concept, the synthesis of PIB-*b*-PVFc diblock copolymer was attempted by employing haloallyl chain-end functionalized PIB (PIB-AllylX) and living PVFc, as outlined in Scheme 1. A chloroallyl chain-end functionalized PIB (PIB-AllylCl) was synthesized by the capping reaction of living PIB cation with 1,3-butadiene in Hex/MeCl (60/40, v/v) at −80 °C followed by instantaneous ion collapse as described elsewhere.[28] In the first experiment, PIB-AllylCl (M_n = 15 900, PDI = 1.06) was reacted with a 1.8-fold excess of poly(vinylferrocenyl)lithium (PVFcLi, M_n = 6220, PDI = 1.17) in THF at 0 °C for 16 h. The GPC RI and UV traces of the coupled product show a large amount of unreacted homo PVFc. Since UV source can only detect PVFc segments, the coupling efficiency (CE = 25%) could be determined from the UV traces. The results are summarized in Table 2.

The more reactive PIB-AllylBr (M_n = 15 600, PDI = 1.07) was next employed in coupling reactions with PVFcLi (M_n = 3600−4200, PDI = 1.08−1.11) in THF at different temperatures, −78, −20, and 0 °C, at the ratio [PVFcLi]/[PIB-AllylBr] = ∼2. The reaction was sluggish at −78 °C, reaching only 8% CE (UV) even after 24 h. On the other hand, the CE increased to 90% (UV) at −20 °C after 40 h. The coupling reaction readily proceeded at 0 °C with 65% (UV) CE after only 1 h and with 91% (UV) after 16 h. The results are summarized in Table 2. Figure 3 shows the GPC RI and UV traces of the product obtained at 0 °C after 16 h. In the traces there are two peaks corresponding to PIB-*b*-PVFc (higher M_n) and unreacted homo PVFc (lower M_n) used in excess (Figure 3A). In order to isolate PIB-*b*-PVFc from the mixture, a THF solution of the product was poured into 2-butanone (THF/2-butanone = 1/5, v/v). The CE could also be determined by comparing the weight ratio of PIB-*b*-PVFc and homo PVFc after isolation giving 85%. Unexpectedly, the GPC UV trace of the insoluble part in THF/2-butanone (1/5, v/v) shows a side peak probably due to PVFc dimer formation (∼10 mol %) (Figure 3C). We suggest that it arises by undesired lithium−halogen exchange during the coupling reaction, resulting in the generation of PVFc bearing a bromine atom at the chain end followed by coupling with PVFcLi. This side reaction is significant when iodoallyl chain-end functionalized PIB (PIB-AllylI) was used (see Figure 4). In this case, the yield of PIB-*b*-PVFc is only 12% after 16 h at 0 °C. A DPE capping approach is known to reduce lithium−halogen exchange in the coupling reaction between polystyryllithium and halobenzyl functionalities.[30] Unfortunately, living PVFc did not react with DPE at all under normal conditions probably due to steric hindrance or low nucleophilicity of the propagating chain end. It can be concluded that PIB-*b*-PVFc could be prepared by employing PIB-AllylBr with relatively high CE (>85%) with minor homo PVFc contamination.

Coupling Reaction of α,ω-Bromoallyl Difunctionalized PIB with Living PVFc. To synthesize ABA triblock copolymer (A = PVFc and B = PIB), the coupling reaction of α,ω-bromoallyl difunctionalized PIB (AllylBr-PIB-AllylBr, M_n = 35 200, PDI = 1.07, bromoallyl functionality = 1.98) with a 2.34-fold excess of PVFcLi (M_n = 9500, PDI = 1.17) toward the bromoallyl functionality has been carried out in THF at 0 °C for 24 h. As shown in Figure 5, the GPC trace of the product shows a major peak of the expected ABA triblock copolymer

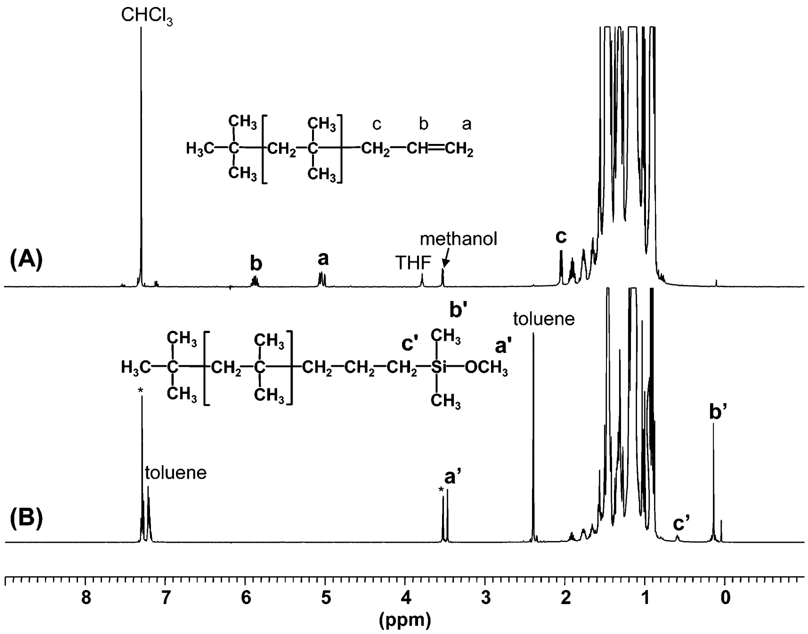


Figure 7. ^{1}H NMR spectra of (A) allyl chain-end functionalized polyisobutylene and (B) methoxysilyl chain-end functionalized polyisobutylene.

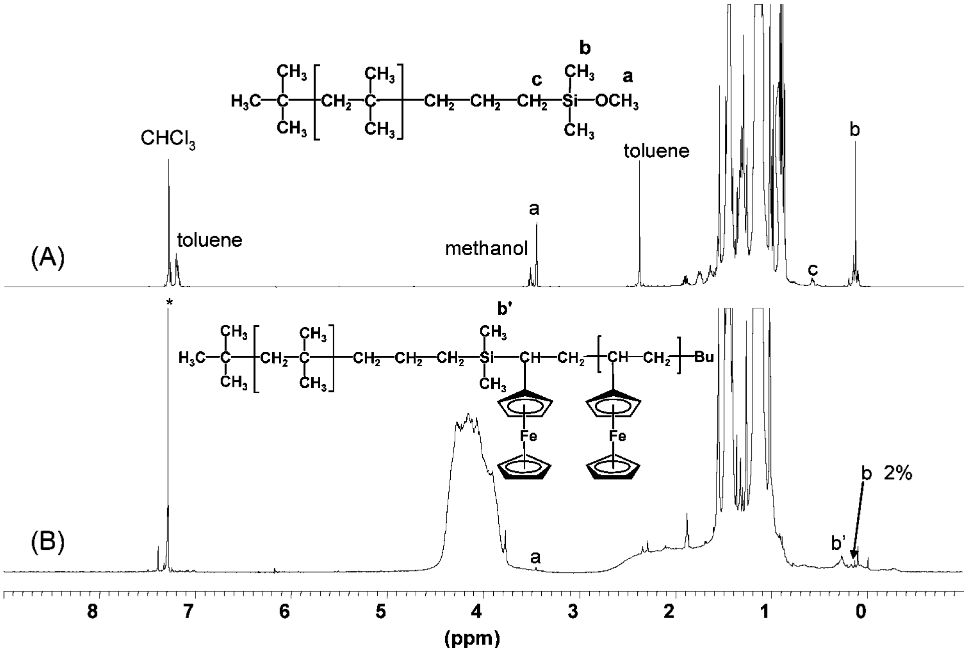


Figure 8. ^{1}H NMR spectra of (A) methoxysilyl chain-end functionalized polyisobutylene and (B) the product obtained by the coupling reaction of chlorosilyl chain-end functionalized polyisobutylene with poly(vinylferrocenyl)lithium at 0 °C at [poly(vinylferrocenyl)lithium]/[chlorosilyl chain-end functionalized polyisobutylene] = 2.6.

Table 3. Coupling Reaction of Chlorosilyl Chain-End Functionalized Polyisobutylene with Poly(vinylferrocenyl)lithium in Tetrahydrofuran at 0 °C

		homo-poly(vinylferrocene)		after coupling reaction				
				M_n			CE (%)[a]	
time (h)	[PVFcLi]/[PIB-SiCl]	M_n GPC-MALLS	PDI	calcd	GPC-MALLS[b]	PDI	UV	^{1}H NMR[c]
0.5	2.6[d]	2800	1.10	18 600	18 700	1.06	99	98
1	1.8[e]	3000	1.10	17 200	16 800	1.04	95	94

[a] Coupling efficiency. [b] Measured after isolation of PIB-*b*-PVFc. [c] Determined by comparing the signal intensities at 0.13 ppm assignable to the silylmethyl protons of PIB-SiOMe and ones at 0.40−0.20 ppm assignable to the silylmethyl protons at the junction between PIB and PVFc segments. [d] PIB-SiCl (M_n = 15 800, PDI = 1.07) was used. [e] PIB-SiCl (M_n = 14 200, PDI = 1.06) was used.

and homo PVFc used in excess accompanied by a significant higher MW shoulder which possibly corresponds to the mixture of ABBA and AB...BA multiblocks as well as the large dimeric PVFc peak. These byproducts may be caused by the lithium−halogen exchange between PVFcLi and both chain ends of AllylBr-PIB-AllylBr. Therefore, it can be seen that there is a limitation in the coupling reaction using haloallyl functionalized PIBs, especially for the synthesis of ABA triblock copolymers.

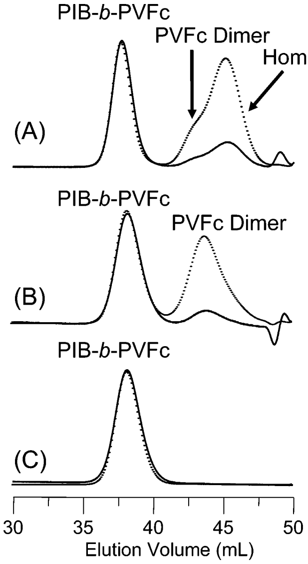


Figure 9. Gel permeation chromatography traces of (A) the product obtained by the coupling reaction of chlorosilyl chain-end functionalized polyisobutylene with poly(vinylferrocenyl)lithium at 0 °C at [poly(vinylferrocenyl)lithium]/[chlorosilyl chain-end functionalized polyisobutylene] = 2.6, (B) at [poly(vinylferrocenyl)lithium]/[chlorosilyl chain-end functionalized polyisobutylene] = 1.8, and (C) the isolated poly(isobutylene-*b*-vinylferrocene) (M_n = 16 800, PDI = 1.04): solid line, refractive index; dotted line, UV.

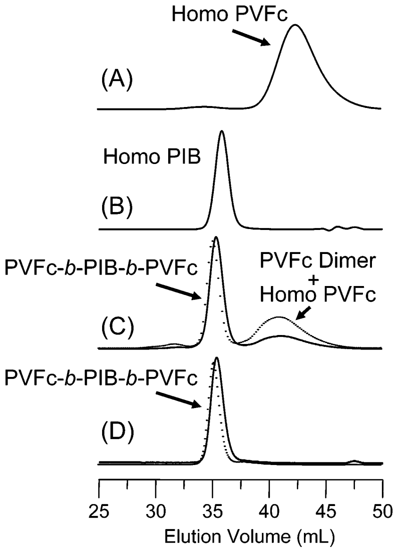


Figure 10. Gel permeation chromatography traces of (A) homo poly(vinylferrocene), (B) the product after treating α,ω-chlorosilyl difunctionalized polyisobutylene with methanol, (C) the product obtained by the coupling reaction of α,ω-chlorosilyl difunctionalized polyisobutylene with poly(vinylferrocenyl)lithium at 0 °C for 3 h, and (D) the isolated poly(vinylferrocene-*b*-isobutylene-*b*-vinylferrocene): solid line, refractive index; dotted line, UV.

Synthesis of PIB-*b*-PVFc by Coupling Reaction of Chlorosilyl Chain-End Functionalized PIB with Living PVFc. Silyl halide compounds are well-known to react with living anionic polymers of styrenes and dienes cleanly and quantitatively. In practice, Hadjichristidis and co-workers have been using a wide variety of silyl chloride compounds to synthesize block, star, and other branched polymers with well-defined structures.[31] Primary amino chain-end functionalized PSs (PS-NH_2) with a high degree of functionalization could be synthesized by using a chlorosilane compound with a protected amino group as a terminating agent of polystyryllithium (PSLi) followed by deprotection as reported by DeSimone and co-workers[32] and recently by Schlaad and co-workers.[33] More recently, Quirk et al. have developed a facile synthetic methodology for PS-NH_2 without protection−deprotection process via the hydrosilation reaction between allylamine and silyl hydride chain-end functionalized PS prepared by terminating PSLi with DMS-Cl.[33] Since lithium−halogen exchange is absent when chlorosilyl functional compounds are used, we intended to explore coupling reactions of PVFcLi with chlorosilyl functionalized PIBs.

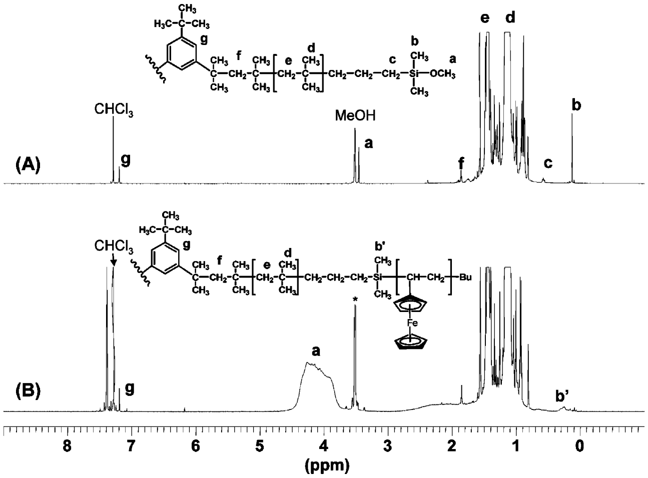


Figure 11. ^{1}H NMR spectra of (A) the product after treating α,ω-chlorosilyl difunctionalized polyisobutylene with dry methanol and (B) the product obtained by the coupling reaction of α,ω-chlorosilyl difunctionalized polyisobutylene with poly(vinylferrocenyl)lithium.

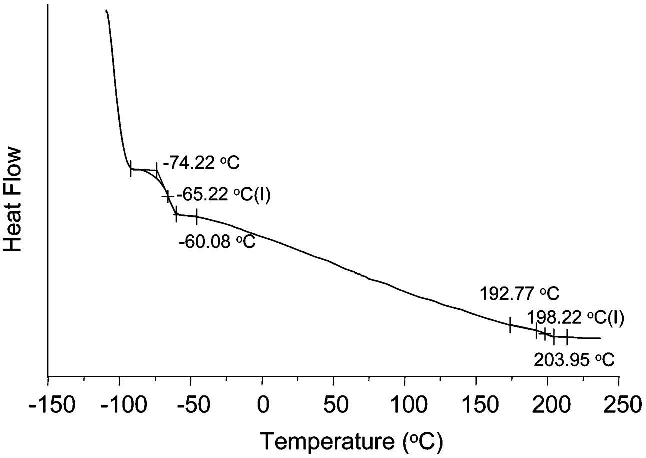


Figure 12. Differential scanning calorimetry thermogram of poly(vinylferrocene-*b*-isobutylene-*b*-vinylferrocene).

As shown in Scheme 2, we prepared a chlorosilyl chain-end functionalized PIB (PIB-SiCl) by the hydrosilation reaction between DMS-Cl and an allyl chain-end functionalized PIB (PIB-Allyl) which can easily be prepared by reacting living PIB cation ($PIB^+Ti_2Cl_9^-$) with allyltrimethylsilane, as described elsewhere.[29] Karstedt's Pt(0) catalyst, $Pt_2[CH_2{=}CHSi(CH_3)_2OSi(CH_3)_2CH{=}CH_2]$, was used for the hydrosilation. PIB-Allyl (M_n = 15 800, PDI = 1.11, allyl functionality = 1.00) was stirred with a 10-fold excess of DMS-Cl and 100 ppm (toward PIB-Allyl by weight) of the Pt(0) catalyst in dry toluene at 95 °C for 3 h under a dry argon atmosphere in a round-bottom flask equipped with a break-seal. Within 5 min after injection of the catalyst, a light yellow color appeared, indicating the formation of active colloidal species;[35] the color remained unchanged after 3 h. A small portion of the solution was taken out and quenched with dry methanol in such a way that PIB-SiCl could be converted to a more stable methoxysilyl chain-end functionalized

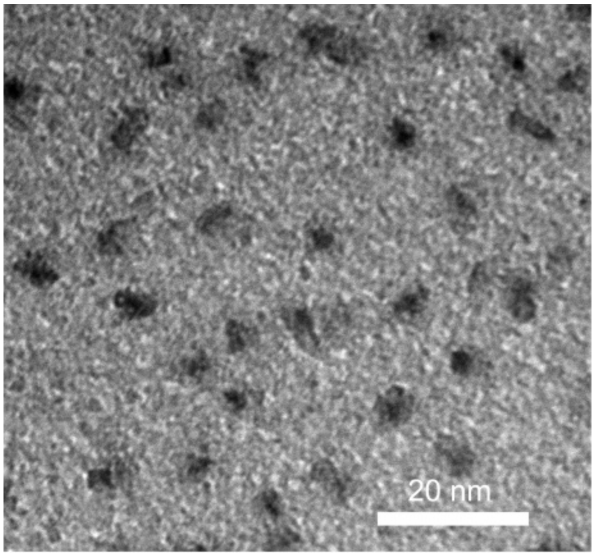


Figure 13. Transmission electron micrograph of poly(vinylferrocene-*b*-isobutylene-*b*-vinylferrocene) thin film.

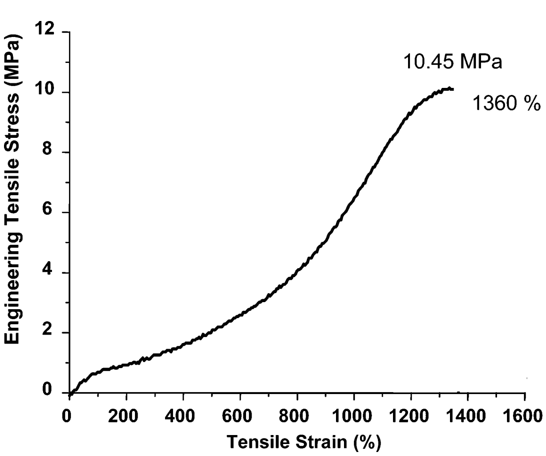


Figure 14. Stress−strain plot for the film of poly(vinylferrocene-*b*-isobutylene-*b*-vinylferrocene).

PIB (PIB-SiOMe) for characterizations by GPC-MALLS and ^{1}H NMR. The polymers before and after hydrosilation exhibit monomodal GPC RI traces without changes in their shape and position (Figure 6).

In the ^{1}H NMR spectrum after hydrosilation (Figure 7), characteristic resonances of allyl groups, the two methylene protons ($-CH_2-CH=$ and $=CH_2$) and the one methine proton ($-CH=$) at 2.05, 5.05, and 5.88 ppm, respectively, completely disappeared, while distinct resonances from the six methyl protons ($-Si(CH_3)_2-$), the two methylene protons ($-CH_2-Si$), and three methoxy protons ($-SiOCH_3$) at 0.16, 0.60, and 3.47 ppm, respectively, of dimethylmethoxysilylmethyl groups were clearly observed. Thus, the hydrosilation proceeded quantitatively to afford the expected PIB-SiCl.

As PIB-SiCl ($M_n = 15\,800$, PDI = 1.07) contained a large excess of DMS-Cl, the azeotropic distillation from its absolute toluene solution was performed twice followed by drying under high-vacuum condition ($<10^{-6}$ Torr) for 24 h. The in-situ coupling reaction of PIB-SiCl with a 2.6-fold excess of PVFcLi ($M_n = 2800$, PDI = 1.10) was carried out in THF at 0 °C. This reaction was much faster than that with PIB-AllylBr achieving excellent CE (UV: 99%) only after 30 min. The ^{1}H NMR spectrum of the polymer mixture confirmed the efficient coupling reaction showing a very small (2%) signal at 0.13 ppm assignable to the six silylmethyl protons of PIB-SiOMe, which was generated by quenching the unreacted PIB-SiCl with dry methanol, while showing a relatively broad signal at 0.2−0.35 ppm corresponding to the six silylmethyl groups at the junction between both PIB and PVFc segments (see Figure 8). By comparing those signals, the CE = 98% was determined. As can be seen in Figure 9A, GPC RI and UV traces of the product show three peaks corresponding to PIB-*b*-PVFc, homo PVFc used in excess, and the unexpected PVFc dimer. The dimer may possibly be formed not by the lithium−halogen exchange but by the coupling between homo PVFcLis used in excess and difunctional low-MW byproducts such as dichlorodimethylsilane or dichlorotetramethyldisilane[36] generated during the hydrosilation reaction. To minimize homo PVFc contaminations in PIB-*b*-PVFc, we reduced the ratio, [PVFcLi]/[PIB-SiCl], from 2.6 to 1.8. The GPC RI and UV traces of the product show two main peaks of PIB-*b*-PVFc and the mixture of PVFc dimer and a very small peak of homo PVFc (detectable in UV) used in excess (see Figure 9B). The CE was still good being 95% close to the value (94%) determined from ^{1}H NMR. The expected pure PIB-*b*-PVFc free of homo PVFc as well as its dimer could be successfully obtained by the fractional precipitation using THF/2-butanone (1/4, v/v) in 80% yield. The purified PIB-*b*-PVFc shows a single, sharp, and symmetrical peak in either RI or UV GPC trace (see Figure 9C). These results are summarized in Table 3.

That the PIB-*b*-PVFc is structurally homogeneous after isolation is indicated by the fact that the measured M_n values are in good agreement with those calculated on the basis of M_n values of PIB-SiCl and PVFc, with very narrow PDIs (<1.06). In addition, the weight compositions, PIB/PVFc, of the isolated PIB-*b*-PVFcs determined from ^{1}H NMR agreed well with those calculated. For instance, the composition of PIB-*b*-PVFc ($M_n = 16\,800$, PDI = 1.04), 82.6/17.4 (w/w) calculated from the ^{1}H NMR spectrum is close to the calculated one, 83.5/16.5. Thus, we have succeeded in synthesizing PIB-*b*-PVFc with excellent CEs ($>94\%$), controlled molecular weights, predictable compositions, and narrow PDIs.

Synthesis of PVFc-*b*-PIB-*b*-PVFc by Coupling Reaction of α,*ω*-Chlorosilyl Difunctionalized PIB with Living PVFc. On the basis of the successful results in AB diblock copolymer synthesis, we next targeted ABA triblock copolymers where A and B were PVFc and PIB segments, respectively. The procedure and conditions employed here are the same as in the AB diblock copolymer synthesis, except for using α,*ω*-chlorosilyl difunctionalized PIB (SiCl-PIB-SiCl) instead of monofunctionalized PIB-SiCl. SiCl-PIB-SiCl was successfully synthesized by the hydrosilation of α,*ω*-allyl difunctionalized PIB ($M_n = 38\,500$, PDI = 1.05, allyl functionality = 2.00) with 10-fold excess of DMS-Cl. The in-situ coupling reaction of SiCl-PIB-SiCl ($M_n = 38\,600$, PDI = 1.04) was then carried out with 1.8-fold excess of PVFcLi ($M_n = 10\,200$, PDI = 1.27) toward SiCl groups in THF at 0 °C for 3 h. As shown in Figure 10C, the GPC RI and UV traces of the product show two peaks corresponding to the expected ABA triblock and the mixture of homo PVFc and its dimer. By comparing the two peak areas in the UV trace, the C.E. was 98%. The excellent CE (99.2%) was confirmed by the ^{1}H NMR spectrum displaying negligible signal at 0.13 ppm assignable to the 12 silylmethyl protons of the SiOMe group at both chain ends (see Figure 11). The expected PVFc-*b*-PIB-*b*-PVFc could be isolated by the fractional precipitation using THF/2-butanone (1/1, v/v) in 73% yield. Both RI and UV GPC traces (see Figure 10D) show monomodal, sharp, and symmetrical peaks, indicating the absence of homo PVFc contamination. The $M_n = 55\,600$ of the isolated PVFc-

b-PIB-*b*-PVFc agrees well with the calculated value (55 600), and the PDI is low (1.08). Furthermore, the weight composition of PIB/PVFc (70/30) determined from ^{1}H NMR spectroscopies is close to the calculated one, 69/31. Thus, well-defined novel PVFc-*b*-PIB-*b*-PVFc ABA triblock copolymer was synthesized for the first time with excellent CE (>98%).

The ABA triblock copolymer has good solubility in common solvents such as benzene, toluene, THF, and chloroform (see Supporting Information). It is also well soluble in cyclohexane and methylcyclohexane that are selective solvents for PIB segment. On the other hand, the ABA triblock copolymer is insoluble in 2-butanone, which is a selective solvent for PVFc segment.

A DSC thermogram of the ABA triblock copolymer (8.3K-39K-8.3K) shows two glass transition temperatures: one at −65 °C corresponding to PIB and the other at 198 °C corresponding to PVFc which may suggest microphase-separated morphology (see Figure 12). To gain insight into the morphology, the ABA triblock copolymer thin film was studied by TEM. Staining is unnecessary, as the high electron density associated with iron atoms in the side chain provided sufficient contrast for TEM micrographs. The electron micrograph of ultrathin sections of the sample is shown in Figure 13. PVFc areas are dark whereas PIB areas are lighter in the TEM image. A typical disordered spherical morphology with 5−8 nm diameter where the PVFc domains are dispersed in the PIB matrix is clearly observed. Stress−strain/dynamic-mechanical measurement performed with a solvent-cast film (from toluene) of the same sample is shown in Figure 14. The sample possesses a good elastomeric property showing 1360% elongation at break. However, the tensile strength at break is 10.45 MPa, which is lower than that expected for typical PIB-based TPEs. For instance, the best SIBS showed 23−25 MPa tensile strength as reported by our group.[12] In addition, the initial modulus is very low. To improve the tensile strength, higher volume fraction of PVFc segment exhibiting cylindrical morphology would be required.

Conclusions

Living anionic polymerizations of VFc initiated with ^{n}BuLi in THF at −28 and 0 °C yielded well-defined PVFcs with predictable M_n and narrow PDI (1.10−1.22) when the targeted MW was less than 18K. New AB diblock copolymers comprised of PIB and PVFc segments could be synthesized by the coupling reaction between PIB-AllylBr and PVFcLi with high CE (∼85%); however, a side reaction that thought to involve lithium−halogen exchange complicated the reaction. The limitation of this method is the concurrent side reaction that yields significant amount of byproducts, especially in the synthesis of ABA triblock copolymer, PVFc-*b*-PIB-*b*-PVFc, by coupling of AllylBr-PIB-AllylBr and PVFcLi. On the other hand, excellent CEs (>94%) have been accomplished in the syntheses of PIB-*b*-PVFc as well as PVFc-*b*-PIB-*b*-PVFc by employing PIB-SiCl and SiCl-PIB-SiCl, respectively, instead of haloallyl functionalized PIB. GPC-MALLS and ^{1}H NMR analyses of the resulting block copolymers confirmed their well-defined structures and low degrees of compositional heterogeneity. The two glass transition temperatures of PVFc-*b*-PIB-*b*-PVFc at −65 and 198 °C observed in the DSC thermogram suggest microphase separation. The typical disordered spherical morphology of a PVFc-*b*-PIB-*b*-PVFc thin film was characterized by TEM. The stress−strain plot of a PVFc-*b*-PIB-*b*-PVFc film showed elastomeric behavior with a 10.45 MPa tensile strength and 1360% elongation at break.

Acknowledgment. Dr. Earl T. Ada is acknowledged for his assistance with the transmission electron microscopy imaging. The authors also thank Dr. Umaprasana Ojha for assisting the preparation of polymer sample film. Financial support by Boston Scientific Corp. is gratefully acknowledged.

Supporting Information Available: Table showing solubility of PVFe-*b*-PIB-*b*-PVFe. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA070903D