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Living Anionic Polymerization of 2-Isopropenylthiophene Derivatives

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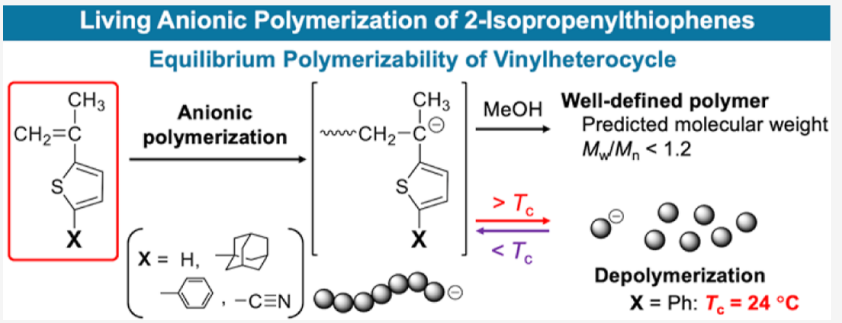

ABSTRACT: The anionic polymerization of 2-isopropenylthiophene (**1**), 2-(1-adamantyl)-5-isopropenylthiophene (**2**), 5-phenyl-2-isopropenylthiophene (**3**), and 2-cyano-5-isopropenylthiophene (**4**) was performed in tetrahydrofuran (THF) with various initiators including *sec*-BuLi, oligo(α-methylstyryl)lithium, potassium naphthalenide, and diphenylmethylpotassium at −78 °C. The anionic polymerization of **2**−**4** proceeded quantitatively to provide novel polymers with the predicted molecular weights and narrow molecular weight distributions (M_w/M_n < 1.2), whereas the polymerization of **1** often suffered from side reactions, probably due to proton abstraction on the thiophene ring. After the complete polymerization at −78 °C, the propagating carbanion of the resulting polymers of **2**−**4** can be depolymerized to give the starting monomer by elevating the temperature to 0 °C. In particular, **3** showed a reversible equilibrium polymerizability similar to that of α-methylstyrene by varying the temperature of the polymerization system. From the plot of logarithm of equilibrium monomer concentration, $\ln[M]_e$, against reciprocal temperature, the thermodynamic parameters, ΔH and ΔS, and the ceiling temperature (T_c) of the anionic polymerization of **3** in THF were estimated to be −8.09 ± 0.22 kcal mol^{-1}, −27.3 ± 0.9 cal mol^{-1} K^{-1}, and 24 °C, respectively.

INTRODUCTION

Equilibrium polymerization is an intriguing system in which the reversible polymerization of a monomer occurs by changing the temperature to shift the equilibrium. Ideally, the system can regenerate the starting monomer from the resulting polymer chain end almost quantitatively and can polymerize the regenerated monomer again.[1−4] The related research of the equilibrium polymerization focused on the simple polymerization behavior and the development of an effective chemical recycle system such as self-immolative polymers.[5−17]

α-Methylstyrene (αMS) is a vinylidene-type monomer and shows the typical equilibrium polymerization behavior with a low ceiling temperature[18] (T_c = 5 °C) under the anionic conditions (Figure 1A).[19−26] Notably, the resulting poly(αMS) showed an ease of thermal degradation compared to a polystyrene without an α-methyl substituent on the main chain. A series of para-substituted αMS derivatives also undergo anionic equilibrium polymerization in tetrahydrofuran (THF), as shown in Figure 1B.[27−31] The anionic polymerizabilities, the electrophilicity of the C═C double bond, of these αMS monomers largely differ and can be predicted by the Hammett parameter (σ_p) of the substituents,[32−35] while various αMS derivatives exhibit close T_c values independent of the σ_p value. Conversely, the isopropenyl heterocyclic monomers show significantly higher T_c values than the αMS derivatives (Figure 1C).[36,37] All of these monomers possessed the isopropenyl group as the (de)polymerizable function, and the heterocycle skeletons such as oxazole, thiazole, and pyridine rings should have a significant influence on the equilibrium polymerizability. Although molecular structures of heterocycles including heteroatoms, ring members, and π-electron density compared with the benzene ring of the αMS derivatives seemed essential to determine the T_c value and the equilibrium polymerizability, there are no reports for the π-

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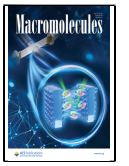

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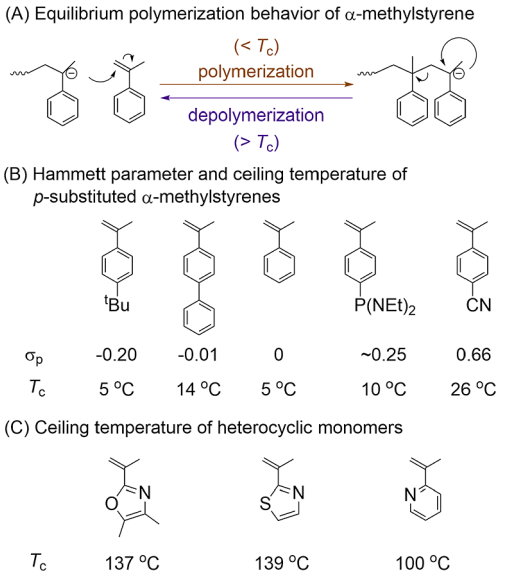
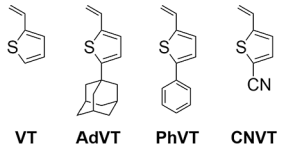


Figure 1. Equilibrium polymerization behaviors of various isopropenyl monomers in the anionic polymerization.

sufficient heterocyclic monomers having the isopropenyl group, not only on the equilibrium polymerizability but also on the anionic polymerization behavior. Whereas the free radical, cationic, and coordination polymerizations of 2-isopropenylthiophene (**1**) possessing a π-sufficient thiophene ring was attempted, the formation of a low molecular weight oligomer was reported.[38] To the best of our knowledge, the anionic polymerization of **1** has not been reported.

Very recently, we performed the anionic polymerization of 2-vinylthiophene (**VT**), a vinyl counterpart of **1**, with various initiators in tetrahydrofuran (THF) at −78 °C to give the polymers possessing predicted molecular weights and narrow molecular weight distribution (M_w/M_n < 1.2).[39] However, after the completion of the polymerization of **VT**, partial deactivation of the propagating carbanion was observed probably due to the abstraction of the relatively acidic proton on the 5-position of the thiophene ring (pK_a = 32.5−33.5).[40,41] In contrast, we succeeded in the living anionic polymerization of a series of 5-substituted **VT** derivatives bearing 1-adamantyl (**AdVT**), phenyl (**PhVT**), and cyano (**CNVT**) groups on the thiophene ring (Chart 1). In these cases, because the acidic

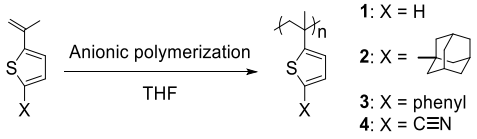
Chart 1. 2-Vinylthiophenes (VTs) Capable of Anionic Polymerization



position of the thiophene ring was masked by the substituents, stable propagating carbanions were unequivocally formed to give the tailored polymers quantitatively. The bulkiness of the 1-adamantyl group, longer π-conjugation system of the phenyl group, and strong electron-withdrawing property of the cyano group might play very important roles in preventing possible side reactions.

In this study, we investigated the anionic polymerization of **1** and 5-substituted 2-isopropenylthiophenes (**IPT**) bearing 1-adamantyl (**2**), phenyl (**3**), and cyano (**4**) groups to expand the range of monomers capable of anionic polymerization (Scheme 1). As explained above, since these substituents of

Scheme 1. Anionic Polymerization of 2-Isopropenylthiophenes (IPTs)



VT derivatives could tolerate the living anionic polymerizations at −78 °C,[39] the anionic polymerization of **2**−**4** should also be possible under suitable conditions. However, the acidic hydrogen at the 5-position of the thiophene ring in **1** may cause a side reaction similar to that of **VT**. Because stable propagating chain ends derived from **2**−**4** were successfully obtained, we further examined their depolymerizability and equilibrium polymerizability. Among them, **3** showed ideal reversible polymerizability owing to the π-stabilized carbanion, and the thermodynamic parameters could also be determined.

RESULTS AND DISCUSSION

Anionic Polymerization of 1. Anionic polymerization of **1** was first attempted using *sec*-butyllithium (*sec*-BuLi) as the initiator in tetrahydrofuran (THF) at −78 °C for 20 h (run 1, Table 1, and Scheme 2). Upon the addition of **1** to *sec*-BuLi, the color of the reaction solution immediately changed from colorless to pale orange. The color was maintained until the reaction was terminated using methanol. However, no polymeric product was obtained even after 20 h of reaction, and the monomer was recovered almost quantitatively. We then changed the initiator to oligo(α-methylstyryl)lithium (*sec*-BuLi/αMS), which was prepared using *sec*-BuLi and 3−4-fold α-methylstyrene (αMS), to reduce the basicity and nucleophilicity of the carbanion compared to that of *sec*-BuLi. It has been reported that the resulting benzylic carbanion of *sec*-BuLi/αMS effectively reduced side reactions to the reactive carbon−bromo bond in 4-bromostyrene because of the π-conjugated structure and its bulkiness.[42] In the initiation of **1** with *sec*-BuLi/αMS, the reaction mixture immediately turned from red to dark red, similar to that of anionic living polystyrene. The polymerization of **1** by *sec*-BuLi/αMS proceeded at −78 °C, and the conversion reached 69% after 5 min (run 2). Furthermore, a longer polymerization time of 1 h resulted in the complete consumption of **1** at −78 °C within 1 h to give poly(**1**) quantitatively (run 3). The polymer obtained after 1 h possessed a rather narrow molecular weight distribution (MWD: M_w/M_n = 1.14) (Figure 2A, B). The observed molecular weights (M_n) were close to the predicted M_n values based on the molar ratios of the monomer and initiator, indicating that M_n was controlled during polymerization by *sec*-BuLi/αMS. The polymerization of **1** was also examined using lithium naphthalenide (Li-Naph), a typical radical anion (run 5). This system also produced a polymer with a narrow MWD (M_w/M_n = 1.11, Figure 2C) within 1 h in a quantitative yield, similar to *sec*-BuLi/αMS. It is noted that a small shoulder in the size exclusion chromatography (SEC) curves of polymers obtained by *sec*-BuLi/αMS and Li-Naph was observed after the completion of polymerization, suggesting that an intermolecular side reaction with increasing

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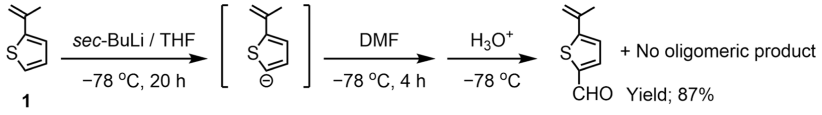
Table 1. Anionic Polymerization of 1−4 in THF at −78 °C

run	monomer (mmol)	initiator (mmol) (equiv)	M/I[a]	time (h)	conversion[b] (%)	M_n (kg/mol) calcd[c]	M_n (kg/mol) obsd[d]	M_w/M_n[e]
1	**1**, 5.93	*sec*-BuLi, 0.0696	85	20	0			
2	**1**, 4.29	*sec*-BuLi, 0.0784/*α*MS, 0.320 (4.1)	55	5 min	69	5.2	5.3	1.09
3	**1**, 4.25	*sec*-BuLi, 0.0642/*α*MS, 0.212 (3.3)	66	1	100	8.7	12	1.14
4	**1**, 4.15	*sec*-BuLi, 0.0661/*α*MS, 0.280 (4.2)	63	24	100	8.4	12	1.13
5	**1**, 6.26	Li-Naph, 0.115	37	1	100	8.7	10	1.11
6	**1**, 5.35	K-Naph, 0.159	34	15 min	∼30	2.5	3.4	1.15
7	**1**, 4.36	K-Naph, 0.140	31	1	86	6.6	6.0	1.56
8	**1**, 3.77	K-Naph, 0.139	27	20	100	6.7	7.8	1.66
9	**2**, 2.02	*sec*-BuLi, 0.0718	28	5 min	78	5.7	8.1	1.20
10	**2**, 2.06	*sec*-BuLi, 0.0681	30	15 min	86	6.8	11	1.15
11	**2**, 1.60	*sec*-BuLi, 0.0622	26	1	100	6.7	10	1.17
12	**2**, 1.96	Li-Naph, 0.191	10	1	100	5.3	14	1.26
13	**2**, 1.98	*sec*-BuLi, 0.0642/*α*MS, 0.225 (3.5)	31	1	100	8.4	9.5	1.19
14	**2**, 1.56	K-Naph, 0.132	12	20	100	6.1	6.8	1.13
15	**2**, 3.70	K-Naph, 0.0986	37	20	100	19	20	1.09
16	**2**, 1.64	Ph_2CHK, 0.0879	19	20	0			
17	**3**, 2.51	*sec*-BuLi, 0.108	23	1	21	1.0	1.2	1.07
18	**3**, 2.40	*sec*-BuLi, 0.0937	26	48	94	4.9	5.0	1.06
19	**3**, 2.68	Li-Naph, 0.104	26	72	97	10	8.9	1.14
20	**3**, 2.40	K-Naph, 0.0932	26	1	20	2.1	1.5	1.09
21	**3**, 2.63	K-Naph, 0.122	22	48	93	8.0	6.4	1.06
22	**3**, 5.18	K-Naph, 0.111	47	96	83	16	15	1.05
23	**3**, 2.37	Ph_2CHK, 0.0729	33	96	94	6.3	6.2	1.07
24	**3**, 2.63	Ph_3CK, 0.0912	29	100	6	0.6	17	1.06
25	**4**, 3.39	Ph_2CHLi, 0.0933	36	2	13	0.9	0.7[e]	
26	**4**, 2.99	Ph_2CHLi, 0.0673	44	72	91	6.2	8.7	1.08
27	**4**, 2.99	Ph_2CHK, 0.0871	34	2	52	2.8	2.2	1.03
28	**4**, 2.30	Ph_2CHK, 0.0712	32	20	95	4.7	5.0	1.05
29	**4**, 3.47	Ph_2CHK, 0.0491	71	48	95	10	14	1.03
30	**4**, 3.84	Ph_3CK, 0.0884	43	48	95	6.4	7.9	1.07
31	**4**, 3.43	Li-Naph, 0.169	20	72	93	5.6	5.4	1.14
32	**4**, 3.63	K-Naph, 0.116	31	20	94	8.8	14	1.10
33	**4**, 3.44	*tert*-BuOK, 0.182	19	100	96	2.8	18	1.10

[a]M/I = [monomer]/[initiator]. [b]Conversion determined by ^{1}H NMR. [c]M_n(calcd.) = (MW of monomer) × M/I + (MW of initiator residue). [d]M_n(obsd) was determined by SEC-RALLS equipped with triple detectors including refractive index (RI), light scattering (LS), and viscometer detectors. [e]M_w/M_n (M_n(obsd)) was determined by SEC calibration using polystyrene standards in THF.

Scheme 2. Reaction of 1 with *sec*-BuLi and the Following Reaction with DMF



molecular weight might occur to some extent. Nevertheless, the shape of the SEC curve of poly(**1**) obtained with *sec*-BuLi/*α*MS even after 24 h was identical to that after 1 h (run 4, Figure S21A), indicating that this side reaction was minor. On the other hand, potassium naphthalenide (K-Naph), possessing a larger potassium cation than the lithium cation, gave poly(**1**) having a narrow MWD (run 6, M_w/M_n = 1.15, Figure 2D) at −78 °C after 15 min in 30% conversion. The polymerization using K-Naph did not complete within 1 h (run 7), and it was slower than that with the organolithium initiators. Quantitative polymerization of **1** was attained within 20 h (run 8), and the SEC curve of the polymer became broader with a long tailing in the low molecular weight region (M_w/M_n = 1.66, Figure 2E). These results suggest that the polymerization of **1** by K-Naph is accompanied by a side reaction during the propagation.

Although these results indicated that *π*-conjugated *sec*-BuLi/*α*MS and the radical anion lithium initiator were preferable for polymerizing **1** in a controlled fashion, we could not explain the reason why no polymer was obtained on the initiation with *sec*-BuLi (run 1). Then, we attempted to react *sec*-BuLi and 2.2 equiv of **1** in THF at −78 °C for 20 h, and an excess amount of *N*,*N*-dimethylformamide (DMF) was added and reacted at −78 °C for 4 h (Scheme 2). The reaction was quenched with acetic acid, and the volatile components were removed in vacuo. Column chromatography of the residue afforded 2-formyl-5-isopropenylthiophene in 87% isolated yield without oligomer formation. This indicated that the strong basic *sec*-butyl anion readily abstracted the relatively acidic hydrogen at the 5-position (pK_a = 32.5−33.5)[40,41] of the thiophene ring of **1** to form the corresponding thienyl anion prior to the initiation reaction, as shown in Scheme 2. Formation of the

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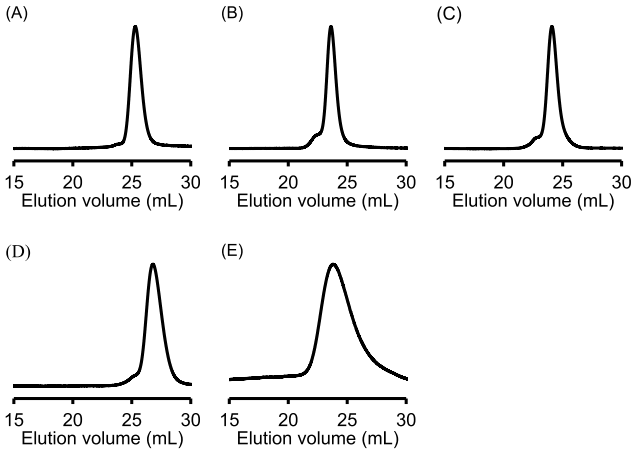

Figure 2. SEC curves of poly(**1**) obtained in THF at −78 °C: (A) run 2 (*sec*-BuLi/αMS for 5 min), (B) run 3 (*sec*-BuLi/αMS for 1 h), (C) run 5 (Li-Naph for 1 h), (D) run 6 (K-Naph for 15 min), and (E) run 8 (K-Naph for 20 h).

thienyl anion was confirmed by the corresponding aldehyde, and the isopropenyl group of **1** remained intact toward *sec*-BuLi. In contrast, proton abstraction was effectively eliminated using *sec*-BuLi/αMS because of its relatively low basicity, and alternative initiation of **1** occurred quantitatively. Once the initiation of **1** occurred, propagation proceeded smoothly to give the polymer a well-defined chain structure without apparent termination. It should be noted that **VT**, possessing a similar acidic proton at the 5-position of the thiophene ring, was quantitatively polymerized with *sec*-BuLi in THF at −78 °C within 5 min to give a well-defined polymer.[39] This contrast polymerization result using *sec*-BuLi would be derived from the different electrophilicities of the vinyl group of **VT** and isopropenyl group of **1**. The only difference was the α-methyl group on the vinyl group, but the electrophilicity of the carbon−carbon double bond was significantly changed by the steric and electronic effects of the electron-donating methyl group. The β-carbon chemical shifts (C_β) of the carbon−carbon double bonds in the ^{13}C NMR spectra were observed at 111.5 ppm (**1**) and 113.3 ppm (**VT**), respectively. The C_β signal of the isopropenyl group was observed at a higher magnetic field, indicating an electron density higher than that of the vinyl group. The relationship between **VT** and **1** is very similar to that between styrene and αMS.

Anionic Polymerization of 2−4. Next, we examined the anionic polymerization of a series of **IPT** derivatives possessing 1-adamantyl (**2**), phenyl (**3**), and cyano (**4**) groups at the 5-position of the thiophene ring in **1**. In each case, the acidic protons of **1** were masked by the corresponding substituents. Since it has been reported that the anionic polymerizations of the corresponding **VT** derivatives[39] and para-substituted styrenes[29,35,43−45] proceeded in living fashions, the three substituents in **2**−**4** would prevent the undesirable side reactions and tolerate the anionic polymerization.

At first, the anionic polymerization of **2**, containing a bulky 1-adamantyl group, was examined using *sec*-BuLi as the initiator in THF at −78 °C for 5 min, as in run 9. The polymerization system of **2** was dark red, indicating the presence of a propagating carbanion. After the reaction mixture was terminated with methanol, ^1H NMR spectroscopy of the reaction mixture revealed that the conversion of **2** was 78% after 5 min. As expected, the conversion of **2** increased by 86 and 100% after 15 min and 1 h, respectively (runs 10 and 11). The resulting poly(**2**) has a relatively narrow MWD (M_w/M_n < 1.20), and the M_n value is slightly higher than the calculated value. The observed polymerization behavior of **2** toward *sec*-BuLi differed from that of **1**, as described above. Similarly, when the polymerization of **2** was performed by Li-Naph, the polymer with a slightly broader MWD (M_w/M_n = 1.26) and a M_n significantly higher than the calculated value was produced (run 12). In contrast, the polymerization with *sec*-BuLi/αMS, the lower nucleophilic initiator, allowed control of both the molecular weight and the MWD of poly(**2**) (run 13). Similarly, K-Naph quantitatively produced well-defined poly(**2**)s with predicted M_n values and narrow MWDs (M_w/M_n < 1.13) within 20 h (runs 14 and 15). The well-defined structure of the resulting poly(**2**) was also confirmed by matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) measurements (Figure S28) since the spectrum showed only one series of peaks corresponding to the target polymer structure.

We then employed diphenylmethylpotassium (Ph_2CHK), a bulky and π-conjugated low nucleophilic initiator, for the polymerization of **2** to investigate the relative reactivity of the monomer. No polymerization of **2** indeed occurred with Ph_2CHK at −78 °C even after 20 h, and **2** was quantitatively recovered from the polymerization system (run 16). It is reported that Ph_2CHK could initiate the polymerization of styrene, αMS, and even 2-(1-adamantyl)-5-vinylthiophene in a 13, 2.5, and 11% efficiency, respectively.[39,46,47] The observed anionic polymerizability, electrophilicity of C═C bonds, of **2** was apparently lower than those of these monomers based on the result using the Ph_2CHK initiator. Notably, the α-methyl substituent on the vinyl group of **2** significantly reduces the anionic polymerizability compared with that of the vinyl counterpart, 2-(1-adamantyl)-5-vinylthiophene (**AdVT**, Chart 1).

We next polymerized **3**, containing a longer π-conjugation system including a phenyl substituent, with *sec*-BuLi and K-Naph in THF at −78 °C for 1 h (runs 17 and 20). The reaction mixture exhibited a typical violet color, indicating the formation of a propagating carbanion. For each initiator, the conversion of **3** was not quantitative and was approximately 20%, suggesting a remarkably slow propagation rate. In fact, the polymerization of **3** quantitatively proceeded at −78 °C after 48−96 h to afford poly(**3**)s with tailored M_ns and narrow MWDs by the initiation with *sec*-BuLi, Li-Naph, and K-Naph (runs 18, 19, 21, and 22). In contrast to that of **2**, anionic polymerization of **3** was initiated with Ph_2CHK (run 23). Interestingly, the resulting polymer possessed the predicted molecular weight and a very narrow MWD (M_w/M_n = 1.07), indicating the quantitative initiation efficiency of Ph_2CHK. Furthermore, triphenylmethylpotassium (Ph_3CK), a π-conjugated carbanion bulkier than Ph_2CHK, initiated the polymerization of **3** (run 24), whereas the conversion of the monomer was only 6% even after 100 h. In this case, the observed M_n (17 kg/mol) of the resulting polymer was much higher than the calculated value (0.6 kg/mol), suggesting an extremely low initiation efficiency. Nevertheless, the results obtained with the Ph_2CHK and Ph_3CK initiators indicated that the anionic polymerizability of **3** was significantly higher than that of **2**.

Finally, anionic polymerization of **4**, a monomer bearing a strong electron-withdrawing cyano group, was attempted in THF at −78 °C. Since we anticipated that the anionic

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Table 2. Postpolymerization of 2−4 in THF at −78 °C[a]

run	monomer		initiator	M/I[b]	time (h)	M_n (kg/mol) calcd[c]	M_n (kg/mol) obsd[d]	M_w/M_n[e]
34	**2**	prepolymer	K-Naph	8	20	4.0	5.1	1.17
		postpolymer		10	20	9.1	12	1.09
35	**3**	prepolymer	K-Naph	12	72	4.9	4.4	1.08
		postpolymer		18	48	12	11	1.06
36	**4**	prepolymer	Ph_2CHK	38	20	5.6	6.2	1.05
		postpolymer		47	20	12	12	1.04

[a]Conversion ∼100%. [b]M/I = [monomer]/[initiator]. [c]M_n(calcd.) = (MW of monomer) × M/I + (MW of initiator residue). [d]M_n(obsd) was determined by SEC-RALLS equipped with refractive index (RI), light scattering (LS), and viscometer detectors. [e]M_w/M_n was determined by SEC calibration using polystyrene standards in THF.

polymerizability of **4** would be enhanced by the cyano group, we employed low nucleophilic anionic initiators such as diphenylmethyllithium (Ph_2CHLi) and Ph_2CHK for the polymerization (runs 25−29). Although the polymerization of **4** occurred with Ph_2CHLi and Ph_2CHK in THF at −78 °C, the conversion of **4** was 13 and 52% even after 2 h of reaction, respectively. The polymerization of **4** using an organolithium initiator seemed slower than that using the organopotassium initiator but was almost completed at −78 °C within 72 h (run 26). This is probably due to the different dissociation condition of the propagating carbanion between the lithium cation and potassium cation in THF. It is noteworthy that tailored poly(**4**) was produced by Ph_3CK with quantitative initiation efficiency because of the high electrophilicity of the carbon−carbon double bond of **4** (run 30). As expected, highly reactive radical anions, Li-Naph and K-Naph, could quantitatively give tailored poly(**4**)s (runs 31 and 32). The remarkably high anionic polymerizability of **4** was further demonstrated since even potassium *tert*-butoxide (*t*-BuOK), a typical alkoxide anion, could initiate the polymerization of **4** at −78 °C. Polymerization was completed within 100 h, but the initiation efficiency was low (run 33). These observed electrophilicities of **4** are remarkably higher than that of other monomers, such as **2**, **3**, St, and αMS, and are similar to that of the corresponding **CNVT** carrying the strong electron-withdrawing cyano group (Chart 1).[39] This effect also decreased the nucleophilicity of the resulting poly(**4**) anion, thereby suppressing the side reactions with the reactive cyano groups during the polymerization.

Postpolymerization of 2−4. The results of the homopolymerization of **2**−**4** indicated that molecular weight control was achieved in the resulting polymer, similar to the living anionic polymerization of **VT** monomers. To clarify the living character of the polymerization, we attempted the postpolymerization of **2**−**4**. For instance, **2** was reacted with K-Naph in THF at −78 °C for 20 h to complete the polymerization, and a second portion of **2** was added to the polymerization system (Table 2, run 34). Then, the system was allowed to react at −78 °C for another 20 h to complete the second-stage polymerization of **2**. The prepolymer and postpolymer yields were quantitative. Figure 3A shows that the SEC curve of the postpolymer of **2** shifts from that of the prepolymer to the high molecular weight side while maintaining a narrow MWD. This means that the propagating poly(**2**) is sufficiently stable in THF at −78 °C even after 20 h to reinitiate the second-stage polymerization. The postpolymerization of **3** and **4** was similarly conducted in THF at −78 °C under the corresponding suitable conditions for run 35 (**3**) using K-Naph after 72 h and for run 36 (**4**) using Ph_2CHK

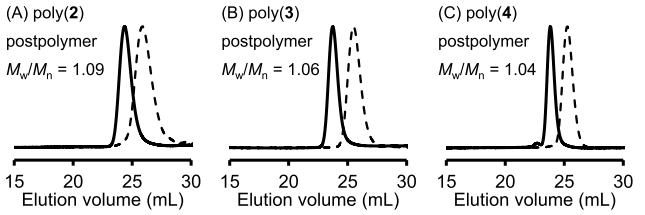

Figure 3. SEC curves of poly(**2**) (A: run 34), poly(**3**) (B: run 35), and poly(**4**) (C: run 36) at the first-stage polymerization (prepolymer, broken line) and at the second-stage polymerization (postpolymer, solid line). The M_w/M_n values of the postpolymers are shown.

after 20 h (Figure 3B and C). In both cases, after the completion of the first-stage polymerization, reinitiation reactions of the propagating carbanion to the second-feed monomer occurred quantitatively to form a postpolymer with well-defined structures. These results successfully demonstrated the stability of the chain-end carbanions of the living polymers derived from **2**−**4**.

Reversible Polymerization of 2−4. Based on the living character of the polymerization, we investigated the depolymerizability and equilibrium polymerizability of **2**−**4**. First, the polymerization of **2** was performed by using K-Naph in THF at −78 °C for 20 h to completely consume the monomer (Table S1). Then, the polymerization system was warmed to 0 °C for 1 h. After increasing the temperature, the polymerization system maintained red coloration, indicating the presence of carbanions. The ^{1}H NMR measurement of the system at 0 °C after 1 h revealed that the conversion of the monomer decreased from 100 to 14%, and monomer **2** was certainly recovered by the depolymerization. The SEC curve of the polymer (Figure 4A: M_n = 9.0 kg/mol) completely

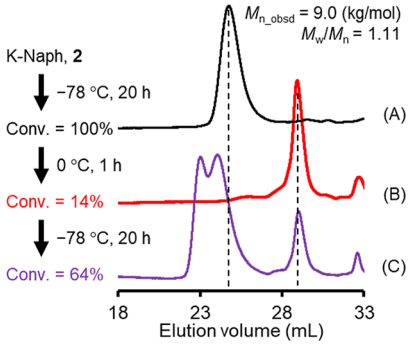

Figure 4. SEC curves of poly(**2**)s at −78 °C for 20 h (A), after heating at 0 °C for 1 h (B), and after cooling at −78 °C for 20 h (C).

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disappears at 0 °C, and a methanol insoluble part is confirmed as an oligomer by the SEC measurement (Figure 4B: M_n = 0.8 kg/mol). Finally, the depolymerized system at 0 °C was recooled to −78 °C for 20 h to shift the equilibrium state. After termination with methanol, the monomer conversion increased from 14 to 64% but not quantitatively. Figure 4C shows the SEC trace of the reaction mixture after cooling to −78 °C. The multimodal SEC trace suggests that the propagating carbanion of poly(**2**) is not completely stable at 0 °C for 1 h and is partially deactivated under the depolymerization conditions. In fact, the SEC trace in the oligomer region was in accordance with that of the depolymerized oligomer at 0 °C, and the bimodal SEC shape of the high molecular weight region was derived from the bifunctional living oligomer and the monofunctional living oligomer after partial deactivation. Since the concentration of the propagating carbanions significantly decreased by the partial deactivation at 0 °C, **2** was not completely consumed at −78 °C even after 20 h and the molecular weight of the replicated poly(**2**) was significantly greater than that of the original polymer.

Next, we similarly examined the equilibrium polymerizability of **3** with K-Naph. The results for **3** are in sharp contrast to those for **2**. As shown in Figure 5A and B, ideal

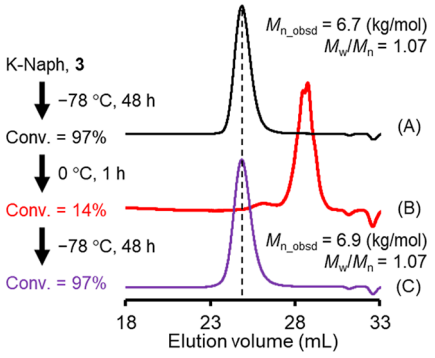

Figure 5. SEC curves of poly(**3**)s after the reaction at −78 °C for 48 h (A), after heating at 0 °C for 1 h (B), and after cooling at −78 °C for 48 h (C).

depolymerization behavior was observed in the SEC curves upon warming the polymerization system to 0 °C for 1 h. As expected, the conversion of **3** decreases from 97% to 14%. Furthermore, by cooling again to −78 °C for 48 h after the depolymerization, the polymerization proceeded again, and the depolymerized monomer was almost consumed (97% conversion). Interestingly, the SEC trace of poly(**3**) reproduced at −78 °C (Figure 5C) was identical to that before depolymerization (Figure 5A). Thus, it can be seen that **3** exhibits the behavior of ideal equilibrium polymerization, and the chain-end carbanion of poly(**3**) is stable under the depolymerization conditions at least at 0 °C for 1 h.

We then performed a similar experiment on **4** using the polymerization system obtained with Ph_2CHK in THF at −78 °C for 20 h (Figure 6A). However, a 58% yield of poly(**4**) was obtained as a methanol-insoluble part after warming the reaction mixture to 0 °C for 1 h. The broadened SEC curve of polymer as shown in Figure 6B indicated that the propagating chain end of **4** seemed to be in the equilibrium state at 0 °C. We then elevated the temperature from −78 to 30 °C to further investigate the depolymerizability of **4**. After warming

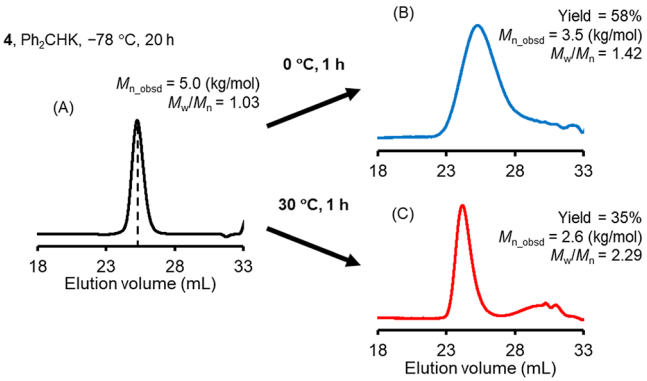

Figure 6. SEC curves of poly(**4**)s after the reaction at −78 °C for 20 h (A), after heating to 0 °C for 1 h (B), and after heating to 30 °C for 1 h (C).

to 30 °C for 1 h, the polymer was still obtained in 35% yield. Figure 6C shows the SEC trace containing the major high molecular weight and minor oligomer fractions. The former is the starting polymer deactivated before warming to 30 °C, and the latter is derived from the depolymerization of the living polymer. These results indicated that the terminal carbanion of poly(**4**) is not completely stable at 30 °C. Notably, some termination reactions occurred at 30 °C without broadening the MWD during depolymerization.

Thus, the depolymerization behavior of **2**−**4** 5-substituted **IPTs** was strongly influenced by the substituent at the 5-position of the thiophene ring. Only **3** afforded the stable propagating carbanion even at an elevated temperature at 0 °C and showed typical reversible equilibrium polymerizability depending on the polymerization temperature, similar to αMS and its derivatives. This is probably due to the extended π-conjugation system in **3**, which induces effective stabilization of the propagating carbanion and high electrophilicity of the monomer. Conversely, the active chain ends of **2** and **4** suffered from the inherent deactivation at 0−30 °C, although the propagating carbanions were proved to be stable at −78 °C from the results of the postpolymerization.

Thermodynamic Analysis of Anionic Polymerization of 3. It is demonstrated in the previous section that the chain-end carbanion of poly(**3**) is sufficiently stable not only at −78 °C but also at the elevated temperature of 0 °C under the depolymerization conditions. This allowed us to perform thermodynamic analysis of the anionic polymerization of **3** at different temperatures. Then, anionic polymerization of **3** was performed at temperatures ranging from −60 to −20 °C, and the reaction was terminated with methanol after an appropriate time to trace the conversion and the molecular weight.

We first carried out two polymerizations of **3** at −40 °C with K-Naph under different monomer concentrations ($[M]_0$), as shown in Table 3 (series 1,2). After initiation with K-Naph at −78 °C in the all-glass apparatus, the reaction solution was immediately divided and sealed in several ampules. Then, the sealed ampules were allowed to stand at −40 °C to follow the time conversion. The conversion of **3** was determined by gas chromatography (GC) and was found to increase with polymerization time, as expected. The conversion reached 88% at −40 °C within 24 h, but no further increase was detected, even after a longer reaction time. The propagation of **3** was followed by changes in the SEC curves of the resulting polymers (Figure 7). In fact, these were unimodal and shifted

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Table 3. Anionic Polymerization of 3 in THF at −40 °C[a]

run	time	conversion[b] (%)	$[M]_t$[b] (M)	M_n (kg/mol) calcd[c]	M_n (kg/mol) obsd[d]	M_w/M_n[e]
	Series 1, $[M]_0$ = 0.220 M, $M_{n,Calcd.}$ = 9.6 (kg/mol)					
A	1 h	72.6	0.054	7.0	7.1	1.10
B	2.2 h	80.2	0.038	7.7	8.3	1.08
C	6 h	86.3	0.026	8.3	8.3	1.11
d	24 h	88.8	0.022	8.5	8.3	1.24
e	48 h	88.2	0.023	8.5	8.4	1.33
f	72 h	87.0	0.025	8.4	8.1	1.34
	Series 2, $[M]_0$ = 0.192 M, $M_{n,Calcd.}$ = 9.0 (kg/mol)					
g	6 min	34.7	0.109	3.1	2.6	1.13
h	12 min	39.5	0.101	3.5	3.5	1.11
i	30 min	53.2	0.078	4.8	5.1	1.11
j	24 h	85.7	0.023	7.7	7.2	1.22

[a]Initiator: K-Naph. [b]Conversion and $[M]_t$ were measured by GC. [c]M_n(calcd.) = (MW of monomer) × M/I + (MW of initiator residue). [d]M_n(obsd) was determined by SEC-RALLS equipped with refractive index (RI), light scattering (LS), and viscometer detectors. [e]M_w/M_n was determined by SEC calibration using polystyrene standards in THF.

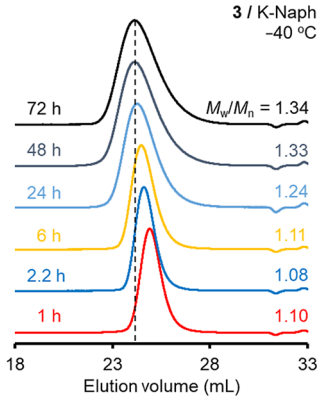

Figure 7. SEC curves of poly(3)s produced at −40 °C (Table 3, series 1).

to the high molecular weight side as the polymerization proceeded. It is noteworthy that the SEC curves gradually became broad ($M_w/M_n \approx 1.3$) after reaching the monomer conversion to be constant at −40 °C. This characteristic phenomenon of the MWD broadening has been predicted for the reversible equilibrium polymerization system in the literature,[48−50] while the MWD of the resulting polymer was initially narrow under the kinetic control. These results strongly indicated that the polymerization system at −40 °C reached the typical equilibrium state, where the polymerization and the reversible depolymerization coexist to result in the shuffling of the MWD.[48−50] In each experiment, similar equilibrium monomer concentrations ($[M]_e$ = 0.024 M) were obtained (Table 4).

Similar to the experiment at −40 °C, we performed the polymerizations of **3** by changing the temperature to −60, −50, −30, and −20 °C to determine the $[M]_e$ values, as summarized in Table 4 (Table S2). A long reaction time was required for each experiment to achieve an equilibrium state. The $[M]_e$ values under the equilibrium increased from 0.005 to 0.098 M as the polymerization was performed at −60 to −20 °C. Figure 8 shows a good linear relationship between $\ln[M]_e$

Table 4. Equilibrium Monomer Concentration of 3 in THF[a]

polymerization temp. (°C)	conversion (%)	$[M]_0$ (M)	$[M]_e$ (M)
−20[b]	46.1	0.170	0.098 ± 0.008
−30[c]	73.6	0.173	0.046 ± 0.008
−40[c]	86.2	0.176	0.024 ± 0.001
−50[b]	94.6	0.174	0.010 ± 0.001
−60[b]	97.5	0.178	0.0048 ± 0.0004

[a]Initiator; K-Naph. [b]Series 3; $M_{n,Calcd}$ = 9.0 (kg/mol). [c]Series 4; $M_{n,Calcd}$ = 8.4 (kg/mol).

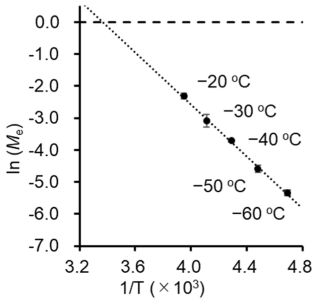

Figure 8. Plot of the equilibrium monomer concentration $[M]_e$ against T^{-1} for the polymerization of **3** in THF with K-Naph.

and the reciprocal temperature. The relationship between $[M]_e$ and the thermodynamic parameters is given by

$$\ln[M]_e = \Delta H/RT - \Delta S/R$$

where ΔH and ΔS are the enthalpy of polymerization and entropy, respectively, for a 1 M solution. From the good linear relationship shown in Figure 8, ΔH, ΔS, and the ceiling temperature (T_c) (=$\Delta S/\Delta H$) of **3** in THF were, respectively, estimated to be −8.09 ± 0.22 kcal mol^{-1}, −27.3 ± 0.9 cal mol^{-1} K^{-1}, and 24 °C. Thus, we demonstrated that **3** is a new vinyl monomer with typical reversible polymerizability under anionic conditions.

Table 5 summarizes the thermodynamic parameters of **3** and various isopropenyl monomers.[27−31,39] The calculated ΔH and ΔS values of **3** were close to the reported values of para-substituted α-methylstyrenes but were largely different from those of 2-isopropenylpyridine (ΔH = −6.2 kcal mol^{-1}, ΔS = −16.6 cal mol^{-1} K^{-1}). The obtained T_c value of **3** (24 °C) was in the range of those of para-substituted α-methylstyrenes (T_c = −3−27 °C), which was far from the value of 2-isopropenylpyridine (T_c = 100 °C) and 2-isopropenylthiazole (T_c = 139 °C). Thus, we successfully designed novel heteroaromatic compounds capable of reversible anionic polymerization by substituting the depolymerizable isopropenyl group in the thiophene framework. The isopropenyl substituent played a crucial role in decreasing the T_c value significantly and in achieving depolymerizability under anionic conditions, similar to αMS. The π-sufficient thiophene ring shows effects similar to those of benzene rings on the thermodynamic properties and the ceiling temperature in a series of isopropenyl monomers, in contrast to the properties of isopropenyl monomers possessing π-deficient rings such as pyridine and thiazole.

Solubility and Thermal Properties. Finally, we checked the solubility and thermal properties of novel polymers derived from **1**−**4**. The solubilities of the polymers of **IPTs** are very similar to those of their counterparts in **VT** derivatives with the corresponding substituents (Table 6). poly(**1**−**3**) were soluble

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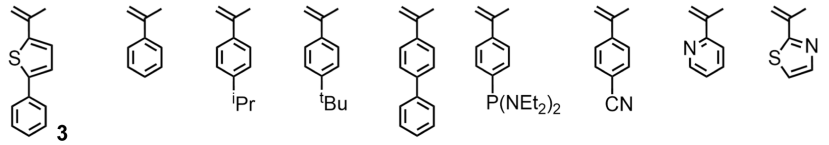
Table 5. Reported Kinetics Values of Isopropenyl Monomers



ΔH	(kcal mol−1)	−8.09±0.22	−8.02	−6.80	−7.10	−8.11	−6.51	−7.64	−6.2	−6.8
ΔS	(cal mol^{-1} K^{-1})	−27.3 ± 0.9	−28.8	−25.2	−25.5	−28.3	−23.0	−25.5	−16.6	−16.5
T_c	(°C)	24	5	−3	5	13	10	27	100	139
	reference	this study	19	27	28	29	30	31	37	37

Table 6. Solubilities and Thermal Properties of Polymers of IPTs and Polystyrene[e]

		solvent								
polymer	poly(IPTs)	poly(VTs)								
R	H (1)	Ad (2)	Ph (3)	CN (4)	H	Ad	Ph	CN	poly styrene	poly(αMS)
n-hexane	I	I	I	I	I	I	I	I	I	I
cyclohexane	I	S[a]	I	I	S[a]	S	I	I	S[a]	I
benzene	S	S	S	I	S	S	S	I	S	S
$CHCl_3$	S	S	S	Sw	S	S	S	Sw	S	S
THF	S	S	S	S	S	S	S	Sw	S	S
DMF	S	I	S	S	S	I	S	S	S	S
dimethyl sulfoxide	I	I	I	S	S	I	I	S	I	I
MeOH	I	I	I	I	I	I	I	I	I	I
water	I	I	I	I	I	I	I	I	I	I
T_g[b] (°C)	133	212	153	182	90	198	100	124	100[d]	167[d]
T_1[c] (°C)	256	268	297	289	359	362	359	337		
T_{10}[c] (°C)	300	321	319	319	382	386	380	370	398[d]	322[d]

[a]Above 40 °C. [b]By DSC measurement in the second heating scan, heating rate 20 °C/min. [c]By TGA measurement, heating rate 20 °C/min. [d]Reference 47. [e]I, insoluble; S, soluble; Sw, swelling.

in benzene, chloroform, and THF but insoluble in dimethyl sulfoxide (DMSO), methanol, and water. poly(**2**) possessing an alicyclic 1-adamantyl group was soluble in cyclohexane over 40 °C but insoluble in DMF, indicating the rather low polarity. In contrast, poly(**4**) with a cyano group exhibited polarity as it was insoluble in benzene and swollen in chloroform. In contrast, poly(**4**) is soluble in aprotic polar solvents such as THF, DMF, and DMSO.

The thermal properties of poly(**1**−**4**) were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). All the polymers of **1**−**4** started to decompose below 300 °C, while the corresponding poly(**VTs**) were stable until 340 °C. The 10% weight loss temperature (T_{10}) of polymers were observed between 300 and 321 °C, independent of the substituents. These T_{10} values were 50−80 °C lower than those of poly(**VTs**). The glass transition temperature (T_g) values of poly(**1**), poly(**2**), poly(**3**), and poly(**4**) were observed at 133, 212, 153, and 182 °C in the DSC profiles (Figure S27), respectively. These T_g values of poly(**IPTs**) were significantly higher (14−58 °C) than those of the polymers of **VT** derivatives carrying the same substituents (Table 6), indicating the clear effect of the α-methyl substituent on the main chain. The effects of the α-methyl substituent on the T_g values are well-known in the relationship between polystyrenes and the corresponding polymers of the αMS derivatives. In summary, the polymers of **IPTs** showed T_g values higher than those of the corresponding poly(**VTs**), but the(**IPTs**) exhibited ease of degradation under heating conditions. Both features were derived from the α-methyl substituents on the main chain.

CONCLUSIONS

In conclusion, we expanded the range of vinyl heterocycles capable of anionic polymerization. It was demonstrated that a series of novel 2-isopropenylthiophenes, **1**−**4**, underwent anionic polymerization in THF at −78 °C. Under suitable reaction conditions for each monomer, a polymer with the predicted molecular weight and narrow molecular weight distribution (M_w/M_n < 1.2) was obtained. Nevertheless, it was noted that considerable care regarding the initiator choice was necessary to polymerize **1** because a strong basic initiator such as *sec*-BuLi caused the inherent side reaction of the relatively acidic proton on the thiophene ring. The anionic polymerizability of **1**−**4**, **IPTs**, and the stability of the propagating carbanion were significantly affected by the substituents, similar to the case of the corresponding **VTs**. In particular, **3** and **4** showed fairly high polymerizability owing to the expanded π-electron system and the strong electron-withdrawing cyano group. Although the propagating carbanions derived from **2**−**4** were stable at −78 °C, only the propagating carbanion of poly(**3**) was stable even at 0 °C. Consequently, the equilibrium polymerization behavior of **3** similar to that of αMS was successfully demonstrated by changing the polymerization temperature between 0 and −60 °C. Thus, the T_c value of the anionic polymerization of **3** was determined to be 24 °C, which was close to the value of the αMS counterpart (4-isopropenylbiphenyl, T_c = 13 °C). The poly(**IPTs**) always demonstrated higher T_g values than the corresponding poly(**VTs**), while the poly(**IPTs**) started to decompose at temperatures below 300 °C. The anionic polymerizability of **IPTs** and their living characteristics should allow the synthesis

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of various architectural polymers containing thiophene rings in the poly(**IPTs**) segments.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.4c02845.

Experimental procedures, preparation of the chemical materials, synthesis of the polymers, schemes of synthesis, NMR spectra, reversible polymerization of **2**−**4** in THF, anionic polymerization of 3 in THF, and SEC, TGA, and DSC curves (PDF)

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Notes

The authors declare no competing financial interest.

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