Macromolecules

Stable and Highly Regioselective Anionic Polymerization of (Z)-1-Phenyl[3]dendralene

Tsukasa Takagi, Tomoyuki Toda, Masamitsu Miya, and Katsuhiko Takenaka*



reported 2-phenyl[3]dendralene (P3D), in terms of the nucleophilicity of the active chain end and regioselectivity in the propagation reaction.

INTRODUCTION

Dendralene, a hydrocarbon with an acyclic cross-conjugated structure,¹ is an interesting monomer for addition polymerization due to its conjugated system based on multiple 1,3dienyl frameworks (Figure 1). Since all dienyl structures can



Figure 1. Molecular structures of the dendralene family: (a) [n]dendralene, (b) [3]dendralene, (c) 2-phenyl[3]dendralene (P3D), (d) 2-(4-methoxyphenyl)[3]dendralene (MP3D), and (e) 2-hexyl[3]dendralene (H3D).

potentially undergo polymerization similar to 1,3-butadiene, a variety of microstructures can be formed in the resulting polymer. Earlier, we reported the successful polymerization of several 2-substituted [3]dendralene derivatives (Figure 1c-e) to afford well-defined linear polymers with predictable molecular weights and narrow molecular-weight distributions using anionic initiators such as potassium naphthalenide (K-Naph) and sec-butyllithium (s-BuLi).^{2,3} In the case of poly(P3D), two conjugate addition structures (1,4 and 4,6 structures) were observed, and their ratio was constant regardless of the polymerization conditions, while the vinyl addition structure was not detected. This indicated that the [3]dendralene derivatives underwent conjugate addition during anionic polymerization and that the polymerizabilities of the two conjugated systems contained in P3D are similar to those in anionic polymerization.

1,3-Butadiene derivatives with phenyl substituents can be applied as models to understand the polymerization of P3D because the molecular structure of 2-phenyl[3]dendralene is equivalent to that of 3-vinyl-substituted 2-phenyl-1,3-butadiene

Received:February 2, 2021Revised:April 6, 2021Published:April 30, 2021





pubs.acs.org/Macromolecules

(Scheme 1). The polymerization of several phenyl-substituted butadiene derivatives has been investigated by $cationic_i^{4,5}$

Scheme 1. Structural Similarity between Phenylbutadiene and Phenyl[3]dendralene



anionic,^{6–16} and coordination polymerization.^{17,18} Takegami et al. reported the relationship between the microstructure of the resulting polymer and the chemical reactivities of the monomer and propagating chain end for the anionic polymerization of 1phenyl-1,3-butadiene (1PB) and 2-phenyl-1,3-butadiene (2PB). The polymer obtained by the anionic polymerization of 2PB mainly contained the 1,4 structure and a small amount of the 1,2 structure, whereas that derived from 1PB contained a conjugate addition structure and a 3,4 addition structure.⁶ Further, when tert-butyllithium (t-BuLi) reacts with these butadiene derivatives, nucleophilic addition of the t-Bu carbanion occurs mainly at the C1 position for 2PB but only at the C4 position for 1PB.^{8,9} These results indicate that the olefinic carbon atoms are susceptible to nucleophilic addition and the microstructure of the resulting polymer is affected by the position of the phenyl substituent. Such a change in regioselectivity in nucleophilic addition is expected to occur in phenyl-substituted [3]dendralene, inspiring us to attempt the anionic polymerization of 1-phenyl[3]dendralene, a structural isomer of P3D.

1-Phenyl[3]dendralene was obtained by Sherburn and coworkers via the Wittig reaction as a mixture of the E/Zisomers. However, the E isomer ((E)-1-phenyl[3]dendralene) was highly unstable and underwent Diels–Alder dimerization even before it could be isolated.¹⁹ Thus, (Z)-1-phenyl[3]dendralene (1Z-P3D) was a likely candidate for the study of anionic polymerization of 1-phenyl[3]dendralene. However, the stereoselective synthesis of 1Z-P3D has not been reported. Earlier, various 2-substituted [3]dendralene derivatives were synthesized by nickel-catalyzed Kumada–Tamao–Corriu cross-coupling of 1,3-butadien-2-ylmagnesium chloride with alkenyl halides.²⁰ Based on this method, the cross-coupling reaction of butadienyl Grignard reagents with alkenyl halides, such as (Z)- β -bromostyrene, is expected to selectively afford 1Z-P3D under suitable conditions.

We first attempted to selectively synthesize 1Z-P3D by the cross-coupling of (Z)- β -bromostyrene with a Grignard reagent derived from chloroprene. Then, the anionic polymerization of 1Z-P3D was carried out with K-Naph in THF. In addition, the

effect of polymerization temperature and the microstructure of the resulting poly(1Z-P3D) was investigated using sizeexclusion chromatography and NMR spectroscopy. Herein, the difference in polymerization of P3D and 1Z-P3D is discussed with specific reference to the extent of delocalization of the propagating chain end.

EXPERIMENTAL SECTION

Materials. 2-Chloro-1,3-butadiene (chloroprene, 50% THF solution) was kindly donated by DENKA Co. Ltd., Japan. Before use, it was washed with 1000 mL of water to remove the solvent and dried over anhydrous magnesium sulfate, followed by distillation under reduced pressure. *trans*-Cinnamic acid was purchased from Kishida Chemical Co., Ltd., Japan. Other reagents were purchased from Tokyo Chemical Industry Co., Ltd., unless otherwise stated. (*Z*)-1-Phenyl[3]dendralene was synthesized by a procedure, as shown in Scheme 2. 2,3-Dibromo-3-phenylpropanoic acid and (*Z*)- β -





bromostyrene were synthesized by a procedure reported by Das et al.²¹ 1,3-Butadien-2-ylmagnesium chloride was prepared by a reported procedure using chloroprene and magnesium turnings in the presence of $ZnCl_2$.^{22,23} The cross-coupling reaction of 1,3-butadien-2-ylmagnesium chloride with (Z)- β -bromostyrene was carried out in reference to the procedure reported by Sherburn et al.²⁰ THF used as the polymerization solvent was purified by distillation from a sodium naphthalenide solution under high vacuum.

2,3-Dibromo-3-phenylpropanoic Acid. *trans*-Cinnamic acid (29.10 g) (196.4 mmol) and AcOH (100 mL) were placed in a two-necked round bottom flask charged with N₂ gas. Then, 43.39 g of bromine (216 mmol) was added dropwise to the solution. After stirring for 2 h, the reaction was quenched by pouring 100 mL of 1 M Na₂S₂O₃ aq. 2,3-Dibromo-3-phenylpropanoic acid was obtained quantitatively by filtration followed by washing with cold chloroform. The brominated product was used for the next step without further purification.

(Z)- β -Bromostyrene. Fifty grams of 2,3-dibromo-3-phenylpropanoic acid (162.3 mmol) and 180 mL of DMF were placed in a twonecked round bottom flask filled with N₂ gas. Triethylamine (Et₃N) (44.7 mL) (320 mmol) was added dropwise at 0 °C. Then, the mixture was stirred for 5 h at room temperature. The resultant mixture was treated with 100 mL of water and extracted using *n*pentane. The combined organic layer was washed with water and brine. The washed mixture was dried over by magnesium sulfate and concentrated in vacuo. Finally, (*Z*)- β -bromostyrene was isolated by fractional distillation (yield 87%, pale-yellow liquid, bp 61.2 °C/5 mmHg). **1,3-Butadien-2-ylmagnesium Chloride.** Magnesium turnings (7.97 g) (328 mmol) and anhydrous THF (120 mL) were placed in a two-necked round bottom flask equipped with a reflux condenser under N_2 gas. Prior to use, the magnesium surface was activated with 1 mL of 1,2-dibromoethane. After the activation was completed, ZnCl₂ (2.71 g) (19.9 mmol) was added to the mixture. A mixture of chloroprene (19.35 g) (219 mmol), anhydrous THF (80 mL), and a small amount of 1,2-dibromoethane was added dropwise with gently heating the flask. Then, the mixture was refluxed at 90 °C for 1 h.

(Z)-1-Phenyl[3]dendralene. (Z)- β -Bromostyrene (20.04 g) (109.3 mmol), Ni(dppp)Cl₂ (1.32 g) (2.42 mmol), and anhydrous THF (70 mL) were placed in a two-necked round bottom flask under N2 gas. 1,3-Butadien-2-ylmagnesium chloride (ca. 219 mmol) was added dropwise over 1 h at 0 °C. The mixture was then stirred for 1 h at the same temperature. The resulting mixture was treated with ice water and extracted using ethyl ether. The combined organic layer was washed with 1 M HCl, sat. NaHCO3 aq., and brine. The washed mixture was dried over magnesium sulfate and concentrated in vacuo. Finally, 1Z-P3D was isolated by fractional distillation. (yield 63%, clear liquid, bp 54.5 °C/4 mmHg) ¹H NMR (CDCl₃): $\delta = 5.19-5.13$ $(3H, m, H_{c}, H_{d}, H_{o}), 5.38 (1H, d, J = 17.4 H_{u}, H_{f}), 6.21 (1H, d, J =$ 12.3 Hz, H_b), 6.48 (1H, dd, J = 17.4, 10.5 Hz, H_c), 6.59 (1H, d, J =12.3 Hz, H_a), 7.21–7.41 (5H, m, H_h, H_i, H_i), ¹³C NMR (CDCl₃): δ = 115.6, 118.1, 127.0, 127.9, 128.0, 128.8, 131.7, 136.8, 137.6, 143.9 (Scheme 3).

Scheme 3. Chemical Structure of 1Z-P3D



Anionic Polymerization. The synthesized monomer was purified by distillation under high vacuum in the presence of phenylmagnesium bromide, diluted with THF, and then sealed in ampules with breakable seals. All anionic polymerizations were carried out under high vacuum using the break-seal method.²⁴ First, a THF solution of the initiator (K-Naph) was introduced into the reactor and cooled to -78 °C. Then, the entire monomer solution was added to the reactor at the same temperature, and the reactor was placed in an aimed constant-temperature bath and held for a fixed time. Finally, degassed ethanol was added to terminate the polymerization.



Measurements. All NMR spectra were recorded in CDCl₃ using a JEOL JNM-AL-400 spectrometer. The solvent peak was used as a reference. One-dimensional ¹H and ¹³C spectra were obtained with 32 768 data points, 15 and 220 ppm spectral widths, 45 and 30° pulse widths, and 7 and 5 s repetition times, respectively. A 2D H–H COSY spectrum was obtained with 1024 raw data points and 256 column data points with zero filling. A 2D C–H HMQC spectrum was obtained with 512 raw data points and 512 column data points. GC-MS spectra were obtained using a Shimadzu QP-2010plus instrument with electron impact ionization. A size-exclusion chromatogram (SEC) was obtained at 40 °C using a TOSOH HLC-8220 instrument equipped with three polystyrene gel columns (TOSOH TSKgel G4000H_{HR}, G3000H_{HR}, and G2000H_{HR} (7.8 mm × 30 cm)), UV (254 nm), and refractive index (RI) detectors. THF was used as the carrier solvent at a flow rate of 1 mL/min.

RESULTS AND DISCUSSION

Anionic Polymerization of 1Z-P3D. The anionic polymerization of 1Z-P3D was carried out in THF using K-Naph as an initiator. Upon addition of 1Z-P3D, the characteristic green color of K-Naph immediately changed to dark red. This color was unchanged and disappeared only when a small amount of ethanol was added to terminate the reaction. The polymer was obtained by pouring the solution into a large excess of methanol; no insoluble fraction was formed during polymerization. Table 1 summarizes the results of the anionic polymerization of 1Z-P3D under various conditions. Polymers of predictable molecular weights based on the monomer-to-initiator ratio were obtained at -78 °C, with narrow molecular-weight distribution $(M_w/M_n < 1.26)$. The conversion increased with time and 24 h were required to achieve quantitative conversion. Although a slight increase in $M_{\rm w}/M_{\rm n}$ was observed with time, the shape of the SEC chromatogram remained unimodal. It is worth noting that the polymerization rate of 1Z-P3D was significantly lower than that of P3D. According to a previous study, the anionic polymerization of P3D was complete in ~90 min under THF/ K-Naph conditions at -78 °C. The SEC chromatograms of poly(1Z-P3D)s produced under different conditions (Figure 2) showed that the molecular-weight distributions remained unimodal during 24 h in the polymerizations carried out at -78 °C. This indicated that side reactions, such as nucleophilic addition of a propagating carbanion to a conjugated double bond in the polymer chain, did not occur. Surprisingly, the polymerization of 1Z-P3D proceeded without broadening of the molecular-weight distribution, even at -40 and 0 °C,

1Z-P3D		K-Naph						$M_{\rm n}~({\rm kg/mol})$		
mol/L	mmol	mol/L	mmol	[M]/[I]	temp. (°C)	time (h)	conv. ^{<i>a</i>} (%)	calcd ^b	SEC	$M_{ m w}/M_{ m n}$
0.576	4.33	0.0702	0.143	30	-78	1	57	5.4	5.2	1.19
0.576	4.98	0.0702	0.206	24	-78	6	94	7.1	7.4	1.22
0.576	6.12	0.0702	0.199	31	-78	12	95	9.2	9.4	1.21
0.576	7.08	0.0702	0.278	25	-78	24	100	7.9	8.2	1.26
0.576	6.15	0.0702	0.229	27	-40	6	97	8.1	8.3	1.17
0.576	6.34	0.0702	0.194	33	0	6	99	10.1	9.3	1.16
0.576	6.99	0.0719	0.270	26	40	6	100	8.1	3.2 ^c	1.68 ^c
0.576	7.73	0.0719	0.154	50	-78	48	100	15.7	16.3	1.21
0.669	10.4	0.0719	0.070	149	-78	168	100	46.3	68.7	1.23

^{*a*}Calculated from the amount of residual 1Z-P3D estimated by GC in a methanol solution after precipitation. ^{*b*} M_n (calcd) = 2 × [M]/[I] × (MW of 1Z-P3D) × (conversion)/100. ^{*c*}For low-molecular-weight samples, other polystyrene gel columns (TOSOH TSKgel G3000H_{HR}, G2000H_{HR}, and G1000H_{HR}) were used.

https://doi.org/10.1021/acs.macromol.1c00260 Macromolecules 2021, 54, 4326-4332

Article



Figure 2. SEC chromatograms of poly(1Z-P3D) prepared under different polymerization conditions. (a) -78 °C, 1 h, (b) -78 °C, 6 h, (c) -78 °C, 24 h, (d) -40 °C, 6 h, (e) 0 °C, 6 h, and (f) 40 °C, 6 h.

indicating the low reactivity of the propagating chain end to produce a high-molecular-weight fraction. On the other hand, the anionic polymerization of P3D at 0 °C yielded a polymer with broad and multimodal molecular-weight distribution in just 10 min. This was presumably due to the nucleophilic addition of the propagating species to the dienyl structure in another polymer chain. When polymerization was carried out at 40 °C, the M_n value of the resulting poly(1Z-P3D) was much smaller than the calculated value, and the molecularweight distribution was much broader. The increase in the lowmolecular-weight fraction at high temperature suggested that the ideal propagation was inhibited by some side reactions such as the Diels-Alder cycloaddition of monomers and β hydride elimination from the propagating species during polymerization. However, the shape of the SEC chromatogram was still unimodal and the formation of high-molecular-weight fractions was not observed, indicating that nucleophilic addition of the propagating chain end to other polymer chains did not occur. Compared with typical anionic polymerization, the molecular-weight distribution of poly(1Z-P3D) prepared at -78 °C was relatively broad. Since $M_{\rm w}/M_{\rm n}$ was decreased by elevating polymerization temperature, it is assumed that the initiation of 1Z-P3D was slow relative to typical hydrocarbon monomers and it resulted in the broadening of molecularweight distribution. Polymerization with a high monomer/ initiator ratio ([M]/[I] = 50, 149) was also successfully carried out at -78 °C to afford the polymer with narrow and unimodal molecular-weight distributions. These experiments clearly indicate that the nucleophilicity of the propagating chain end derived from 1Z-P3D is much lower than that of P3D. Presumably, the anionic polymerization of 1Z-P3D proceeded with much higher stability than that of P3D due to the delocalization of the negative charge on the propagating chain end (Scheme 4), attributed to the phenyl group at the terminal position of the butadienyl framework. As reported earlier by us, the electron-deficient character of the central C = C double

Scheme 4. Schematic Illustration of Negative Charge Delocalization on the Active Chain End in the Polymerization of 1Z-P3D for Nucleophilic Attack



bond of 2-phenyl[3]dendralene was indicated by the ¹³C NMR chemical shift of the monomer. Thus, the C4 position of 2phenyl[3]dendralene derivatives is expected to be the most favorable for nucleophilic attack. In the case of P3D, the negative charge produced by the addition of a propagating anion to the C4 position can be delocalized only within the [3]dendralene framework. In other words, the phenyl ring in P3D does not participate in the conjugated system, and the 4,1-anion is stabilized by resonance. Thus, we expect the reactivity of the propagating chain end derived from 1Z-P3D to be significantly lowered by the effective conjugation between the butadienyl structure and the phenyl ring. If the resonance with a phenyl substituent affects the polymerization behavior of [3]dendralene, it could also influence the ease of polymerization of butadienyl structures in [3]dendralene molecules. In such a case, the microstructure of the resulting polymer would be significantly affected by the phenyl

Scheme 5. Possible Microstructures Expected to be Formed by the Polymerization of 1Z-P3D





substituent. Therefore, the microstructure of the obtained poly(1Z-P3D) was studied in detail.

Microstructure. [3]Dendralene derivatives are able to form multiple microstructures because of their unique conjugated system when they are polymerized. Because these unsaturated hydrocarbons contain two cross-conjugated butadienyl frames, the resulting polymers can display complex microstructures involving five possible structures (Scheme 5). We carefully analyzed the microstructure of poly(1Z-P3D) using NMR spectroscopy. In the aliphatic proton region of the ¹H NMR spectrum of the obtained polymer (Figure 3), signals of allylic methylene protons were observed at 1.6–2.3 ppm. In the olefinic region, two signals attributed to vinyl protons were observed at 5.1 (= CH_2) and 6.5 ppm (=CH-). A shoulder peak observed at 5.3 ppm could be attributed to another double bond in the polymer, which is not the vinyl group of

the side chain. Aromatic proton signals were observed at 6.5-7.4 ppm. Interestingly, a characteristic resonance that was not seen in poly(P3D) was observed at 3.7 ppm in the ¹H NMR spectrum of poly(1Z-P3D). This was likely an allylic methine proton signal, which shifted downfield due to the effect of the neighboring phenyl group. Among the possible microstructures of poly(1Z-P3D), such a methine proton is contained only in the 1,4 structure. If this signal is indeed due to the 1,4 structure, its content was estimated as >90% from the ratio of intensities of the signal at 3.7 ppm and the aromatic proton signals. In a previous study, it was reported that poly(P3D) is composed of only the conjugate addition structure and that the contents of 1,4 and 4,6 structures were almost equal. Thus, the anionic polymerization of 1Z-P3D is highly regioselective compared to that of P3D.



Figure 5. 2D NMR spectra of poly(1Z-P3D): (a) C-H HMQC and (b) H-H COSY.

To confirm that the signal at 3.7 ppm corresponds to the allylic methine proton, we carried out a detailed structural analysis based on distortionless enhancement by polarization transfer (DEPT) and 2D NMR spectroscopy. Figure 4 shows the ¹³C NMR spectrum of poly(1Z-P3D). A comparison of the ordinary complete proton-decoupled spectrum and the DEPT135 spectrum showed secondary carbon signals at 41 $(-CH_2-)$ and 114 ppm (=CH₂). Interestingly, the upward signal at 42 ppm, even in DEPT135, indicated a tertiary carbon. This implied that poly(1Z-P3D) prepared by anionic polymerization contains both aliphatic methine and methylene structures. In the C-H HMQC spectrum (Figure 5a) of poly(1Z-P3D), the proton signal at 3.7 ppm exhibited a cross peak with the tertiary carbon signal at 42 ppm, indicating that it could be attributed to the aliphatic methine proton. In the H-H COSY spectrum (Figure 5b) of poly(1Z-P3D), the methine proton signal at 3.7 ppm exhibited cross peaks with the signals at 2.2 $(-CH_2-)$ and 5.3 ppm (=CH-), further establishing that the signal at 3.7 ppm was due to the allylic methine proton of the 1,4 structure. Considering these results, the two conjugated systems of 1Z-P3D appeared to possess significantly different reactivities; the 1,4 conjugated system exhibited much higher polymerizability compared to the 4,6 conjugated system, and thus, the resulting polymer contained a predominant amount of the 1,4 structure. The different reactivities of the two conjugated systems could be explained by the effective conjugation between the terminal phenyl group and the butadienyl framework on the propagating chain end of poly(1Z-P3D). The delocalization energy due to resonance with the phenyl group reduces the activation energy of the next 1,4 addition; thus, the reaction kinetics is faster than that of 4,6 addition. Consequently, poly(1Z-P3D) had a large 1,4 structure content, and the anionic polymerization of 1Z-P3D was highly regioselective. Further investigations of the kinetics of propagation of these monomers using DFT calculations are underway. The details will be reported in the near future.

CONCLUSIONS

(Z)-1-Phenyl[3]dendralene (1Z-P3D) was successfully synthesized by the cross-coupling reaction of (Z)- β -bromostyrene with 1,3-butadien-2-ylmagnesium chloride in the presence of Ni(dppp)Cl₂. The anionic polymerization of 1Z-P3D using K-Naph as an initiator in THF afforded the polymer with predictable molecular weight and narrow molecular-weight distribution. The rate of polymerization of 1Z-P3D was significantly slow and the active chain-end carbanion was very stable over a wide temperature range from -78 to 0 °C, suggesting that the chain-end carbanion was effectively stabilized by the resonance effect of the phenyl substituent introduced at the C1 position. The microstructure of the resulting poly(1Z-P3D) exhibited a higher content of the 1,4 addition structure (>90%), indicating that 4,1 conjugate addition occurred preferentially in the propagation. Thus, the anionic polymerization of 1Z-P3D was significantly more stable and regioselective than that observed for P3D.

AUTHOR INFORMATION

Corresponding Author

Katsuhiko Takenaka – Department of Materials Science and Technology, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan; Email: ktakenak@ vos.nagaokaut.ac.jp

Authors

- Tsukasa Takagi Department of Materials Science and Technology, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan; orcid.org/0000-0002-5780-1779
- **Tomoyuki Toda** Department of Materials Science and Technology, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan
- Masamitsu Miya Department of Materials Science and Technology, Nagaoka University of Technology, Nagaoka, Niigata 940-2188, Japan

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.macromol.1c00260

Notes

The authors declare no competing financial interest.

REFERENCES

(1) Payne, A. D.; Bojase, G.; Paddon-Row, M. N.; Sherburn, M. S. Practical Synthesis of the Dendralene Family Reveals Alternation in Behavior. *Angew. Chem., Int. Ed.* **2009**, *48*, 4836–4839.

(2) Takenaka, K.; Amamoto, S.; Kishi, H.; Takeshita, H.; Miya, M.; Shiomi, T. Anionic Polymerization of 2-Phenyl[3]Dendralene and 2-(4-Methoxyphenyl)[3]Dendralene. *Macromolecules* **2013**, *46*, 7282–7289.

(3) Takamura, Y.; Takenaka, K.; Toda, T.; Takeshita, H.; Miya, M.; Shiomi, T. Anionic Polymerization of 2-Hexyl[3]Dendralene. *Macromol. Chem. Phys.* **2018**, *219*, No. 1700046.

(4) Asami, R.; Hasegawa, K.; Onoe, T. Cationic Polymerization of Phenylbutadienes. I. Cationic Polymerization of Trans-1-Phenyl-1,3-Butadieiie. *Polym. J.* **1976**, *8*, 43–52.

(5) Asami, R.; Hasegawa, K. Cationic Polymerization of Phenylbutadienes. III. Cationic Polymerization of 2-Phenyl-1,3-Butadiene. *Polym. J.* **1976**, *8*, 67–73.

(6) Suzuki, T.; Tsuji, Y.; Takegami, Y. Microstructure of Poly(1-Phenylbutadiene) Prepared by Anionic Initiators. *Macromolecules* **1978**, *11*, 639–644.

(7) Suzuki, T.; Tsuji, Y.; Takegami, Y.; Harwood, H. J. Microstructure of Poly(2-Phenylbutadiene) Prepared by Anionic Initiators. *Macromolecules* **1979**, *12*, 234–239.

(8) Suzuki, T.; Tsuji, Y.; Watanabe, Y.; Takegami, Y. Characterization of Living Anion Chain End of Oligomeric 1-Phenyl-1,3-Butadienyllithium. *Polym. J.* **1979**, *11*, 651–660.

(9) Suzuki, T.; Tsuji, Y.; Watanabe, Y.; Takegami, Y. Characterization of Living Anion Chain End of Oligomeric 2-Phenyl-1, 3-Butadienyllithium. *Polym. J.* **1979**, *11*, 937–945.

(10) Tsuji, Y.; Suzuki, T.; Watanabe, Y.; Takegami, Y. Active Species in Anionic Polymerization of Phenylbutadienes—Reactivity of Model Anions—. *Polym. J.* **1981**, *13*, 1099–1110.

(11) Tsuji, Y.; Suzuki, T.; Watanabe, Y.; Takegami, Y. Anionic Block Copolymerization of Phenylbutadienes with Styrene or Butadiene. *Macromolecules* **1981**, *14*, 1194–1196.

(12) Ambrose, R. J.; Hergenrother, W. L. Structure of Anionic Poly(2-Phenylbutadiene). *Macromolecules* **1972**, *5*, 275–279.

(13) Kase, T.; Imahori, M.; Komiyatani, T.; Itoh, K.; Isono, Y.; Fujimoto, T. Molecular Characterization of Poly(2-Phenyl-1,3-Butadiene) Prepared by Anionic Living Polymerization. *Kobunshi Ronbunshu* **1990**, 47, 17–24.

(14) Hirao, A.; Sakano, Y.; Takenaka, K.; Nakahama, S. Anionic Living Polymerization of 2,3-Diphenyl-1,3-Butadiene. *Macromolecules* **1998**, 31, 9141–9145.

(15) Tsuji, Y.; Suzuki, T.; Watanabe, Y.; Takegami, Y. Anionic Polymerizations of 1-(2-Methoxyphenyl)-1,3-Butadiene and 1-(4-Methoxyphenyl)-1,3-Butadiene—Microstructures of Polymers and Characterizations of Living Anion Chain Ends—. *Polym. J.* **1981**, *13*, 651–656.

(16) Kosaka, Y.; Kawauchi, S.; Goseki, R.; Ishizone, T. High Anionic Polymerizability of Benzofulvene: New Exo-Methylene Hydrocarbon Monomer. *Macromolecules* **2015**, *48*, 4421–4430.

(17) Pragliola, S.; Cipriano, M.; Boccia, A. C.; Longo, P. Polymerization of Phenyl-1,3-Butadienes in the Presence of Ziegler-Natta Catalysts. *Macromol. Rapid Commun.* **2002**, *23*, 356–361.

(18) Jiang, Y.; Kang, X.; Zhang, Z.; Li, S.; Cui, D. Syndioselective 3,4-Polymerization of 1-Phenyl-1,3-Butadiene by Rare-Earth Metal Catalysts. ACS Catal. 2020, 10, 5223–5229.

(19) Toombs-Ruane, H.; Pearson, E. L.; Paddon-Row, M. N.; Sherburn, M. S. On the Diels-Alder Dimerisation of Cross-Conjugated Trienes. *Chem. Commun.* **2012**, *48*, 6639–6641.

(20) Bradford, T. A.; Payne, A. D.; Willis, A. C.; Paddon-Row, M. N.; Sherburn, M. S. Cross-Coupling for Cross-Conjugation: Practical Synthesis and Diels–Alder Reactions of [3]Dendralenes. *Org. Lett.* **2007**, *9*, 4861–4864.

(21) Das, S. K.; Roy, S.; Khatua, H.; Chattopadhyay, B. Ir-Catalyzed Intramolecular Transannulation/C(Sp 2)–H Amination of 1,2,3,4-Tetrazoles by Electrocyclization. *J. Am. Chem. Soc.* **2018**, *140*, 8429–8433.

(22) Sultanov, N. T.; Mekhtiev, S. D.; Efendieva, T. G.; Kodzhaeva, Sh. Ya.; Alieva, M. A.; Balakishieva, M. M.; Mamedov, F. A. 2-Chloromagnesium-1,3-butadiene. *Chem. Abstr.* **1971**, *74*, No. 142040.

(23) Nunomoto, S.; Yamashita, Y. Reaction of 2-(1,3-Butadienyl)
 Magnesium Chloride with Carbonyl Compounds and Epoxides. A
 Regioselectivity Study. J. Org. Chem. 1979, 44, 4788–4791.

(24) Uhrig, D.; Mays, J. W. Experimental Techniques in High-Vacuum Anionic Polymerization. J. Polym. Sci., Part A: Polym. Chem. 2005, 43, 6179–6222.