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Anionic Living Polymerization of 2,3-Diphenyl-1,3-butadiene

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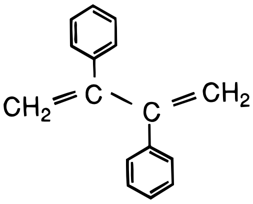
ABSTRACT: The anionic polymerization of 2,3-diphenyl-1,3-butadiene (**1**) was investigated in THF at −78 °C as well as in benzene at 40 °C. Compound **1** was found to undergo anionic living polymerization in THF with cumylpotassium or *s*-BuLi to afford quantitatively the polymers of well-controlled molecular weights and narrow molecular weight distributions ($M_w/M_n < 1.1$). Each of the microstructures of the polymers was observed to be only the 1,4-addition product of poly(2,3-diphenyl-1,3-butadiene). Furthermore, the polymer consisted of 90% cis and 10% trans 1,4-structures, although the assignment of these configurations was tentative. It was observed by DSC that the polymer showed a glass transition temperature of 98 °C and a melting point of 170 °C. Surprisingly, on standing for a few hours the polymer precipitated completely from the polymer solution in THF. The polymer thus precipitated became insoluble in most organic solvents except for hot toluene and *o*-dichlorobenzene. This may therefore be due to the crystallization of the polymer, but not cross-linking as previously reported.

Introduction

Anionic polymerizations of 1,3-diene monomers have so far been extensively investigated.[1,2] Under the appropriate conditions of polymerization, 1,3-butadiene, isoprene, and many 2-alkyl- and 2-aryl-substituted 1,3-butadiene derivatives are known to undergo anionic living polymerization to afford the poly(1,3-diene)s with controlled molecular weights and narrow molecular weight distributions.[2] Furthermore, block copolymers of styrene with 1,3-butadiene or isoprene prepared by anionic living polymerization are commercially available as thermoplastic elastomers.[3] The stereochemistry of anionic polymerization of dienes depends on the polymerization variables such as initiator, solvent, and temperature and can be controlled to a certain extent. For example, a high *cis*-1,4 polyisoprene analogous natural rubber can be obtained by the polymerization of isoprene with organolithium compounds in hydrocarbon solvents.[4]

Little attention has been, however, paid to the polymerization of 2,3-diphenyl-1,3-butadiene (**1**). To the best of our knowledge, only two studies on the polymerization were previously reported.[5,6] Vogl and coworkers first demonstrated in 1977 that **1** underwent AIBN-initiated free-radical polymerization to afford the polymers in 60−96% yields, while (t-Bu)$_3$Al−TiCl$_4$ and (i-Bu)$_3$Al−TiCl$_4$ Ziegler type initiators were not effective for the polymerization.[5] The resulting polymer was shown to be 57% *trans*-1,4-poly(2,3-diphenyl-1,3-butadiene) and 43% *cis*-1,4-poly(2,3-diphenyl-1,3-butadiene), and the 1,2-isomeric structure was not observed by IR or ^{1}H and ^{13}C NMR analyses. Later, similar results on the radical polymerization of **1** were reported by Asami and co-workers.[6]



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Vogl and co-workers also attempted to polymerize **1** anionically with either *n*-butyllithium (*n*-BuLi) or sodium naphthalenide.[5] Unfortunately, *n*-BuLi was not effective and the polymer yields were less than 10% yields. On the other hand, a nearly quantitative conversion of the monomer in the polymer was observed with sodium naphthalenide in THF at 30 °C. It turned out, however, that the polymer was completely insoluble in organic solvents and totally cross-linked. Unfortunately, no further information was available in the literature. From these results, it is considered that **1** possess anionic polymerizability to a certain extent. However, we believe that the polymerization temperature of 30 °C in THF might be unusual as a general condition of the anionic polymerization. It therefore occurred to us that it should be possible to control the polymerization of **1**, affording a soluble polymer, even with molecular weight control by carefully setting the condition of anionic polymerization.

We present in this paper our successful results of the anionic living polymerization of **1** in THF at −78 °C. The microstructures of the resulting polymers will be discussed.

Experimental Section

Materials. Styrene, α-methylstyrene, isoprene, methyl methacrylate (MMA), THF, heptane, and benzene were purified by the procedures reported previously.[7]

2,3-Diphenyl-1,3-butadiene (1). The monomer **1** was previously synthesized by Vogl and co-workers.[5,8] In this study, we synthesized **1** by the following new method using a nickel-mediated coupling reaction between α-bromostyrene and 1-phenylvinylmagnesium bromide, prepared from α-bromostyrene and Mg in THF. To 30 mL of a dry ether solution of α-bromostyrene (4.91 g, 26.8 mmol) and NiCl$_2$−bis(diphenylphosphino)propane (40 mg, 0.10 mmol) was added dropwise a THF solution of 1-phenylvinylmagnesium bromide (40 mL of a 0.69 M THF solution, 27.6 mmol) at 0 °C under an atmosphere of nitrogen. The resulting mixture was stirred for 12 h at room temperature. It was then hydrolyzed with 2 N HCl and extracted with ether (30 mL × 3). The ether layer

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was washed with 10% $NaHCO_3$ and H_2O and dried over $MgSO_4$. After evaporation, the residual oil was fractionally distilled twice at 98−99 °C (1 Torr) to give 2.53 g (12.3 mmol, 46% yield) of **1** as a colorless liquid which crystallized on standing. It was further purified by repeating recrystallization from methanol, mp 48.5−49.0 °C (lit.[5] mp 49−50 °C). The purity of **1** thus obtained was analyzed by GC to be more than 99.3%: ^1H NMR ($CDCl_3$) δ 7.54−7.18 (10H, m, Ar), 5.53 (2H, d, $J = 1.65$ Hz, $CH_2{=}$), 5.31 (2H, d, $J = 1.65$ Hz, $CH_2{=}$); ^{13}C NMR ($CDCl_3$) δ 149.9 ($CH_2{=}C$), 140.1 (C3 of Ar), 128.2 (C5 and C6 of Ar), 127.5 (C4 of Ar), 116.3 ($CH_2{=}$); IR (KBr) 3030, 3023, 1608, 1573, 1495, 1443, 1096, 1071, 1028, 904, 776, 704 cm^{-1}.

Compound **1** thus synthesized was dried under high-vacuum condition (10^{-6} Torr) in the presence of P_2O_5 for 48 h. It was diluted with THF (0.05 M) or benzene (0.15 M) on a vacuum line and divided into ampules with breakseals that were prewashed with potassium naphthalenide in THF or 1,1-diphenylhexyllithium in benzene.

Polymerization Procedure. Polymerizations were carried out under high-vacuum condition in all-glass apparatus with breakseals in the usual manner. The resulting polymers all were first soluble in THF after terminating with a few drops of degassed methanol, but they precipitated completely on standing after a few hours. The polymers that precipitated were insoluble in not only THF but also most organic solvents. They were soluble only in hot *o*-dichlorobenzene. The polymers with M_ns of less than 7000 were also soluble in hot toluene.

The polymerization mixtures soon after terminating with a few drops of degassed methanol were directly injected into a SEC instrument to characterize the molecular weights and molecular weight distributions of the polymers using polystyrene calibration.

Block Copolymerization. Block copolymerizations were conducted by the sequential addition of two monomers in THF at −78 °C. The block copolymer of poly(styrene-*b*-**1**) was prepared in THF at −78 °C with *s*-BuLi by polymerizing styrene first for 30 min and then **1** for 48 h. When **1** was used as a first monomer, the polymerization of **1** was carried out with *s*-BuLi in THF at −78 °C for 48 h, and then either styrene or MMA was added as a second monomer to polymerize in THF at −78 °C for 1 h. In the polymerization of MMA, 5 equiv of LiCl was added prior to the polymerization. With use of isoprene as a second monomer, cumylpotassium instead of *s*-BuLi was used as an initiator in the first polymerization of **1**, and the polymerization mixture was allowed to stand for 5 h in THF at −78 °C after the addition of isoprene.

The block copolymers poly(styrene-*b*-**1**) and poly(**1**-*b*-MMA) thus obtained were soluble and did not precipitate on standing. They could be purified by precipitation from THF to methanol. The block copolymers were characterized by NMR and SEC.

Measurements. IR spectra were recorded on a JASCO IR-G spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL GSX-270 (270 MHz for ^1H and 67.80 MHz for ^{13}C) in $CDCl_3$ and toluene-d_8. Size exclusion chromatography (SEC) was conducted on a TOYO SODA HLC-802 instrument at 40 °C with THF as the carrier solvent. Differential scanning calorimetric (DSC) measurements were carried out with a Perkin-Elmer DSC Model II at a scanning rate of 2 °C/min.

Results and Discussion

Anionic Polymerization of 1. The anionic polymerization of **1** was first carried out in THF at −78 °C with cumylpotassium. On mixing **1** in THF with cumylpotassium, an immediate color change from the bright red characteristic of cumylpotassium to dark red was observed, indicating that the polymerization occurred very rapidly to generate a new carbanion from **1**. This color remained stable as long as the temperature was kept at −78 °C. Only a trace amount of oligomer was obtained after 1 h. A polymer was obtained in 66% yield after 20 h. The polymerization was observed to go to completion in 168 h.

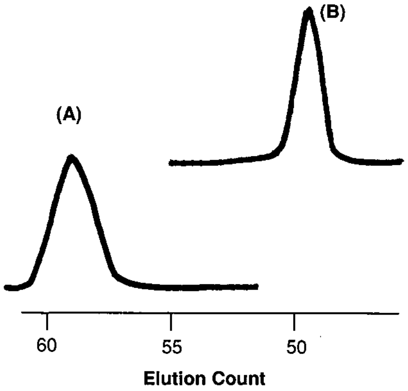


Figure 1. SEC curves of poly(2,3-diphenyl-1,3-butadiene)s (peak A, $M_n = 2600$, $M_w/M_n = 1.07$; peak B, $M_n = 13000$, $M_w/M_n = 1.05$).

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

1, mmol	initiator	mmol	time, h	yield, %	M_n calcd	M_n obsd[a]	M_w/M_n[a]
1.99	cumyl-K[b]	0.128	1	<10			
2.68	cumyl-K	0.156	20	66	2 400	2 600	1.07
2.67	cumyl-K	0.0430	168	100	13 000	13 000	1.05
2.89	K-naph[c]	0.0402	200	90	30 000	44 000	1.11
2.71	*s*-BuLi/α-MeSt[d]	0.102	48	100	6 500	6 500	1.04
2.16	*s*-BuLi	0.0509	20	100	8 800	10 500	1.07
2.20	*s*-BuLi	0.0330	25	100	14 000	16 000	1.06
2.27[e]	*s*-BuLi	0.856	4	49	5 500		

[a] M_n obsd was obtained by SEC using standard polystyrene calibration. [b] Cumylpotassium [c] Potassium naphthalenide. [d] α-Methylstyrene. [e] Polymerization was carried out in benzene at 40 °C.

The polymerization was terminated with a few drops of degassed methanol. It turned out that the polymer completely precipitated from the polymer solution on standing after a few hours at room temperature. The polymer, once precipitated, was not soluble again in THF, even after a long time and at a reflux temperature of 66 °C. Furthermore, the polymer was observed to become insoluble in most organic solvents, such as acetone, benzene, chloroform, dichloromethane, 1,4-dioxane, DMF, and DMSO. The polymer was only soluble in hot *o*-dichlorobenzene. It was also found that the polymers having M_ns of less than 7000 were soluble in hot toluene. Thus, obviously, the polymer precipitation in our case is not attributed to the cross-linking, as reported previously by Vogl et al.[5] The cause for the precipitation will be discussed later.

To characterize the molecular weights and molecular weight distributions of the resulting polymers, the polymer solutions were directly injected into the SEC instrument prior to precipitation of the polymers. Surprisingly, both polymer samples obtained after 20 and 168 h showed symmetrically unimodal SEC peaks without any shoulders and tailings. As shown in Figure 1, their molecular weight distributions are very narrow, the M_w/M_n values being 1.07 and 1.05, respectively, estimated from polystyrene calibration. The M_n values obtained by SEC agreed well with those calculated by [monomer]/[initiator] ratios, as was seen in Table 1. These results, as well as the observation that the polymerization system turned bright red, indicate strongly the living character of the polymerization of **1**.

With use of potassium naphthalenide as a difunctional initiator, the polymerization of **1** gave a polymer in 90% yield in THF at −78 °C for 200 h. The polymer showed two peaks (M_n = 50 000 and 25 000), both of which seemed nearly monodisperse. The M_n observed by SEC was definitely higher than that calculated. This may possibly be caused by partial termination of either the initiator or the propagating chain end with impurities in **1** at the initial stage of the polymerization. More rigorous purification of **1** may be required to obtain the polymers of higher molecular weights.

The polymerization of **1** was similarly carried out in THF at −78 °C with *s*-BuLi or with the living oligomer of α-methylstyrene prepared from *s*-BuLi and α-methylstyrene. The polymerization was also conducted with *s*-BuLi in benzene at 40 °C, since the importance of organolithium-initiated anionic polymerization of 1,3-dienic monomers in hydrocarbon solvents is well-recognized. The results are also summarized in Table 1.

With use of organolithium compounds as initiators, the polymerization appeared to proceed relatively fast and completed within 20 h. The polymers with controllable molecular weights and narrow distributions could be obtained in THF at −78 °C, with both *s*-BuLi and oligo(α-methylstyryl)lithium. These results also indicate that the anionic polymerization of **1** proceeds in a living manner in THF at −78 °C. Again, all the polymers obtained here were observed to precipitate completely from the polymer solutions on standing after a few hours, as was similarly observed in the polymer obtained with cumylpotassium.

On the other hand, the polymerization of **1** with *s*-BuLi in benzene behaves differently. Addition of **1** on *s*-BuLi instantaneously turned the reaction mixture light yellow, which changed to orange after 1 min. A homogeneous polymerization system at first became turbid and a polymer was then precipitated gradually with time. After 1 h, a clear solution was obtained with an orange polymer clinging to the bottom of the reaction vessel. A polymer yield was 49%. The resulting polymer was soluble only in hot *o*-dichlorobenzene and toluene. Therefore, the molecular weight was not measured by SEC in THF, chloroform, or even DMF. The molecular weight can be estimated to be less than 7000 from the fact that the polymer is soluble in hot toluene.

Anionic Block Copolymerization. One of the most important advantages of living polymerization is to be able to synthesize block copolymers with well-defined structures by sequential addition of two or more different monomers. In addition to this synthetic advantage, the reactivities of monomers and their living polymers can be elucidated by the result of sequential polymerizations with other monomers.

At first, a block copolymerization was attempted by the sequential addition method in which styrene was polymerized first and **1** was then added to the polymerization mixture. The polymerization of styrene was carried out with *s*-BuLi in THF at −78 °C for 0.5 h, and after addition of **1** the polymerization mixture was allowed to stand in THF at −78 °C for 48 h. A dramatic change in color from orange to dark red was observed in going from polystyryl anion to the carbanion generated from **1**. A polymer was obtained quantitatively. Figure 2 showed that the SEC peak of the resulting polymer shifted completely to a higher molecular weight side, while the peak for the starting polystyrene disappeared. The molecular weight distribution was narrow, the M_w/M_n value being 1.09. From the closeness of the M_n values calculated and measured by SEC and NMR, it is obvious that the block copolymerization of styrene with **1** occurs as expected to afford a novel well-defined AB diblock copolymer, poly(styrene-*b*-**1**). The results are summarized in Table 2. Interestingly, the block copolymer thus obtained did not precipitated on standing for a long time and could be purified by reprecipitation from THF to methanol.

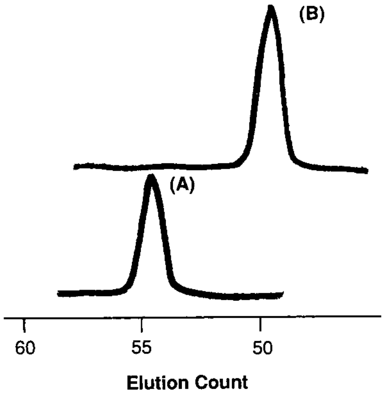


Figure 2. SEC curves of polystyrene at the first polymerization (peak A, M_n = 6500, M_w/M_n = 1.05) and of poly(styrene-*b*-2,3-diphenyl-1,3-butadiene) (peak B, M_n = 12 000, M_w/M_n = 1.09).

Table 2. Block Copolymerization of 1 with Styrene or MMA in THF at −78 °C

	monomer		yield,	M_n		
initiator	1st	2nd	%	calcd	obsd	M_w/M_n
s-BuLi	styrene	**1**	100	12 000 (6 300)[a]	12 000 (6 500)	1.09
s-BuLi	**1**	styrene	100	28 000 (8 800)	11 000 (11 000)	220 000[b]
s-BuLi/LiCl	**1**	MMA	100	22 000 (11 000)	24 000 (10 000)	1.08

[a] The values in parentheses are M_ns of homopolymers obtained at the 1st polymerizations. [b] Two main peaks were observed and their M_w/M_n values were estimated to be around 1.1.

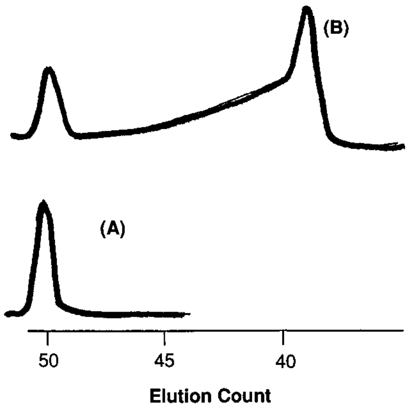


Figure 3. SEC curves of poly(2,3-diphenyl-1,3-butadiene) at the first polymerization (peak A, M_n = 10 500, M_w/M_n = 1.07) and the polymer mixture of poly(2,3-diphenyl-1,3-butadiene) and poly(2,3-diphenyl-1,3-butadiene-*b*-styrene) at the second polymerization (peak B).

On the other hand, the block copolymerization failed in the case where **1** and styrene were added in that order. As can be seen in Figure 3, a bimodal distribution is observed in the resulting polymer. A higher molecular weight sharp peak (M_n = 220 000) with a significant shoulder may correspond to the block copolymer with an unexpected high styrene content. A low molecular weight sharp peak (M_n = 10 000) agreed with that of

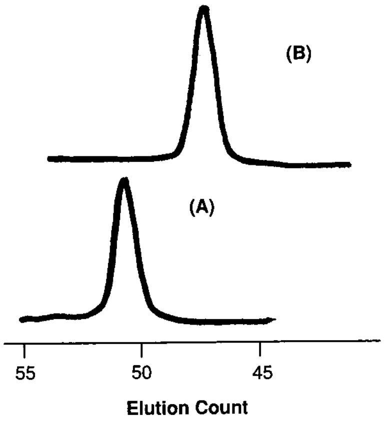


Figure 4. SEC curves of poly(2,3-diphenyl-1,3-butadiene) at the first polymerization (peak A, $M_n = 10\ 000$, $M_w/M_n = 1.05$) and poly(2,3-diphenyl-1,3-butadiene-*b*-methyl methacrylate) (peak B, $M_n = 24\ 000$, $M_w/M_n = 1.08$).

the homopolymer of **1** at the first-stage polymerization. It was estimated from both peak areas and their molecular weights that only around 5% of the living polymer of **1** initiated the polymerization of styrene. This indicates that the carbanion generated from **1** is not reactive enough to initiate the polymerization of styrene quantitatively.

On the basis of this result, we have next employed the more electrophilic methyl methacrylate (MMA) as a second monomer in the block copolymerization. The dark red color for the carbanion from **1** disappeared instantaneously on addition of MMA at the second-stage polymerization. SEC of the resulting polymer revealed that the resulting polymer possessed a unimodal sharp peak, the M_w/M_n value being 1.08, as was seen in Figure 4. No peak corresponding to the homopolymer of **1** was detected at all. There is a fair agreement between the M_n values calculated and measured, as can be seen in Table 2. Thus, a well-defined block copolymer of poly(**1**-*b*-MMA) could be successfully synthesized. It should be emphasized here that the success of this block copolymerization also provides direct evidence for the living character of the anionic polymerization of **1**.

On the other hand, no block copolymer was formed at all by the sequential block copolymerization of **1** with isoprene, which was less electrophilic than styrene. Only the homopolymer of **1** was quantitatively recovered. This implies that the carbanion from **1** has no ability to initiated the polymerization of isoprene under the conditions employed.

From these results of block copolymerizations of **1** with styrene, MMA, and isoprene, it is estimated that the living polymer of **1** is less reactive than those of isoprene and styrene, but similar or more reactive than that of MMA. In general, the monomers that form the more reactive anions are the less reactive monomers in anionic polymerization and vice versa. It can therefore be estimated that the anionic reactivity of **1** is higher than those of isoprene and styrene and similar to or lower than that of MMA.

Characterization of Polymers. The resulting polymers obtained here were characterized by both ^{1}H and ^{13}C NMR spectroscopies in toluene-d_8 at 110 °C. A typical ^{1}H NMR spectrum of the polymer is shown in Figure 5. The ^{1}H NMR spectra of the polymer samples obtained with different initiators in THF are very similar. The resonances at 7.4−6.5 and 2.7−2.1 ppm assigned to phenyl and methylene protons, in addition to those assigned to initiator (*s*-BuLi) residue (around 3, 2, and 1 ppm), were observed in all spectra, while no resonance for terminal methylene protons was detected at all in each case. Thus, these polymers are clearly indicated to be structurally pure 1,4-addition products. The polymer obtained with *s*-BuLi in benzene also consisted of only the 1,4-structure, as shown by the ^{1}H NMR analysis.

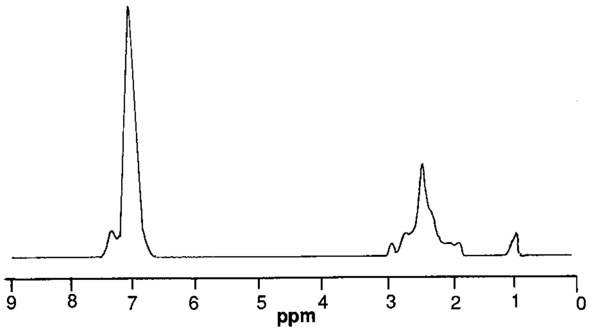
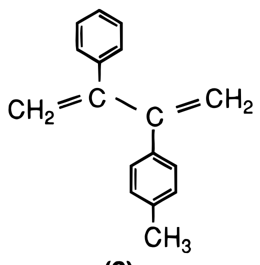


Figure 5. ^{1}H NMR spectrum of poly(2,3-diphenyl-1,3-butadiene) obtained by the polymerization with *s*-BuLi in THF at −78 °C.

In the ^{13}C NMR spectrum of the polymer obtained in THF with *s*-BuLi ($M_n = 6500$), the resonances for only quaternary carbons at 138.8 and 35−34 ppm characteristic for olefinic and methylene carbons were observed. On the other hand, no signal corresponding to the terminal methylene carbon formed by a 1,2-polymerization was observed at 110−120 ppm within analytical limits. Accordingly, ^{13}C NMR analysis also indicated that the polymers consisted of exclusively the 1,4-structure.

In the aliphatic carbon region, a major signal at 34.0 ppm and a minor signal at 35.1 ppm were observed and assigned tentatively to the cis and trans configurations, respectively. The reason for this is that carbons originated from trans configuration are indicated to shift to higher fields than those from cis configuration in the poly(2,3-diphenyl-1,3-butadiene)s obtained by radical polymerization and the related low molecular weight compounds previously reported.[5,9,10] It can be estimated from their peak areas that the polymer consists of approximately 90% cis and 10% trans 1,4-structures. Unfortunately, a further information on configuration was not available from resonances at 139.8 and 138.8 ppm attributed to aromatic C1 and methylene carbons, both of which were not split into two peaks. Therefore, uncertainty still exists regarding the assignment of resonances to the cis and trans configuration.

To obtain more information on the stereochemistry of the polymers of 2,3-diphenyl-1,3-butadiene derivatives, we have preliminarily studied the anionic polymerizations of 2-(4-methyphenyl)-3-phenyl-1,3-butadiene (**2**) and 2-(4-methoxyphenyl)-3-phenyl-1,3-butadiene



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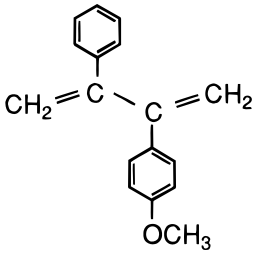

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(**3**) in addition to **1** under the similar conditions employed here. From ^{1}H and ^{13}C NMR analyses of the resulting polymers of **2** and **3**, they are indicated to be also composed of predominantly 1,4-or 4,1-structures. Furthermore, we have newly synthesized their model compounds by stoichiometric reactions of **2** or **3** with *tert*-butyllithium to well characterize the structures of polymers by NMR spectroscopies. Expanded long-range C−H shift correlation spectra and NOE spectra of the polymers and model compounds were measured and compared with each other. From these spectra, for example, it can be concluded that the polymer of **2** and **3** contains 76% *Z*-4,1-structure. More detailed results will be published in the very near future.

These spectral results are similar to those of the polymers obtained by AIBN-initiated radical polymerization reported previously by Vogl and co-workers.[5] Their polymer consisted of 100% 1,4-structure, although the cis and trans configurations were indicated to be 43 and 57%, respectively.

One of the most striking features of the polymer obtained by anionic polymerization is the precipitation of the polymer completely from the solution on standing for a few hours after terminating with a few drops of methanol. The solubility of the polymer changed dramatically before and after the precipitation, as mentioned before. The polymer obtained with cumylpotassium (M_n = 13 000) was characterized by DSC to show a glass transition temperature (T_g) of 98 °C and a reproducible endothermic peak at 170 °C, corresponding to the melting point, as was observed in Figure 6. It was also observed by microscope that the polymer melted at around 170 °C. All the polymers obtained anionically in this study are soluble in *o*-dichlorobenene, although they are not soluble in most organic solvents once precipitated. Accordingly, the cause for the polymer precipitation may possibly be due to the crystallization of polymer, but not the cross-linking as reported previously.[5] This is a marked contrast to the previous result of radical polymerization. The polymer obtained by radical polymerization showed a somewhat high T_g of 116 °C, but no melting point.[5]

In conclusion, the anionic polymerization of **1** proceeded quantitatively in THF at −78 °C with cumylpotassium, *s*-BuLi, or oligo(α-methylstyryl)lithium. The resulting polymers were observed to have predictable M_n values and narrow molecular weight distributions, indicating the living character of the polymerization of **1** under the conditions employed here. Furthermore, this was strongly supported by the success of block copolymerization. The microstructure of the polymer was the 1,4-structure, which consisted of 90% cis and 10% trans configurations, respectively, although their assignment was tentative. The polymer completely precipitated in THF on standing, possibly by the crystallization, and became insoluble in most organic solvents, except for hot *o*-dichlorobenzene and toluene.

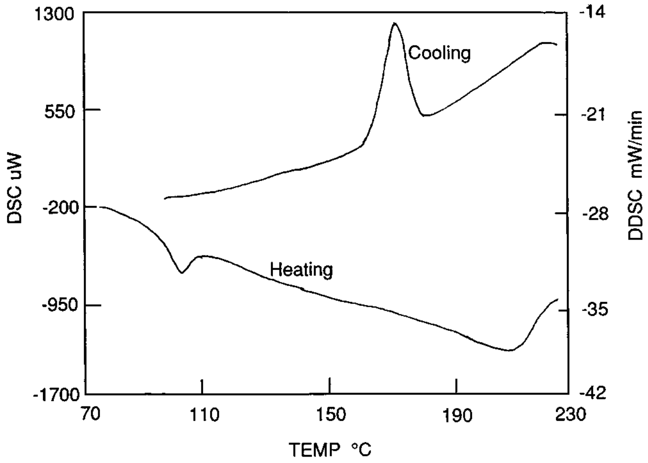

Figure 6. DSC curves of poly(2,3-diphenyl-1,3-butadiene) obtained by the polymerization with cumylpotassium in THF at −78 °C.

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