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Anionic Polymerization of 2-Phenyl[3]dendralene and 2-(4-Methoxyphenyl)[3]dendralene

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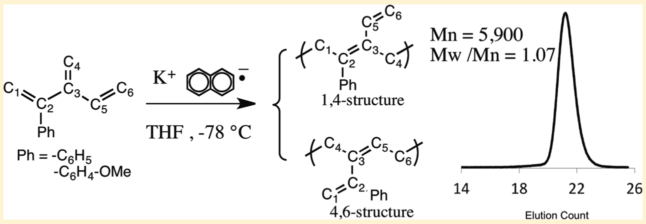
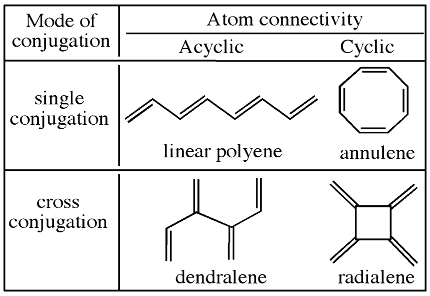
ABSTRACT: Anionic polymerization of two phenyl-substituted trienes containing cross-conjugated carbon−carbon double bonds, 2-phenyl[3]dendralene (**P3D**) and 2-(4-methoxyphenyl)[3]dendralene (**MP3D**), was carried out in THF under a variety of different conditions. Poly(**P3D**) of controlled molecular weight with a narrow molecular weight distribution was obtained when the polymerization reaction was carried out at −78 °C for 30 min. Broadening of the molecular weight distribution to the higher-molecular-weight side was observed if the polymerization mixture was left to stand for 20 h at −78 °C, presumably because of the attack of the propagating chain-end carbanion at the conjugated diene structure in the polymer chain. Similar broadening occurred if the polymerization was performed at a higher temperature. However, under identical conditions, no such a broadening was observed in the polymerization of **MP3D**. Block copolymers of predictable molecular weights and compositions containing a poly(2-vinylpyridine) segment were obtained by the sequential addition of **P3D** and/or **MP3D** to potassium naphthalenide and then 2-vinylpyridine. Only the conjugate addition structure was found in the resulting polymers.



INTRODUCTION

Hydrocarbons containing multiple conjugated carbon−carbon double bonds can be classified into four groups on the basis of their structural differences. Chart 1 shows examples of fundamental hydrocarbon families of oligoalkene structures, where each family differs in the type of atom connectivity (unbranched or branched, cyclic or acyclic). The unbranched acyclic and cyclic systems, namely, linear polyenes and annulenes, respectively, have a single conjugated chain of double bonds. In contrast, the branched acyclics (dendralenes) and cyclics (radialenes) have multiple conjugated systems, where one carbon−carbon double bond belongs to two conjugation systems.[1−3]

Chart 1. Examples of Fundamental Hydrocarbon Families Having Oligoalkene Structures



Among these oligoalkenes, dendralene has been attracting much attention for its unique chemical reactivity. This molecule contains multiple 2- or 2,3-disubstituted 1,3-dienyl frames, providing the potential for it to be used as a substrate for a diene-transmissive Diels−Alder reaction.[4−6] Because the reactivity in the Diels−Alder reaction strongly depends on the electron density and the conformation of the dienyl frame, a variety of substituted dendralenes have been synthesized via the thermal decomposition of certain precursors.[7] Recently, a new route to synthesizing dendralenes, involving the cross-coupling reaction of 1,3-butadien-2-yl magnesium chloride with an appropriate alkenyl halide, was reported.[8] Because this route does not include the thermal decomposition of the precursors, dendralenes of various chain lengths with a range of substituents can be obtained in high yield.

The first and smallest dendralene, [3]dendralene, was synthesized in 1955.[9] Since then, a variety of [*n*]dendralenes up to [8]dendralene have been systematically synthesized. The effect of the number of double bonds in the [*n*]dendralene molecules on their stability has been evaluated, with larger dendralenes appearing more stable and those containing an odd number of carbon−carbon double bonds being less stable than those with an even number.[10] However, the behavior of these molecules in addition polymerization reactions has not been reported thus far.

1,3-Butadiene, the simplest conjugated dienyl monomer, can be considered to be [2]dendralene and can be polymerized by

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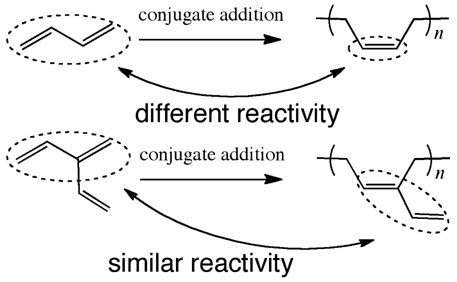
free-radical, anionic and coordination polymerization to give a rubbery material, even though no cross-conjugated double bond is present in the monomer molecule. Because the chemical reactivity of the conjugated carbon−carbon double bond in the monomer and that of the nonconjugated double bond in the resulting polymer are very different, it is easy to obtain polydienes without cross-linking. However, if the dendralene polymerization proceeds via a conjugate addition mode, as shown in Scheme 1, then the newly formed conjugated carbon−carbon double bond in the polymer chain may have similar reactivity to the one in the monomer and could therefore be susceptible to attack of the propagating chain end during polymerization. As a result, it is important to select the polymerization conditions carefully in order to prevent such a side reaction. For this purpose, in this work, we chose the method of anionic polymerization, to be carried out at low temperature.

Scheme 1. Transmission of the Carbon−Carbon Double Bond to Form a New Conjugated Dienyl Structure by the Conjugated Addition of [3]Dendralene



In a previous paper, we reported on the anionic polymerization behavior of various functionalized 1,3-butadiene derivatives.[11−14] Because the anionic polymerization of conjugated 1,3-dienes proceeds smoothly in polar solvents at low temperature, this mechanism was speculated to be useful for the polymerization of dendralenes. Another strategy for controlling the polymerization of dendrarene is to introduce a substituent at a certain position. Although it is known that the nucleophilicity of active chain-end species derived from 2-phenyl-1,3-butadiene[15] and 2,3-diphenyl-1,3-butadiene[16] was too weak to initiate the polymerization of styrene, anionic polymerization of these monomers proceeds in a living manner to give polymers of predictable molecular weights and narrow molecular weight distributions. This indicates that the aromatic substituent on the C2 carbon of the 1,3-butadienyl skeleton can change the nucleophilicity of active chain-end species through conjugation. Because one of the conjugation systems in 2-phenyl[3]dendralene (**P3D**) can be regarded as 2-phenyl-3-vinyl-substituted 1,3-butadiene and the other one can be regarded as 2-(1-phenylethenyl)-1,3-butadiene, active chain-end species derived from **P3D** should have lower nucleophlicity compared to that of ordinary 1,3-dienes, making it possible to distinguish the conjugated double bond in the monomer from the one in the polymer chain. Therefore, 2-aromatic-substituted[3]dendralene would be suitable for studying the anionic addition polymerization behavior of dendralenes. Among 2-substituted[3]dendralene, we chose **P3D** and 2-(4-methoxyphenyl)[3]dendralene (**MP3D**) as the first monomer to polymerize by anionic initiator because the synthesis methodology of these monomers is well established.[8] In this article, we report the first example of anionic polymerization of **P3D** and **MP3D** and discuss the microstructure of the resulting polymers.

■ EXPERIMENTAL SECTION

Materials. 2-Chloro-1,3-butadiene (chloroprene) was kindly donated by Denki Kagaku Kogyo Co. Ltd., Japan as a 50% toluene solution. Prior to use, it was twice purified by fractional distillation under reduced pressure. **P3D** and **MP3D** were prepared according to the reported procedure.[8] Bromine, *p*-bromoanisole, [1,3-bis(diphenylphosphino)propane]dichloronickel(II), and [1,2-bis(diphenylphosphino)ethane]dichloronickel(II) were used as received. α-Bromostyrene was prepared from styrene by the addition of bromine in CCl_4, followed by dehydrobromination using KOH/methanol at 25 °C. 1,3-Butadien-2-yl magnesium chloride was prepared according to a previously reported procedure using chloroprene and ordinary magnesium turnings with continuous activation of the magnesium surface with 1,2-dibromoethane.[17]

Anionic Polymerization. The synthesized monomers were purified by distillation under high-vacuum conditions in the presence of phenylmagnesium bromide. The purified monomers were diluted with THF and then sealed in ampules with breakable seals. All anionic polymerizations were carried out under high vacuum using the well-known break-seal method.[18] First, the THF solution of initiator was introduced into the reactor and cooled to −78 °C. After the addition of the monomer solution to the reactor in one portion at this temperature, the reactor was put in an aimed constant-temperature bath and allowed to stand still for a designed time. Finally, degassed ethanol was added to terminate the polymerization. In the case of block copolymerization, a small portion of the polymerization mixture was transferred to the separated part of the reactor prior to the addition on the second monomer.

Materials Characterization. The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using a JEOL JNM-AL-400 spectrometer. The solvent peak was used as the reference. One dimensional ^1H and ^{13}C 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 row data points and 256 column data points with zero filling. GC−MS data were obtained using a Shimadzu QP-2010plus with electron impact (EI) 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)] and UV (254 nm) and refractive index (RI) detectors. THF was used as the carrier solvent at a flow rate of 1 mL/min. The absolute molecular weights of the polymers were determined using a Viscotek model 270 instrument connected to an SEC.

■ RESULTS AND DISCUSSION

Anionic Polymerization of P3D. The anionic polymerization of **P3D** was carried out in THF using potassium naphthalenide as an initiator. Upon addition of **P3D**, the characteristic green color of the initiator turned immediately to deep red. This color remained unchanged until the end of the polymerization and disappeared instantaneously on the addition of ethanol. No gel was formed during the polymerization, and the polymer was precipitated by pouring the solution into a large excess of ethanol. It was purified by reprecipitation from THF to ethanol an additional two times and finally freeze-dried from benzene. Table 1 summarizes the results of the anionic polymerization of **P3D** under various conditions. When the reaction was performed at −78 °C, the polymerization was not complete in 1 h, whereas in the time frame of 1−10 h, no residual monomer was detected by GC. In all cases, polymers of predictable molecular weights based on the monomer to initiator ratios were obtained with narrow molecular weight distributions, indicating that the olefinic

Table 1. Anionic Polymerization of P3D under Various Conditions

P3D, mmol	K-Naph, mmol	temp, °C	time, h	conv, %	M_n, kg/mol calcd	M_n, kg/mol SEC	M_w/M_n
6.61	0.23	−78	10 min	60	5.4	5.3	1.08
4.43	0.18	−78	0.5	85	6.7	6.4	1.05
6.90	0.41	−78	1	100	5.3	4.7	1.05
5.54	0.29	−78	5	100	6	5.9	1.07
3.60	0.21	−78	10	100	5.4	5.4	1.06
6.80	0.12	−78	20	100	17.7	15.6	1.13
6.61	0.25	−40	0.5	100	8.4	8.1	1.11
5.73	0.32	0	10 min	100	5.6	8.6	multi[a]

[a] Multimodal distribution.

carbon−carbon double bonds in the polymer chain did not react with the propagating chain end under these conditions. However, if the polymerization mixture was left to stand for any length of time after complete consumption of the monomer had occurred, then broadening of the molecular weight distributions toward the higher-molecular-weight side was observed. Figure 1 shows the SEC results for poly(**P3D**) prepared under different polymerization conditions. As will be discussed in a later section, the polymerization of **P3D** proceeded via conjugate addition, forming a conjugated dienyl structure in the polymer chain. Nucleophilic addition of the propagating carbanion to this dienyl structure is therefore likely to be responsible for the broadening of the molecular weight distribution, as shown in Scheme 2. Similar broadening was observed when the polymerization was performed at −40 °C, although the polymerization was complete within 0.5 h. If the polymerization was carried out at 0 °C, then a polymer of multimodal molecular weight distribution was obtained quantitatively, without the formation of a gel. Because the estimated molecular weight corresponding to the sharp peak on the lower-molecular-weight side was close to the value calculated on the basis of the monomer to initiator ratio, nucleophilic addition of the chain-end carbanion to the double bond in the polymer chain may have occurred after the complete consumption of the monomer.

Anionic Polymerization of MP3D. If the nucleophilic attack of the chain-end carbanion on the carbon−carbon double bonds in the polymer was responsible for the broadening of the molecular weight distribution, it was speculated that this could be suppressed by changing the reactivity of both the carbanion and the double bonds. For this purpose, **MP3D**, a **P3D** derivative with an electron-donating methoxy group, was synthesized and polymerized under similar conditions. The color of the system was almost identical to the case of **P3D**. A soluble polymer was obtained by pouring the solution into a large excess of ethanol. Table 2 summarizes the results of the anionic polymerization of **MP3D** under various conditions. SEC chromatograms of poly(**MP3D**) thus obtained are shown in Figure 2. When the reaction was performed at −78 °C, the rate of polymerization was found to be slightly slower than that of **P3D** and was not complete in 1 h. If the polymerization was performed for more than 2 h, then poly(**MP3D**) of a predictable molecular weight based on the monomer to initiator ratio was obtained with a narrow molecular weight distribution. It should be noted that no broadening of the molecular weight distribution was observed, even after 30 h at this temperature. As we discuss in a later section, the electron-donating character of the methoxy group on the phenyl ring increased the electron density of the conjugated double bond in the polymer chain, preventing the nucleophilic attack of the carbanion at the double bond. It is interesting that polymer of relatively narrow molecular weight distributions was also obtained if polymerization was carried out at −40 or 0 °C for 30 min. However, broadening of the molecular weight was observed if polymerization was performed at 0 °C for 5 h, indicating that the above-mentioned electronic effect was not strong enough to suppress the side reaction completely.

Block Copolymerization. As mentioned above, **P3D** and **MP3D** showed some differences in the rate of polymerization. The methoxy group on the phenyl ring may increase the reactivity of the active chain-end species owing to its electron-donating character; however, in addition, it decreased the electrophilicity of the carbon−carbon double bond in the polymer chain. To investigate the reactivity of the chain-end carbanion, block copolymerization of **P3D** and **MP3D** with styrene and/or 2-vinylpyridine as a second monomer was performed. Polymerization of the second monomer was carried out at −78 °C for 2−3 h for 2-vinylpyridine and for 3−18 h for styrene. Table 3 and Figure 3 summarize the results of block copolymerizations. When 2-vinylpyridine was used as the second monomer, a block copolymer of predictable molecular weight with a narrow molecular weight distribution was obtained. The SEC peaks moved to the higher-molecular-weight side, with no residual homo poly(**P3D**) and (**MP3D**) peaks evident. This clearly indicates that the active chain-end carbanions derived from **P3D** and **MP3D** had strong enough nucleophilicity to initiate the polymerization of 2-vinylpyridine to form block copolymers. However, a polymer of bimodal distribution was obtained when styrene, a less-reactive monomer toward the carbanion, was used as the second monomer. A mixture of homo poly(**P3D**) and block copolymer composed of a high-molecular-weight polystyrene segment and

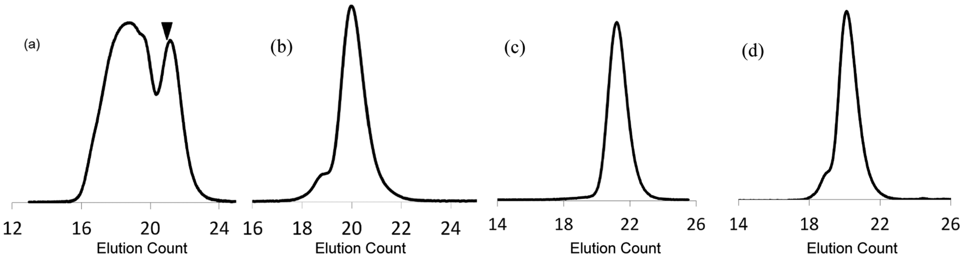


Figure 1. SEC chromatograms of poly(**P3D**) prepared under different polymerization conditions. (a) 0 °C, 10 min, (b) −40 °C, 30 min, (c) −78 °C, 1 h, and (d) −78 °C, 20 h. ▼ in plot a indicates the calculated molecular weight based on the monomer to initiator ratio.

Scheme 2. Nucleophilic Addition of a Propagating Carbanion to the Dienyl Structure in the Polymer Chain Causing the Broadening of the Molecular Weight Distribution

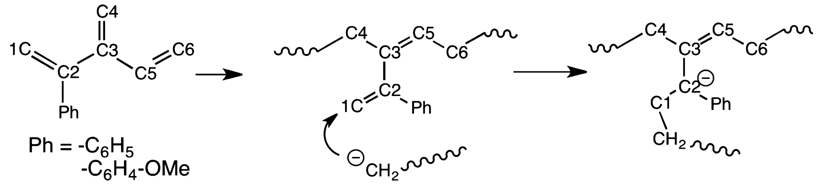


Table 2. Anionic Polymerization of MP3D under Various Conditions

MP3D, mmol	K-Naph, mmol	temp, °C	time, h	conv, %	M_n, kg/mol calcd	M_n, kg/mol SEC	M_w/M_n
3.14	0.26	−78	10 min	40	2.73	2.41	1.19
3.04	0.24	−78	0.5	75	4.06	3.96	1.07
2.96	0.24	−78	1	85	3.95	4.05	1.08
3.58	0.10	−78	2	100	12.80	12.10	1.05
2.96	0.18	−78	5	85	6.06	5.64	1.04
2.75	0.21	−78	10	100	4.80	4.68	1.05
3.16	0.23	−78	15	100	5.12	4.71	1.05
2.75	0.23	−78	30	100	4.45	4.62	1.05
2.61	0.15	−40	0.5	100	6.35	6.82	1.05
2.55	0.19	0	0.5	100	5.00	4.75	1.21
2.65	0.26	0	5	100	3.80	13.53	5.61

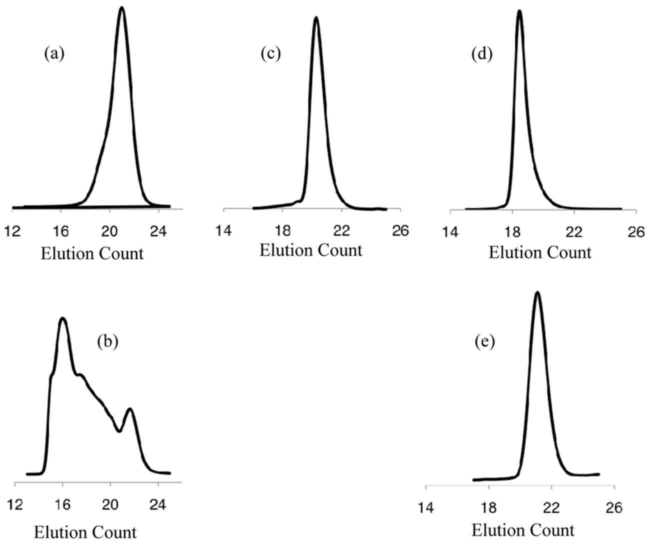


Figure 2. SEC chromatograms of poly(**MP3D**) prepared under different polymerization conditions. (a) 0 °C, 30 min, (b) 0 °C, 5 h, (c) −40 °C, 30 min, (d) −78 °C, 2 h, and (e) −78 °C, 30 h.

a poly(**P3D**) segment was obtained in 3 h. In the case of **MP3D**, the rate of initiation was so slow that only a slight broadening of the SEC peak to the higher-molecular-weight side was observed in 3 h, and the conversion was very low. It was necessary to carry out the polymerization for 18 h to achieve the complete consumption of styrene. This could be explained by the lower nucleophilicity of the carbanion derived from **MP3D** compared to that from **P3D**. This is also in accordance with the results of the homopolymerization discussed above, where the nucleophilic attack of the propagating carbanion at the carbon−carbon double bond in the polymer chain was less likely to occur in the polymerization of **MP3D**. Because it is well known that an ordinary carbanion derived from 1,3-dienes such as 1,3-butadiene and isoprene can initiate the anionic polymerization of styrene, it can be concluded that the nucleophilicities of the propagating chain ends derived from **P3D** and **MP3D** were much lower than those of ordinary 1,3-dienes.

Microstructure of the Resulting Polymers. When diene polymerization is studied, control and analysis of the microstructure of the resulting polymer are of great importance because the physical properties of the polymer strongly depend on the microstructure. Because the [3]dendralene derivatives used in this study contained two cross-conjugated dienyl frames, it was extremely interesting to analyze which double bonds participated in the polymerization. Therefore, the microstructures of the resulting polymers were analyzed by ^{1}H and ^{13}C NMR spectroscopy.

In principle, three vinyl addition structures and two conjugate addition structures can be formed in the polymerization of **P3D** and **MP3D**, as shown in Scheme 3. Among these, only the 5,6 structure has an aliphatic methyne carbon in the polymer chain. In addition, an aliphatic quaternary carbon should be present only in the other two vinyl structures (1,2- and 3,4-). Therefore, ^{13}C NMR analysis can be employed to determine easily if the vinyl structures are present in the synthesized polymers. Figure 4 shows the ^{13}C NMR spectrum of poly(**MP3D**) prepared at −78 °C. In the aliphatic carbon region, only three signals were observed at 55, 33−34, and 25−28 ppm. Though each of the signals appeared as a multiplet, the mode of monomer addition such as the 4,1 and 4,6 addition, geometries of the monomer units, *E* and *Z*, and their distribution might have caused the signal splitting. By comparing the ordinary complete proton-decoupled spectrum to the DEPT135 spectrum, the signal around 55 ppm could be assigned to the methoxy carbon on the phenyl ring, with the others due to methylene carbons. Importantly, no signals attributable to methyne and quaternary carbons were observed in this region, within the detectable limit, indicating that no or very little vinyl addition structure was incorporated into poly(**MP3D**). This was further confirmed using ^{1}H NMR

Table 3. Anionic Block Copolymerization of P3D and MP3D Using Styrene (St) and 2-Vinylpyridine (2-VP) as a Second Monomer at −78 °C

initiator	monomer	time, h	conv, %	M_n, kg/mol calcd	M_n, kg/mol obsd	M_w/M_n
K-Naph	**P3D**	5	100	6.3	7.0	1.06
$2K^+$(**P3D**)$_n^{2-}$	St	3	92	21.3	332.8(7.6)[a]	bimodal
K-Naph	**P3D**	2	100	11.7	12.8	1.07
$2K^+$(**P3D**)$_n^{2-}$	2-VP	2	80	32.6	32.6	1.14
K-Naph	**MP3D**	6	100	7.2	7.2	1.08
$2K^+$(**MP3D**)$_n^{2-}$	St	3	34	19.7	7.6	1.12
K-Naph	**MP3D**	21	100	5.4	7.2	1.07
$2K^+$(**MP3D**)$_n^{2-}$	St	18	100	21.7	395.0 (7.6)[a]	bimodal
K-Naph	**MP3D**	3	100	6.4	5.2	1.19
$2K^+$(**MP3D**)$_n^{2-}$	2-VP	2	84	16.6	15.5	1.13

[a] Molecular weight corresponding to the SEC peak on the higher-molecular-weight side. The value in parentheses corresponds to the peak on the lower-moleculer-weight side.

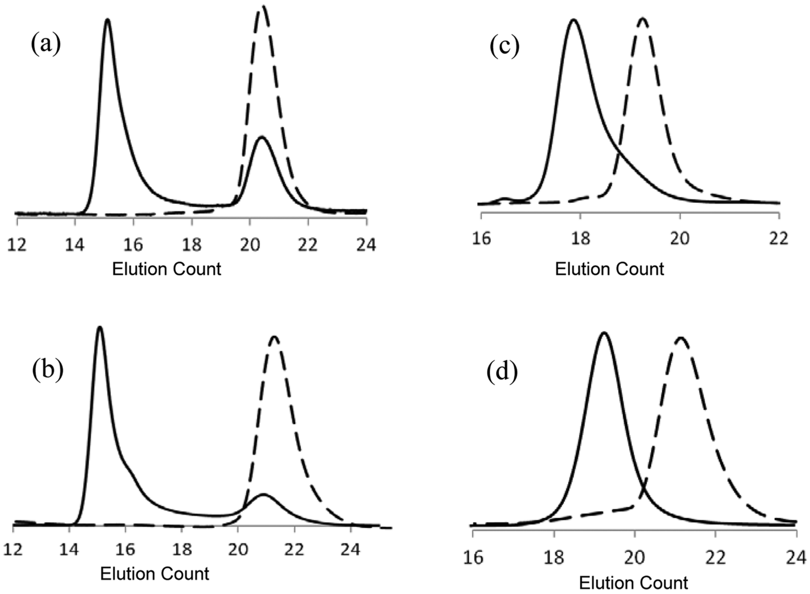
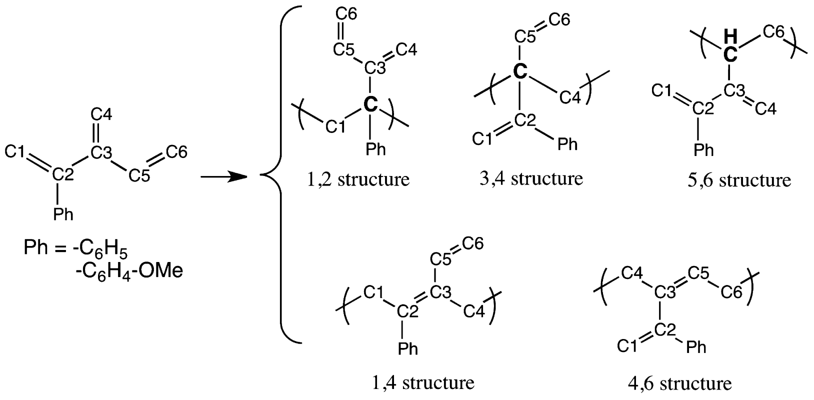


Figure 3. SEC chromatograms of block copolymers (—) and original homopolymer (---). (a) **P3D** anion + styrene, (b) **MP3D** anion + styrene, (c) **P3D** anion + 2-vinylpyridine, and (d) **MP3D** anion + 2-vinylpyridine.

Scheme 3. Possible Microstructures



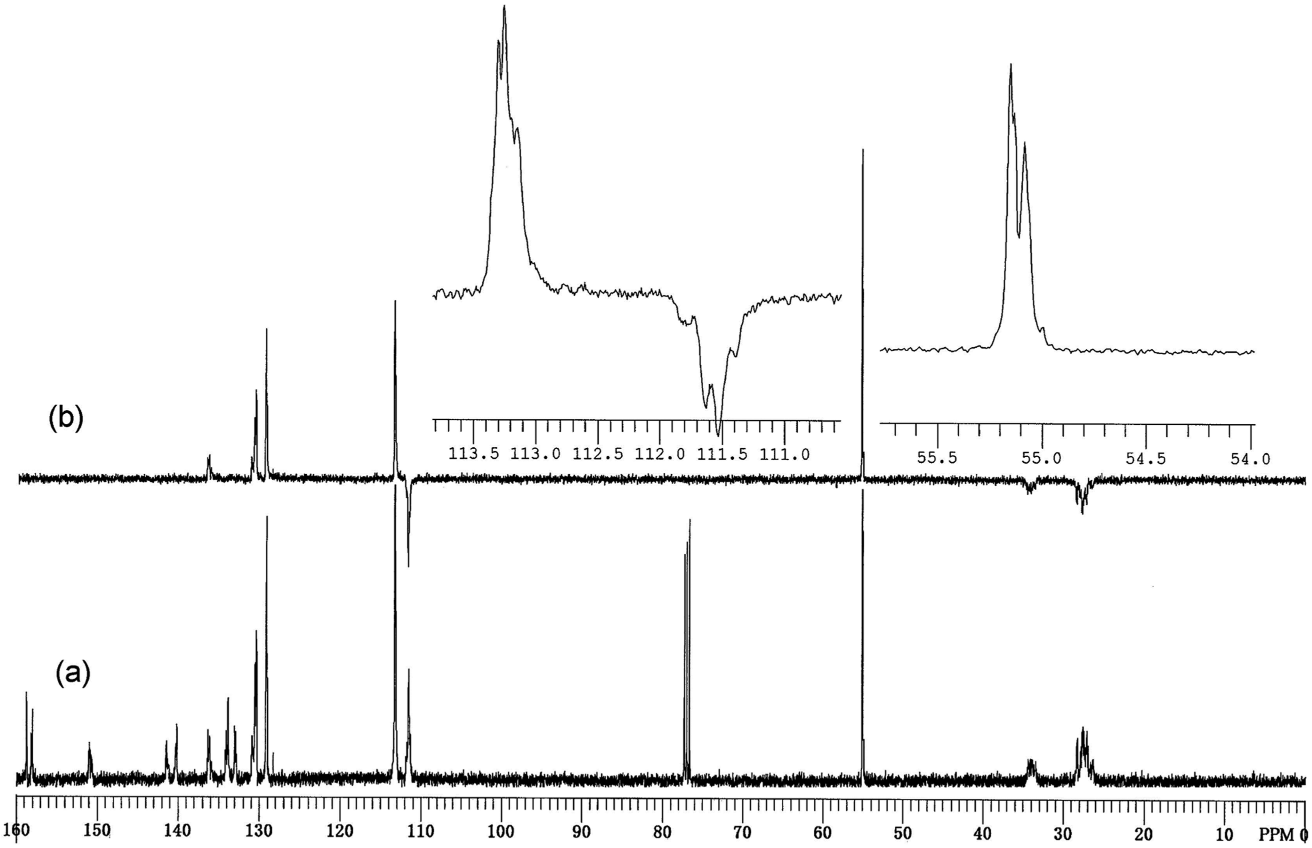


Figure 4. ^{13}C NMR: (a) ordinary complete decoupling and (b) DEPT135 spectra of poly(**MP3D**) prepared at −78 °C.

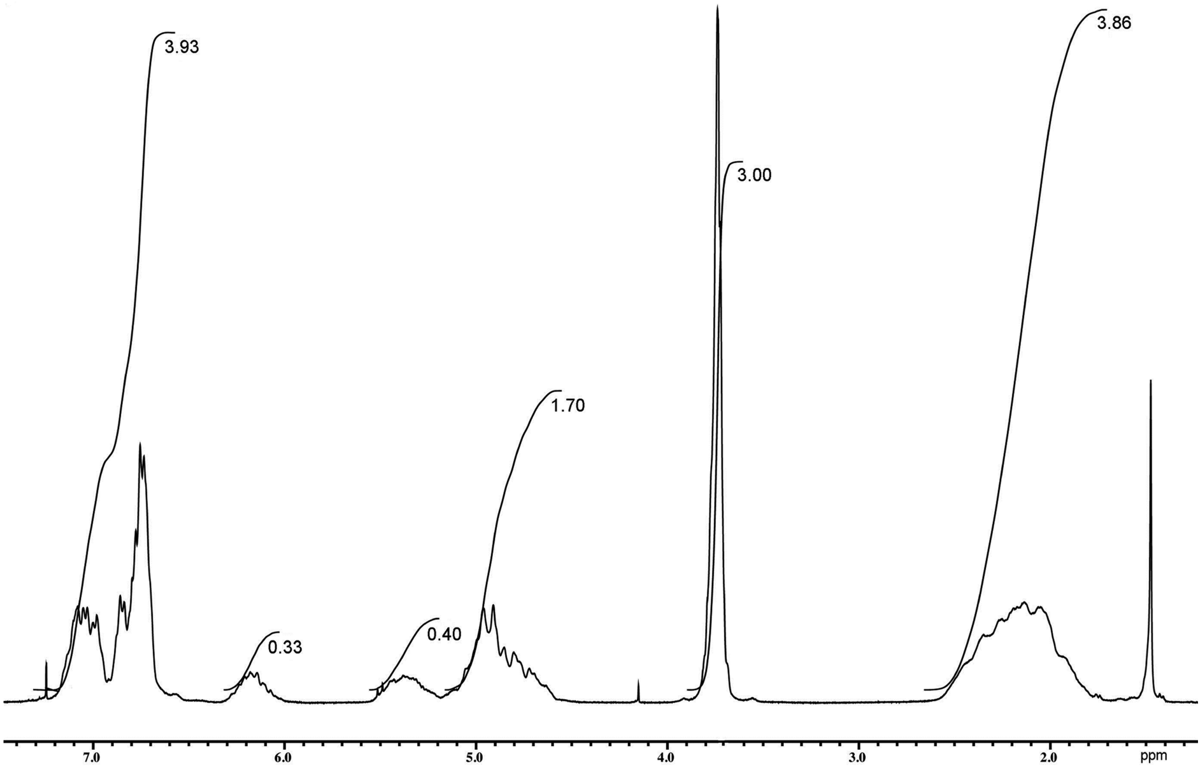


Figure 5. ^{1}H NMR spectrum of poly(**MP3D**) prepared at −78 °C.

analysis. Figure 5 shows the ^{1}H NMR spectrum of poly(**MP3D**) prepared at −78 °C. In the aliphatic proton region, signals attributable to methylene protons adjacent to carbon−carbon double bonds and a methoxy proton were observed at 1.8−2.5 and 3.7 ppm, respectively. Aromatic proton signals were observed at 6.6−7.2 ppm. The relative integrated

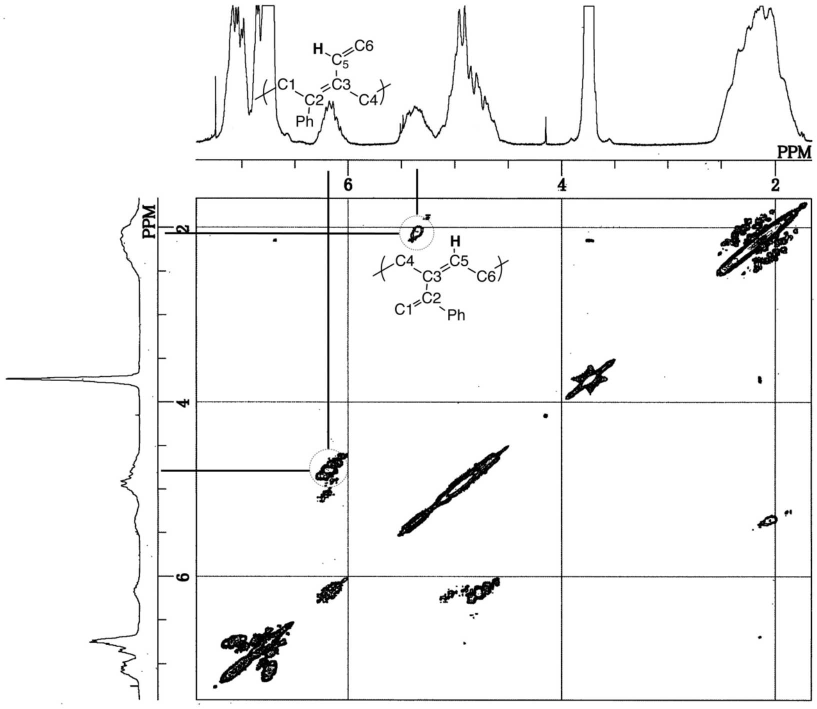
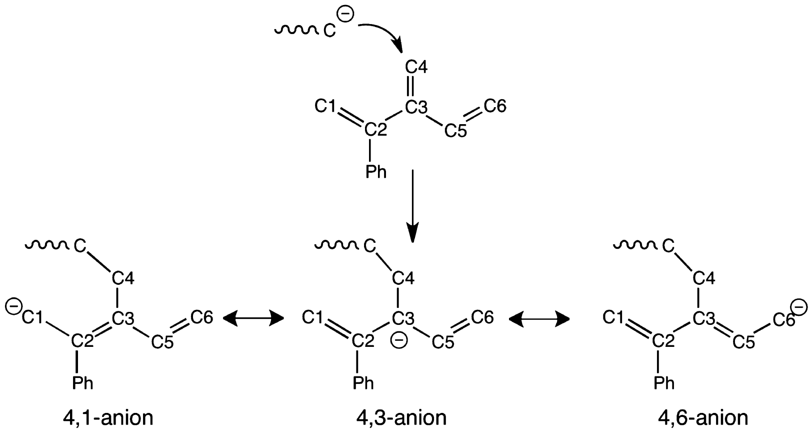


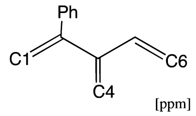
Figure 6. COSY spectrum of poly(**MP3D**) prepared at −78 °C.

Scheme 4. Expected Structure of the Propagating Carbanion



intensities of these signals, 3.9(=C−CH$_2$):3(OCH$_3$):4.0(arom), were close to the ratio based on the premise that only the conjugate addition structure was incorporated. In addition, the fractional number of olefinic proton signals at 5.2 and 6.1 ppm indicated that two or more structures were included in the polymer chain. Figure 6 shows the COSY spectrum of poly(**MP3D**). The olefinic proton signals at 5.2 and 6.1 ppm exhibited cross peaks with the aliphatic proton signal at 2 ppm and the olefinic proton signal at 4.9 ppm, respectively. This indicated that the signal at 5.2 ppm is due to the olefinic methyne proton in the 4,6 structure, with that at 6.1 ppm attributable to the pendant vinyl methyne proton in the 1,4 structure. From the relative integrated intensities of these signals, the 4,6 structure was observed to predominate slightly in poly(**MP3D**). No apparent change in the microstructure was observed when changing the polymerization temperature. In the 1,4 and 4,6 structures, two types of methylene carbons, C6 and C1, respectively, should be present in the side group as shown in Scheme 3. Although multiple olefinic methylene signals were observed at 111.5 ppm in the ^{13}C NMR spectrum shown in Figure 4, we could not assign these signals because their chemical shifts were too close to analyze. The microstructure of poly(**P3D**) was analyzed similarly, and almost equal proportions of the 4,6 and 1,4 structures were found.

Though the microstructure of the polymers was determined to be a mixture of 1,4 and 4,6 structures, the mode of monomer addition was not clear. Each monomer used in this study had three methylene carbons, C1, C4, and C6, that could be attacked by the propagating chain-end carbanion, as shown in Scheme 4. However, because there was no evidence of vinyl components such as 1,2 or 5,6 structures, it is likely that the propagating carbanion attacked at C4 on the monomer to form 4,1 and 4,6 anions, resulting in the formation of the above-mentioned microstructures. The ^{13}C NMR chemical shifts of the monomers shown in Figure 7 are in agreement with this. In general, the chemical shift of an olefinic carbon is mainly affected by the electron density of the double bond. The lower the electron density, the larger the chemical shift. As can be



			[ppm]
P3D	114.8	118.3	117.5
MP3D	113.1	118.2	117.3

Figure 7. ^{13}C NMR chemical shifts of the dienyl skeleton in the monomer.

seen from Figure 7, the C4 methylene carbon resonates at the lowest field, indicating that the carbon is most susceptible to the nucleophilic attack of the carbanion to form a resonance hybrid consisting of 4,3, 4,1, and 4,6 anions. Among these anions, the 4,3 anion should be the most stable because of hybridization; in addition, it is a sterically hindered tertiary anion, making propagation difficult. Thus, only the 4,1 and 4,6 anions participate in propagation, resulting in the formation of the observed 1,4 and 4,6 structures in the polymer.

■ CONCLUSIONS

Anionic polymerization of **P3D** and **MP3D** was carried out in THF with a potassium counterion. Poly(**P3D**) of a narrow molecular weight distribution was obtained if the polymerization was carried out at −78 °C and terminated after an appropriate polymerization time. Broadening of the molecular weight distribution was observed if the polymerization mixture was left to stand for a period of time after complete consumption of the monomer had occurred. In the case of poly(**MP3D**), such broadening did not occur if the reaction was carried out at −78 °C. The nucleophilicities of the carbanions derived from these monomers were too low to initiate the polymerization of styrene but high enough to initiate the polymerization of 2-vinylpyridine. Microstructural analysis of the resulting polymers by NMR revealed that they were mixtures of 1,4 and 4,6 structures, and no vinyl addition was observed in the polymer chain.

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Notes

The authors declare no competing financial interest.

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