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Self-Alternating Polymerization of *m*-Vinyl-1,1-diphenylethylene and Cyclopolymerization of *o*-Vinyl-1,1-diphenylethylene

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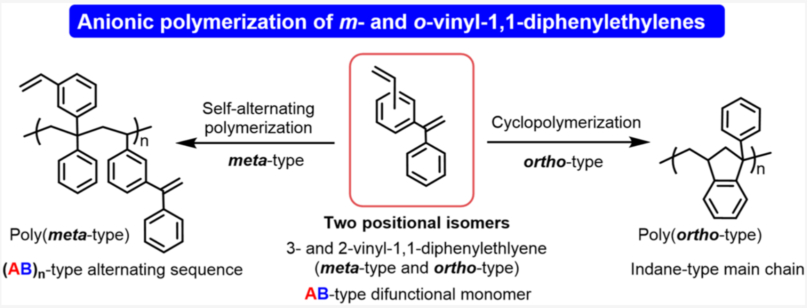

ABSTRACT: 4-Vinyl-1,1-diphenylethylene (***p*-VDPE**)—an AB-type difunctional monomer containing two reactive C═C bonds—undergoes anionic polymerization via intermolecular crossover propagation on styrene and 1,1-diphenylethylene frameworks in an alternating manner. In this study, the anionic polymerization behavior of the positional isomers of ***p*-VDPE**, 3-vinyl-1,1-diphenylethylene (***m*-VDPE**), and 2-vinyl-1,1-diphenylethylene (***o*-VDPE**) was investigated under various conditions in tetrahydrofuran. Their anionic polymerization produced soluble polymers with predictable molecular weights and relatively narrow molecular weight distributions (M_w/M_n = 1.14−1.44). The polymer of ***m*-VDPE** possessed a unique polymeric structure corresponding to the $(AB)_n$-type sequence, indicating that the anionic self-alternating polymerization of ***m*-VDPE** proceeded similarly to that of ***p*-VDPE**. In contrast, the polymer of ***o*-VDPE** had an annular Indane-type main chain with a cyclization efficiency of 68−82%, suggesting that ***o*-VDPE** undergoes cyclopolymerization involving an intramolecular cyclization reaction. Thus, the substitution position of the vinyl group in **VDPE** framework strongly affects the polymerization behavior of the AB-type difunctional monomer.

■ INTRODUCTION

Difunctional vinyl monomers, such as *p*-divinylbenzene, ethylene glycol di(meth)acrylate, and *N*,*N*′-methylenediacrylamide, are typically used as cross-linking reagents for the addition polymerization of various vinyl monomers, since both vinyl groups in these difunctional monomers participate in the polymerizations to produce insoluble polymers.[1−5] The selective anionic polymerization of *p*-divinylbenzene produces a linear polymer that possesses a predicted molecular weight and narrow molecular weight distribution (MWD; M_w/M_n < 1.1) under specific anionic conditions.[6,7] While such controlled polymerization of symmetric AA-type difunctional vinyl monomers is rather difficult and limited, the A or B vinyl group in the asymmetric AB-type difunctional monomers, such as allyl methacrylate,[8,9] 2-vinyloxyethyl methacrylate,[10,11] oligo(ethylene glycol) methacrylate vinyl ethers,[12,13] 4-vinylbenzyl methacrylate,[14] and 4-isopropenylstyrene,[15] can be chemoselectively polymerized to produce soluble and linear $(A)_n$ or $(B)_n$ polymers, depending on the polymerization conditions.

Another possible polymerization mode for difunctional vinyl monomers is cyclopolymerization, wherein the two vinyl groups participate in both the intramolecular reaction (cyclization) and intermolecular propagation.[16,17] Since the early report on the cyclopolymerization of diallyldimethylammonium salt,[18−20] cyclopolymerization of numerous monomers have been shown to proceed to form five- or six-membered ring structures, such as *N*-substituted di(meth)acrylamides,[21,22] (meth)acrylic anhydrides,[23,24] divinyl acetals,[25,26] and 1,5-hexadiene.[27,28] In an ideal cyclopolymerization of divinyl monomers, the resulting polymer has a fully annulated main chain, and all vinyl groups are fully consumed through the successive reactions of cyclization and subsequent intermolecular propagation. This means that cyclopolymerization is in contrast to the aforementioned selective polymerizations,[6−15] which completely retain the residual vinyl group

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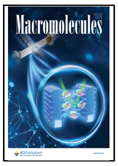

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Scheme 1. Anionic Polymerization of 4-Vinyl-1,1-diphenylethylene (*p*-VDPE) Derivatives, and Positional Isomers (*m*-VDPE and *o*-VDPE) Involving Self-Alternating Polymerization and Cyclopolymerization

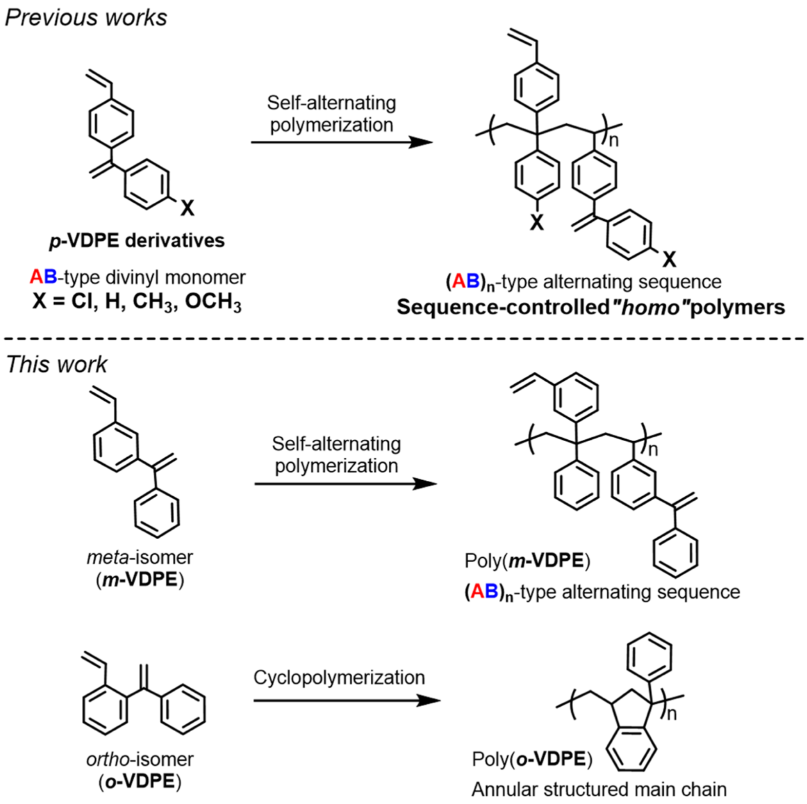


Table 1. Anionic Polymerization of *m*-VDPE and D3-*m*-VDPE in THF

run	monomer (mmol)	initiator (mmol)	temp. (°C)	time (h)	M/I[a]	yield[b] (%)	M_n (kg/mol) calcd.[c]	M_n (kg/mol) SEC[d]	M_w/M_n[d]
p-1[e]	***p*-VDPE**, 2.26	*s*-BuLi, 0.102	−78	72	22	37	1.7	2.4	1.19
m-1	***m*-VDPE**, 2.22	*s*-BuLi, 0.101	−78	72	22	48	2.3	2.2	1.23
m-2	***m*-VDPE**, 1.94	Ph_2CHLi, 0.090	−78	72	22	26	1.3	1.4	1.19
m-3	***m*-VDPE**, 2.16	Ph_2CHK, 0.101	−78	72	21	27	1.3	1.2	1.17
m-4	***m*-VDPE**, 2.27	Ph_2CHK, 0.028	−40	72	81	73	12.2	14.5	1.14
m-5	***m*-VDPE**, 1.88	Ph_2CHK, 0.088	0	3	21	97	4.4	3.3	1.27
m-6	***m*-VDPE**, 2.34	Ph_2CHK, 0.116	0	72	20	100	4.4	4.4	2.06
m-D3-1	**D3-*m*-VDPE**, 2.18	Ph_2CHK, 0.113	−78	72	19	39	1.7	1.8	1.27
m-D3-2	**D3-*m*-VDPE**, 2.10	Ph_2CHK, 0.101	0	3	21	88	4.0	3.7	1.30

[a] M/I = [monomer]/[initiator]. [b] Yield of the polymer after precipitation and freeze-drying from benzene. [c] M_n calcd. = [(MW of the monomer) × (M/I) × Yield] + initiator moiety. [d] Determined by GPC equipped with RI detector using polystyrene standards in THF. [e] From ref 37.

in each repeating unit. However, to improve the efficiency of the cyclopolymerization of difunctional vinyl monomers, intramolecular cyclization is preferred over intermolecular propagation. Various elaborate monomer designs[29−36] have been employed to promote intramolecular cyclization, such as implanting a substrate that induces noncovalent interactions[31,32] and introducing a bulky substituent for the deliberate utilization of steric effects (e.g., Thorpe−Ingold effect).[35,36]

Beyond the conventional examples, including selective and cyclopolymerizations, we have recently proposed and demonstrated a new perspective on the polymerization of the specially designed AB-type difunctional vinyl monomers (Scheme 1).[37,38] The anionic "self-alternating polymerization" of 4-vinyl-1,1-diphenylethylene (***p*-VDPE**), featuring two C=C bonds derived from styrene (St, A) and 1,1-diphenylethylene (DPE, B) frameworks connected with π-conjugation, afforded a well-defined "homo"polymer with an alternating sequence structure. In this novel polymerization mechanism, the A and B frameworks alternatingly participated in propagation in an intermolecular crossover manner to form a polymer carrying two types of residual vinyl groups in a 1:1 ratio. Not only ***p*-VDPE** but also its 4-substituted derivatives carrying chloro (**ClVDPE**), methyl (**MeVDPE**), and methoxy (**MeOVDPE**) groups undergo self-alternating polymerization. The non-homopolymerizable character of DPE and its derivatives are crucial in providing a repeating unit composed of polymerized St and DPE frameworks arranged alternatingly.

In this study, we examine the anionic polymerizations of two positional isomers of ***p*-VDPE**: 3-vinyl-1,1-diphenylethylene (*meta* type, ***m*-VDPE**) and 2-vinyl-1,1-diphenylethylene (*ortho* type, ***o*-VDPE**). We can predict that the two reactive C=C bonds in ***m*-VDPE** and ***o*-VDPE** are closer than those in ***p*-**

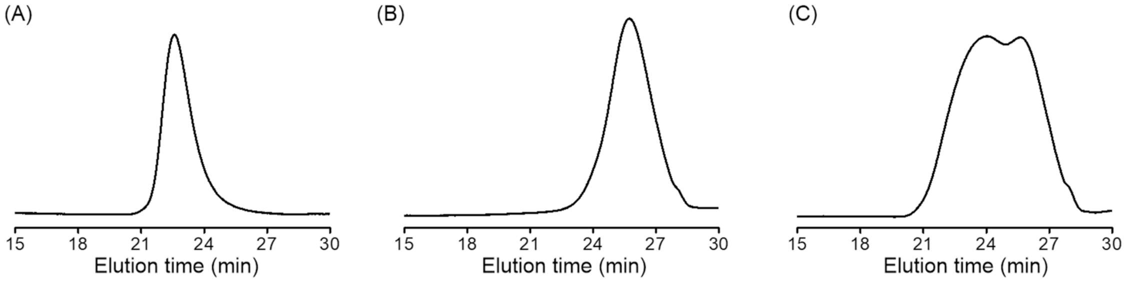


Figure 1. SEC curves of poly(***m*-VDPE**); m-4 (A), m-5 (B), and m-6 (C).

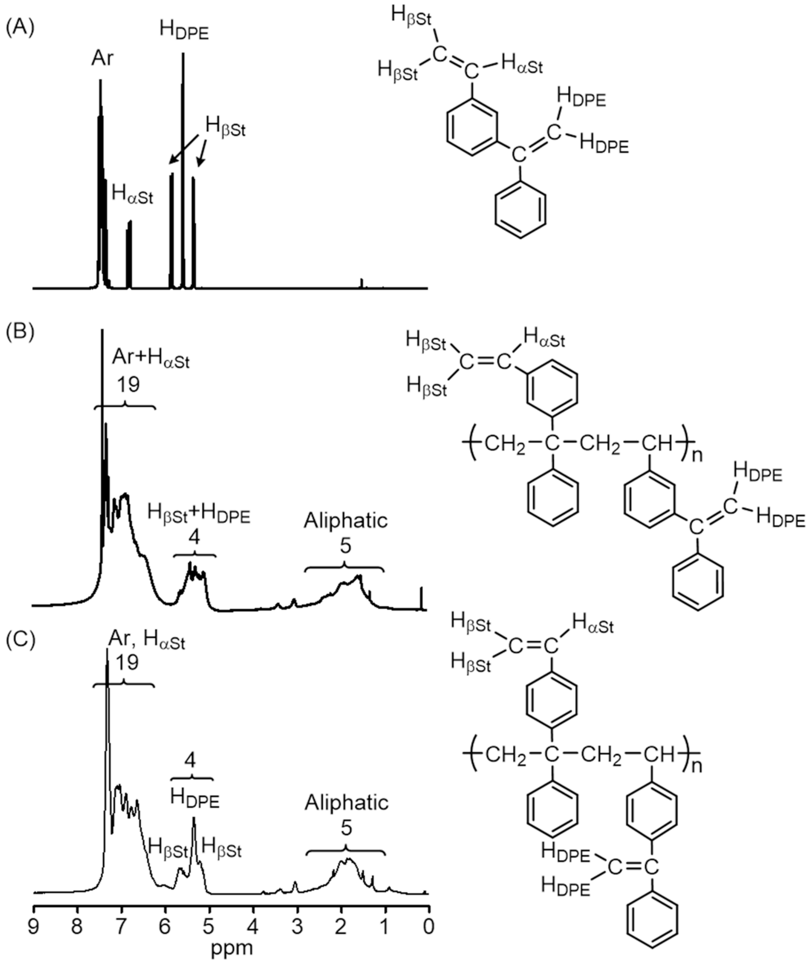


Figure 2. ^{1}H NMR spectra of ***m*-VDPE** (A) poly(***m*-VDPE**) (B, m-3), and poly(***p*-VDPE**) (C, ref 37).

VDPE, suggesting different polymerization behaviors owing to the proximity of the two C═C bonds. Polymerization yields polymers with distinguishable structures depending on the geometry of the monomer. Anionic polymerization of ***m*-VDPE** produced an $(AB)_n$-type sequenced homopolymer via anionic self-alternating polymerization similar to ***p*-VDPE**. In contrast, the anionic polymerization of ***o*-VDPE** formed a main chain with an annular Indane structure via the cyclopolymerization of neighboring vinyl groups.

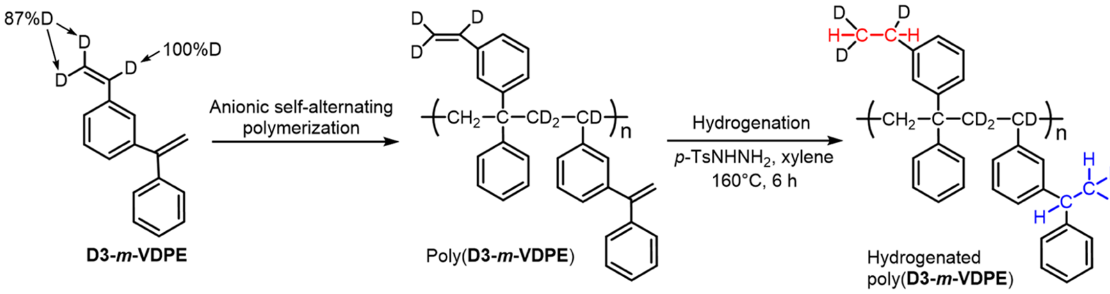
■ RESULTS AND DISCUSSION

Anionic Self-Alternating Polymerization of *m*-VDPE.

The anionic polymerizability of ***m*-VDPE** was first investigated in tetrahydrofuran (THF) at −78 °C for 72 h using *sec*-butyllithium (*s*-BuLi, m-1 in Table 1). Upon introducing ***m*-VDPE** into the initiator solution at −78 °C, a brown color appeared immediately and disappeared shortly after degassed methanol was added for quenching. This characteristic brown color was observed in all polymerizations of ***m*-VDPE**, regardless of the polymerization conditions, such as polymerization time, temperature, and type of initiator. The terminated polymerization solution was poured into excess methanol to precipitate the polymer.

After filtration and freeze-drying from benzene, the polymer was recovered in 48% yield. The resulting polymer was fully soluble in various organic solvents, and size exclusion chromatography (SEC) measurements exhibited a unimodal curve with a predictable molecular weight (M_n = 2.2 kg/mol) and a narrow MWD (M_w/M_n = 1.23). This indicates that the anionic polymerization of ***m*-VDPE** at −78 °C can produce a

Scheme 2. Anionic Self-Alternating Polymerization of D3-*m*-VDPE and the Subsequent Hydrogenation



linear polymer with controlled structure. The observed polymerization rate of run m-1, which was evaluated by polymeric yield, was comparable to that of ***p*-VDPE** conducted under the same polymerization condition (p-1, Table 1). Moreover, all polymerizations with diphenylmethyllithium (Ph_2CHLi) (m-2) at −78 °C or diphenylmethylpotassium (Ph_2CHK) between −78 and 0 °C (from m-3 to m-5) yielded poly(***m*-VDPE**)s with well-controlled structures within the M_n range of 1.2−14.5 kg/mol (Figure 1A,**B**). The polymerization of ***m*-VDPE** could be controlled between −78 and 0 °C and by an organopotassium or organolithium initiator. However, the extended polymerization times to 72 h at 0 °C led to the broadening of the SEC curve of the polymer, possibly due to the intermolecular branching reactions of the propagating carbanion of poly(***m*-VDPE**) toward the pendent vinyl groups in the repeating unit (m-6) (Figure 1C).

Figure 2A is the ^1H nuclear magnetic resonance (NMR) spectrum of ***m*-VDPE** measured in $CDCl_3$. In the ^1H NMR spectrum of the resulting poly(***m*-VDPE**) (Figure 2B), proton signals of the aromatic and vinylic methine (−CH =), vinylic methylene (=CH_2), and aliphatic groups were observed at 7.0, 5.5, and 2.0 ppm, respectively. The proton signal intensity of poly(***m*-VDPE**) was estimated to be 19:4:5, which was in agreement with the intensity ratio of the $(AB)_n$-type sequenced poly(***p*-VDPE**) (Figure 2C).

This suggests that ***m*-VDPE** also polymerizes in a self-alternating manner, similar to the polymerization of ***p*-VDPE**. Because the broadening of the vinyl protons in the polymer restricts the derivation of the specific ratio of the polymerized St or DPE framework units, further clarification of the structure of the $(AB)_n$-type sequenced poly(***m*-VDPE**) is needed. In our previous studies, the polymerization of a purposefully deuterated monomer and hydrogenation of the resulting polymer have successfully reveled the formation of the $(AB)_n$-type sequenced polymer structure.[37,38] Thus, we employed the same toolkits in this study for further characterization of the constructed polymer structure. A selectively deuterated ***m*-VDPE** (**D3-*m*-VDPE**) monomer with CD = CD_2 group in the St framework was synthesized. The deuteration efficiency (%D) in the synthesized **D3-*m*-VDPE** was calculated by ^1H NMR measurement, which was 87%D for $H_{\beta St}$ and 100%D for $H_{\alpha St}$. Under the typical conditions, **D3-*m*-VDPE** was polymerized using Ph_2CHK at −78 °C for 72 h (m-D3−1) and 0 °C for 3 h (m-D3−2) (Scheme 2).

The resulting polymers of **D3-*m*-VDPE** demonstrated polymerization results comparable to those of ***m*-VDPE**, such as polymer yield and a unimodal SEC curve with a predictable M_n value, suggesting that **D3-*m*-VDPE** exhibited the same polymerization behavior as ***m*-VDPE** (Figure S8). As expected, the intensity of the vinyl proton signal in the ^1H NMR spectrum of poly(**D3-*m*-VDPE**) decreased. Proton signals of the aromatic, vinyl, and aliphatic groups were observed at 18:2.26:2.26 (Figure 3A). Considering the calculated deuterated % of **D3-*m*-VDPE**, the observed ratio clearly demonstrates the formation of an $(AB)_n$-type sequence in the repeating unit. Furthermore, the hydrogenation of the pendent $CH_2{=}C$ and $CD_2{=}CD$ groups of poly(**D3-*m*-VDPE**) resulted in four new ^1H NMR signals of CH (3.8 ppm), CDH (2.5 ppm), CH_3 (1.5 ppm), and CD_2H (1.0 ppm), with an estimated ratio of aromatic and aliphatic proton signals of 18:8.26, aligned with the expected alternating polymeric structure of poly(**D3-*m*-VDPE**) (Figure 3B). The hydrogenation of poly(***m*-VDPE**) also showed similar results to those of poly(**D3-*m*-VDPE**), and the related data are shown in the Supporting Information (Figure S9). The constructed main chains of polymers of ***m*-VDPE** and **D3-*m*-VDPE** were also analyzed by ^{13}C NMR measurements. The characteristic carbon signals of the $(AB)_n$-type sequenced main chain were detected as reported previously.[37,38] In particular, the quaternary carbon signal at 51 ppm in the aliphatic region, derived exclusively from the polymerized unit of the non-homopolymerizable DPE framework, strongly supported the alternatingly aligned repeating units of the DPE and St frameworks (Figures S10 and S11). All of the above discussions on the polymerization of ***m*-VDPE** converge to the conclusion that the anionic polymerization of ***m*-VDPE** is

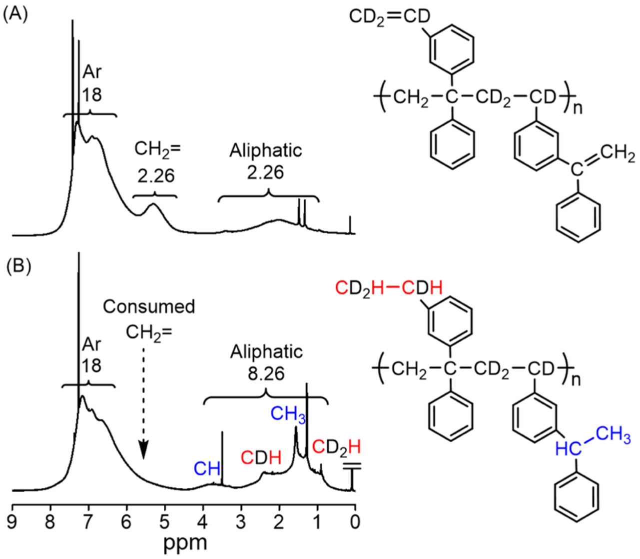


Figure 3. ^1H NMR spectra of poly(**D3-*m*-VDPE**) (A) and hydrogenated poly(**D3-*m*-VDPE**) (B).

Scheme 3. Anionic Self-Alternating Polymerization of *m*-VDPE

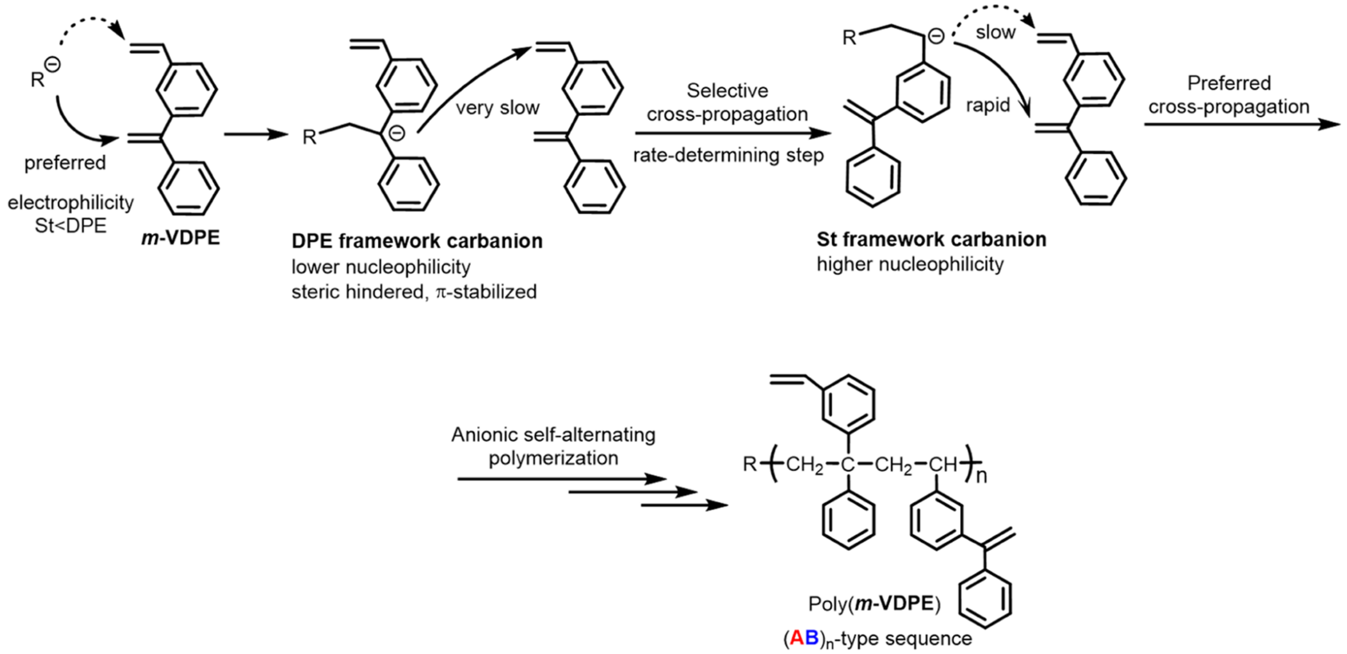


Table 2. Anionic Polymerization of *o*-VDPE in THF[a]

run	*o*-VDPE (mmol)	initiator (mmol)	temp. (°C)	M/I[b]	time (h)	yield[c] (%)	M_n (kg/mol) calcd.[d]	M_n (kg/mol) SEC[e]	M_w/M_n[e]	cyclic ratio[f]
o-1	2.35	*s*-BuLi, 0.117	−78	20	72	∼0				
o-2	2.19	*s*-BuLi, 0.112	0	20	3	78	3.3	2.2	1.70	76−78
o-3	1.97	Ph_2CHLi, 0.093	0	21	3	92	4.2	3.3	1.38	80−82
o-4	2.43	Ph_2CHK, 0.129	0	19	3	50	2.0	1.8	1.45	68−71
o-5	1.95	Ph_2CHCs, 0.123	0	16	3	25	1.0	1.0	1.30	70−73
o-6	3.83	Ph_2CHLi, 0.038	0	101	24	86	17.7	33.3	1.44	72−74
o-7	1.80	Ph_2CHLi, 0.100	0	18	72	90	3.5	3.4	1.49	79−81
o-8	2.15	Ph_2CHLi, 0.093	40	23	3	92	4.6	3.7	1.50	78−80
o-9[g]	2.49	Ph_2CHLi, 0.097	0	26	3	67	3.7	3.2	1.40	73−76
o-10	2.10	Ph_2CHLi, 0.051	−40	41	72	95	8.2	9.1	1.37	69−72

[a] Polymerization was attempted in THF in 0.45 M solution of monomer. [b] M/I = [monomer]/[initiator]. [c] Yield of the polymer after precipitation and freeze-drying from benzene. [d] M_n calcd. = [(MW of the monomer) × (M/I) × Yield] + initiator moiety. [e] Determined by GPC equipped with RI detector using polystyrene standards in THF. [f] Content of annular structured part of the polymer main chain; estimated from the CH_2= signal intensity in the ^{1}H NMR spectrum of the polymer. [g] Polymerization using diluted monomer solution ($[M]_0$ = 0.1 M, $[I]_0$ = 0.05 M).

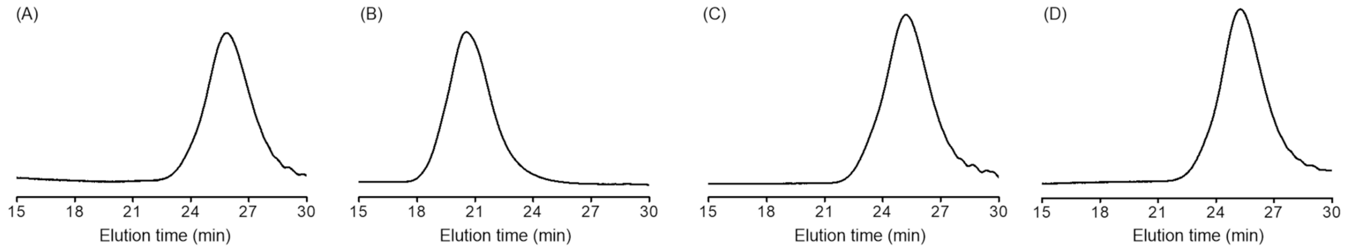


Figure 4. SEC curves of poly(***o*-VDPE**); o-3 (A), o-6, (B), o-7 (C), and o-8 (D).

governed by a self-alternating polymerization mechanism, as described in Scheme 3.

Anionic Polymerization of *o*-VDPE. The anionic polymerizability of ***o*-VDPE** was first investigated at −78 °C for 72 h using *s*-BuLi (Tables 2, o-1). Upon adding the ***o*-VDPE** solution to the initiator solution at −78 °C, an immediate change from colorless to red was observed, indicating the occurrence of a rapid initiation reaction. This characteristic red hue was maintained for 72 h and disappeared shortly after degassed methanol was added. However, no polymeric product was obtained after 72 h, unlike the polymerization results of ***p*-VDPE** and ***m*-VDPE** obtained under the same reaction conditions. Subsequently, the polymerization temperature was elevated to 0 °C to react for 3 h (o-2). This polymerization reaction produced a white precipitate that was insoluble in methanol. After filtration and freeze-drying from benzene, poly(***o*-VDPE**) was obtained in 78% yield. The resulting polymer showed a unimodal SEC curve with M_w/M_n value of 1.70 and predictable M_n (2.2 kg/mol), indicating that the polymerization ***o*-VDPE** is controllable to a certain extent.

Next, we conducted the polymerization using a Ph_2CHLi initiator, which has a lower nucleophilicity than *s*-BuLi. After 3 h of polymerization at 0 °C, poly(***o*-VDPE**) was obtained in 92% yield (o-3). The SEC curve was unimodal (Figure 4A), with a narrow M_w/M_n value of 1.38. The measured M_n value matched the calculated value well, indicating that the Ph_2CH-type initiator was more effective for controlled polymerization. The effect of counter cations on the polymerization of ***o*-VDPE** using the Ph_2CH carbanions was also investigated. By employing Ph_2CHK and diphenylmethylcesium (Ph_2CHCs) initiator (o-4 and o-5), a notable decrease was observed in the yield of the resulting poly(***o*-VDPE**) (50% and 25%) after 3 h.

As the ionic radius of the countercation increased in the order of Li^+ (0.59 Å), K^+ (1.38 Å), and Cs^+ (1.67 Å), the yields of the polymer decreased in the order of 92%, 50%, and 25%,[39] which could be attributed to the ionic radius of the counter cations.[40] As the size of the countercation increases, the dissociation of the ion-pair is expected to retard the propagation due to the hindered solvation in THF. The formation of free ions is suppressed in larger counter cations, thereby decreasing the polymerization rate of ***o*-VDPE**. This tendency for ***o*-VDPE** differs from the polymerization rates of ***p*-VDPE** and ***m*-VDPE**, which are independent of the size of the countercation.[37,38] This observation highlights the significant influence of the selected cation on the polymerization rate of ***o*-VDPE**, indicating a different polymerization mechanism in ***o*-VDPE** compared to its positional isomers, ***p*-VDPE** and ***m*-VDPE**, as discussed later.

Investigation of the anionic polymerizability of ***o*-VDPE** revealed that the Ph_2CHLi initiator was suitable for achieving a narrower M_w/M_n value and faster polymerization. By increasing the initial M/I ratio (o-6), a poly(***o*-VDPE**) with a unimodal MWD (M_w/M_n = 1.44, Figure 4B) was similarly obtained at 0 °C after 24 h, although the M_n (33.3 kg/mol) was higher than the calculated value (17.7 kg/mol). Hence, we presumed that the concentration of the initiator decreased because of the trace amounts of impurities in the monomer during the initial stage of polymerization. Next, the stability of the polymerization system of ***o*-VDPE** was examined. After standing the polymerization system at 0 °C for 72 h (o-7), the obtained poly(***o*-VDPE**) still exhibited a unimodal SEC curve (M_w/M_n = 1.49, Figure 4C), which was comparable with the polymer obtained after 3 h (o-3, Figure 4A). Furthermore, the polymerization at 40 °C for 3 h afforded a polymer with a controlled chain structure of M_w/M_n = 1.50 (o-8, Figure 4D) without the broadening of the MWD. These results indicate that intermolecular side reactions were hindered in the case of ***o*-VDPE**. In contrast, the intermolecular side reactions of the propagating carbanions to the residual C═C bonds occurred slowly after the polymerization of ***p*-VDPE** and ***m*-VDPE**;[37,38] the extended polymerization time resulted in multimodal SEC curves with notably increased M_w/M_n values, as shown in Figure 1C. This observation again emphasizes that the polymerization behavior of ***o*-VDPE** is distinct from that of the other positional isomers of ***p*-VDPE** and ***m*-VDPE**.

Characterization of Annular Structure of Poly(*o*-VDPE). The chemical structure of the synthesized poly(***o*-VDPE**) was characterized by ^1H and ^{13}C NMR spectroscopy. In the ^1H NMR spectra of poly(***o*-VDPE**)s, the intensity of the residual CH_2= groups around 5.0 ppm was significantly weaker than those of poly(***p*-VDPE**) and poly(***m*-VDPE**) (Figure 5). This indicated that the resulting poly(***o*-VDPE**) did not contain any residual CH_2= groups in the repeating units. The significantly weak CH_2= signal implies that the polymer structure of poly(***o*-VDPE**) is distinct from the $(AB)_n$-type alternating sequenced polymer structures derived from ***p*-VDPE** and ***m*-VDPE**. Furthermore, in the ^{13}C NMR spectra (Figure S12), the weak intensity of the characteristic carbon signal of the residual CH_2= groups supports the low content of residual CH_2= groups in poly(***o*-VDPE**). The possibility remains of partial consumption of the residual CH_2= moieties by the nucleophilic addition of the propagating chain ends. However, the polymerization results, such as the unimodal SEC curve and predictable M_n, excludes this possibility. Furthermore, no noticeable changes are observed in the NMR spectra of poly(***o*-VDPE**) before and after hydrogenation, indicating a low content of unreacted C═C bonds in the polymer. A possible explanation for these observations is the formation of an Indane-type annular structure as the major component of the polymer main chain via intramolecular cyclization (Scheme 4).

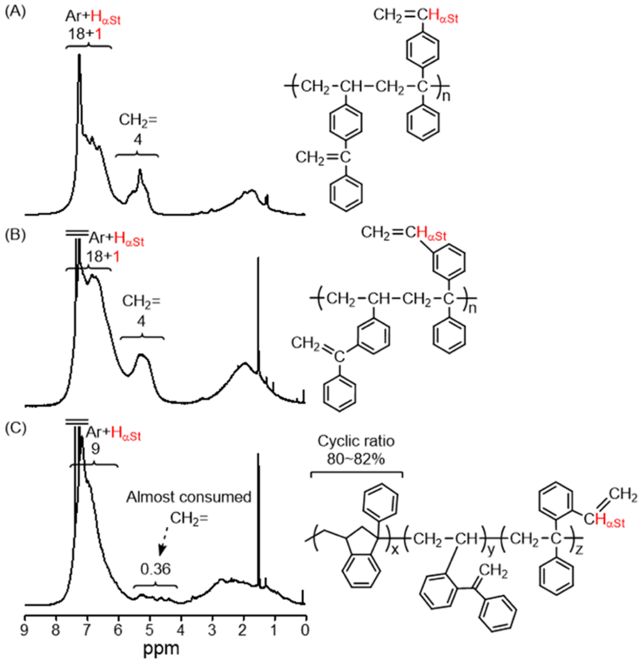
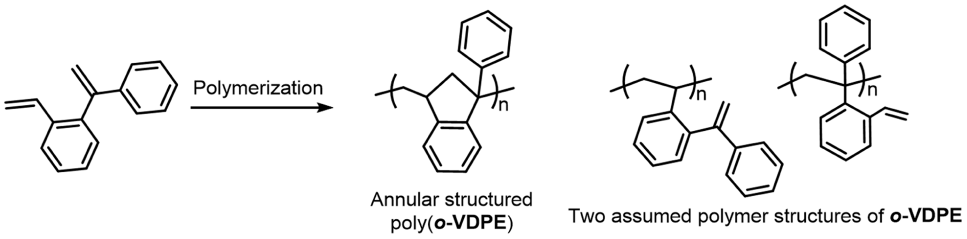


Figure 5. ^1H NMR spectra of poly(***p*-VDPE**) (A), poly(***m*-VDPE**) (B), and poly(***o*-VDPE**) (C).

Figure 6 shows the ^{13}C NMR spectra of the aliphatic region of the polymers. In the spectrum of poly(***o*-VDPE**), several distinct carbon signals were observed at 59, 49, and 35 ppm, which were identified as secondary, quaternary, and primary/tertiary carbons, respectively, using DEPT135 analysis. Notably, their chemical shifts closely matched those of corresponding carbons in a model compound, 1,1,3-trimethyl-3-phenylindane (Figure 6), with the annular structure similar to the proposed repeating unit.[41] A significant point was the detection of the secondary methylene carbon signal (C_c, 59 ppm) in the Indane-type annular structure and the quaternary carbon signal (C_d, 49 ppm) exhibiting the strong intensity among other carbon signals. These results

Scheme 4. Possible Repeating Units of Poly(*o*-VDPE) Obtained by Cyclopolymerization and Intermolecular Propagation



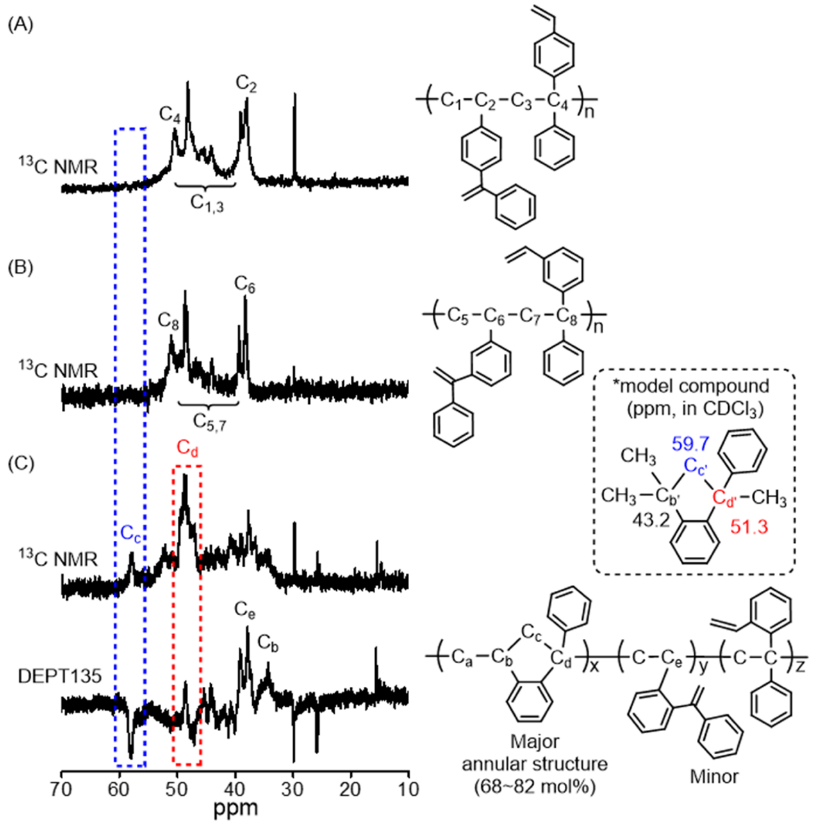


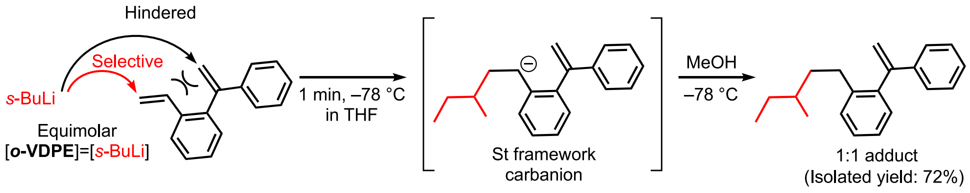
Figure 6. ^{13}C NMR and DEPT135 spectra of poly(***p*-VDPE**) (A), poly(***m*-VDPE**) (B), and poly(***o*-VDPE**) (C).

strongly indicated that the main chain of poly(***o*-VDPE**) was composed of an Indane-type annular structure. Although the detailed chain structure could not be fully characterized owing to overlapping carbon signals in the spectrum, we assumed that poly(***o*-VDPE**) contained an Indane-type main chain as a major component.

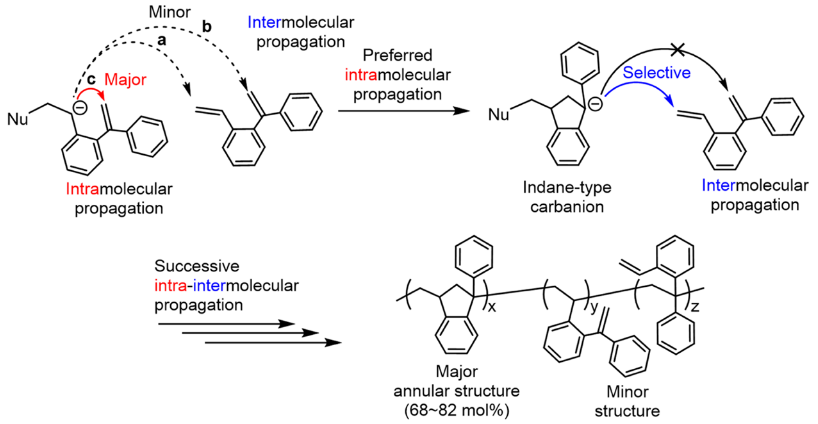
The content of the annular-structured main chain (cyclic ratio) was estimated assuming two extreme structures, as shown in Scheme 4. The extremely weak intensity and broad signal in Figure 5 restricted the accurate estimation of the content of each polymerized unit of the St and DPE frameworks; the detailed estimation method is described in the Supporting Information. Therefore, the cyclic content was calculated as the range between the minimum and maximum values. Consequently, the estimated cyclic content of poly(***o*-VDPE**) (o-3, Figure 5C) was obtained within the 80–82% range. This estimation is considered to fall within an acceptable range, even when accounting for potential measurement errors.

A conventional strategy for increasing the cyclopolymerization content of a difunctional monomer is to perform polymerization under highly dilute conditions to suppress intermolecular propagation and promote intramolecular cyclization. Therefore, the anionic polymerization of ***o*-VDPE** was carried out in THF at 0 °C under dilute conditions (o-9, $[I]_0$ = 0.05 M, $[M]_0$ = 0.1 M), while the usual concentrations of $[I]_0$ and $[M]_0$ were 0.05 and 0.45 M, respectively. Although the polymerization slightly slowed down to form a polymer in 67% yield due to the dilute polymerization condition, the cyclic ratio in the polymer was lowered in the 73–76% range. Thus, the expected promotion of intramolecular cyclization was not achieved under dilute conditions. The effect of polymerization temperature on the cyclization was compared with the polymerizations at 40, 0, and −40 °C, (Table 2, o-8, o-3, and o-10). The cyclic ratios were in the 69–82% range, indicating that the polymerization temperature did not significantly affect the cyclization efficiency. As shown in Table 2, the estimated cyclic ratios of the synthesized poly(***o*-VDPE**)s were in the 68–82% range, exhibiting a feature independent of the various polymerization conditions, including the initiator structure, countercation, concentration of the system, and polymerization temperature.

Scheme 5. 1:1 addition reaction of *o*-VDPE with *s*-BuLi.



Scheme 6. Proposed Cyclopolymerization of *o*-VDPE Involving Successive Intra- and Intermolecular Propagations



Cyclopolymerization Mechanism of *o*-VDPE. Before proposing the polymerization mechanism for ***o*-VDPE**, we attempted a 1:1 addition reaction of *s*-BuLi and ***o*-VDPE** to clarify which framework predominantly reacted to form an Indane-type annular structure (Scheme 5). *s*-BuLi (0.998 mmol) was reacted with equivalent ***o*-VDPE** (1.03 mmol) in THF at −78 °C for 1 min; the reaction was rapidly quenched with methanol. The reaction mixture was concentrated and dried under vacuum to obtain a viscous liquid before further purifications. The ^{1}H NMR spectrum of the crude reaction mixture showed only two singlet proton signals at 5.3 and 5.9 ppm corresponding to the residual $H_{\beta DPE}$ of ***o*-VDPE** along with the complete consumption of the characteristic $H_{\alpha St}$ and $H_{\beta St}$ signals (Figure S13). After purifying the mixture by column chromatography using hexane, the expected 1:1 adduct of ***o*-VDPE** and *s*-BuLi was isolated in 72% yield (Scheme 5). Interestingly, the C═C bond of the DPE framework in the isolated adduct was intact after the formation of the St carbanion of ***o*-VDPE**, indicating that the intramolecular cyclization reaction of the St anion with the residual DPE framework was slow and should be the rate-determining step.

Based on these observations, we proposed a plausible cyclopolymerization mechanism for ***o*-VDPE**, as shown in Scheme 6. As demonstrated, the St framework carbanion is initially formed by selective nucleophilic initiation/propagation toward the St framework in ***o*-VDPE**. The following three reactions, **a**−**c**, are possible for the resulting St carbanion, although this anion is fairly stable. Examples **a** and **b** are intermolecular propagations to either the C═C bond of the St framework or the DPE framework of the next ***o*-VDPE** monomer. However, these should not be dominant because the resulting poly(***o*-VDPE**) has a low residual C═C bond content in the repeating unit. Finally, **c** is an intramolecular cyclization reaction of the St anion with the residual C═C bond of the DPE framework of the same ***o*-VDPE** unit to form the Indane-type tertiary carbanion, which might be stabilized by the two aromatic rings. This intramolecular reaction for the St carbanion should be predominant, considering the high cyclic content and low C═C bond content of poly(***o*-VDPE**). The generated Indane-type tertiary carbanion selectively undergoes intermolecular addition to the C═C bond of the St framework of the next monomer because the non-homopolymerizable property of DPE and its derivatives function similarly in this intermolecular propagation process. These two reaction processes, that is, intramolecular cyclization and intermolecular propagation, are repeated to construct an Indane-type annular structure in poly(***o*-VDPE**), which is a major part of the main chain.

Finally, based on the results of the 1:1 addition, the rate-determining step in the polymerization of ***o*-VDPE** would be the intramolecular cyclization to form the Indane-type framework. The bulky 1-phenylvinyl substituent on the St carbanion of the adduct may play an important role in retarding subsequent intermolecular propagation. In contrast, in the cases of ***p*-VDPE** and **ClVDPE**, the nucleophilic addition reaction of a bulky initiator such as Ph_2CHK occurred chemoselectively on the C═C bond of the DPE framework to afford a *π*-stabilized DPE carbanion, as previously reported.[37,38] The subsequent intermolecular propagation to the St framework slowly proceeded as the rate-determining step because the *π*-stabilized DPE anion derived from ***p*-VDPE** or **ClVDPE** had low nucleophilicity, as mentioned previously for the polymerization of ***m*-VDPE**.

Properties of Polymers. All prepared polymers were white powders and soluble in various organic solvents, including benzene, chloroform, THF, and *N,N*-dimethylformamide. The related experimental and analytical results are shown in **Supporting Information** in Table S1 and Figure S14. The thermal stabilities of the polymers were examined by thermogravimetric analysis. The poly(***m*-VDPE**) began to decompose at approximately 371 °C, and its 10% weight loss ($T_{10\ \mathrm{wt}\ \%}$) was observed at 406 °C. A 15 wt % residue of poly(***m*-VDPE**) still remained even at 600 °C, while the poly(***o*-VDPE**) decomposed completely by 500 °C (Table 3).

Table 3. Thermal Properties of Polymer of VDPE Isomers

	M_n (kg/mol)[a]	T_g (°C)[b]	$T_{10\text{ wt }\%}$ (°C)[c]	residue (wt %)[d]
Poly(***p*-VDPE**)[e]	3.2	158	413	15
Poly(***p*-VDPE**)[e]	16.2	172	420	18
Poly(***m*-VDPE**)	14.5	161	406	15
Poly(***o*-VDPE**)[f]	2.2	265	384	0
Poly(***o*-VDPE**)[f]	2.8	273	387	0

[a] Determined by GPC equipped with RI detector using PS standards in THF. [b] Measured by DSC; polymer samples were annealed to 240 °C before first heating scan, and measurements were carried out under temperature range at 30−260 °C at 20 °C/min. [c] Measured by TGA under temperature range at 30−600 °C at 20 °C/min. [d] Residue at 600 °C. [e] From ref 37. [f] Polymer sample was annealed to 290 °C, and measured under temperature range at 30−300 °C.

The thermal properties of poly(***m*-VDPE**) and poly(***o*-VDPE**) were analyzed by differential scanning calorimetry (DSC). During the first heating scan to 240 °C for poly(***m*-VDPE**), the DSC curve displayed an endothermic heat flow at 161 °C, corresponding to the glass transition temperature (T_g), and a large exothermic heat flow was observed above 220 °C. In the second heating scan, no endo- or exothermic heat flow was observed, probably because of the formation of cross-linked poly(***m*-VDPE**) in the first heating scan, similar to that of poly(***p*-VDPE**).[37]

Conversely, the poly(***o*-VDPE**) exhibited a T_g at 273 °C significantly higher than those of poly(***m*-VDPE**) (T_g = 161 °C) and poly(***p*-VDPE**) (T_g = 172 °C). Furthermore, the T_gs of poly(***o*-VDPE**) were not observed below 300 °C in the samples with higher M_n values (runs 6 and 10). Interestingly, the T_g of poly(***o*-VDPE**) was consistently observable during repeated DSC measurements. The distinct annular-structured main chain and low content of residual C═C bonds contributed to the substantial increase in T_g and reproducibility of the measurements without cross-linking. The observed properties, such as the high T_g and thermal stability of poly(***o*-VDPE**), were attributed to the rigid polymer structures resulting from the proposed cyclopolymerization mechanism.

■ CONCLUSIONS

The influence of the substitution position of the C═C groups on the anionic polymerization behavior of ***m*-VDPE** and ***o*-VDPE** was investigated. In both the cases, the resulting polymers were completely soluble, exhibited relatively narrow MWDs, and possessed predictable molecular weights, indicating the controlled characteristics of anionic polymerization. ***m*-VDPE** was found to undergo the "self-alternating polymerization," yielding $(AB)_n$-type sequenced homopoly(***m*-VDPE**), similar to that in the case of ***p*-VDPE**. The structure of the resulting poly(***m*-VDPE**) was successfully characterized using several experiments, including the NMR measurements, polymerization of purposefully deuterated ***m*-VDPE**, and hydrogenation of the polymer. In contrast, ***o*-VDPE** undergoes cyclopolymerization. The carbanion derived from the C═C bond of the St framework was preferentially generated through intermolecular propagation. The subsequent rate-determining step was the intramolecular reaction of the St framework carbanion with the adjacent C═C bond of the DPE framework to form the Indane-type annular structure of poly(***o*-VDPE**). The Indane-type carbanion then reacted intermolecularly with the St framework of another monomer. These successive intra- and intermolecular reactions were repeated, resulting in the formation of a main chain with a ring structure, with cyclization efficiencies ranging from 68% to 82%. The thermal properties of polymers were strongly dependent on their structures. The $(AB)_n$-type sequenced poly(***m*-VDPE**) showed the T_g at 161 °C and thermal cross-linking property, while the poly(***o*-VDPE**) had the markedly high T_g at 273 °C and high thermal stability, supporting the formation of the rigid annular structured main chain. Thus, the substitution position of the vinyl group in **VDPE** framework strongly affects the polymerization behavior of the AB-type difunctional monomer.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.5c00257.

> Experimental procedures, preparation of the chemical materials, and synthesis of the polymers (Figures S1−S14) (Schemes S1−S2) (Table S1) (PDF)

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Notes

The authors declare no competing financial interest.

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