Anionic Polymerization of 2,3-Dimethylbutadiene

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ABSTRACT: 2,3-Dimethylbutadiene was polymerized in tetrahydrofuran with *n*-BuLi. The content of the 1,2-unit in the polymer varied with the polymerization temperature as follows: 86% at -78°C , 69% at -45°C , 54% at -30°C , and 48% at 0°C . The relationship between $\log(k_{1,2}/k_{1,4})$ and $1/T$ showed a break at -30°C , where $k_{1,2}$ and $k_{1,4}$ are the propagation rate constants leading to the denoted structures, respectively, and T is the polymerization temperature ($^{\circ}\text{K}$). It was postulated that the continuous arrangement of 1,2-units, which is preferential at low temperature, becomes impossible at higher temperatures due to steric hindrance, and the insertion of the 1,4-unit in the sequence of 1,2-units takes place more frequently, resulting in alternating arrangements of the 1,2- and 1,4-unit above -30°C . The NMR spectra of the polymers showed that the chemical shifts of each monomeric unit varied with the difference of the neighboring monomeric units in both sides. The spectrum of the polymer having a 1,2- and 1,4-unit in 1:1 suggested the 1,2-unit being held between the 1,4-units, *i.e.*, both the units being alternate. The polymerization of 2,3-dimethylbutadiene in hydrocarbon solvent gave a polymer rich in the 1,4-unit with *n*-BuLi at 30°C , but formed a similar polymer with K-dispersion as that obtained with *n*-BuLi in tetrahydrofuran at 30°C .

KEY WORDS 2,3-Dimethylbutadiene / Poly(2,3-dimethylbutadiene) / Anionic Polymerization / Microstructure / Alternating Copolymer / NMR /

A number of papers have been published on the anionic polymerizations of butadiene and isoprene. Many of them were concerned with the relationship between the conditions of polymerization and the microstructures of the produced polymers.¹⁻⁴ However, no detailed investigation has been reported on the anionic polymerization of 2,3-dimethylbutadiene (DMB). In the present study, we investigated the microstructure of the poly(2,3-dimethylbutadiene) (PDMB) prepared by anionic polymerization under various conditions, by means of NMR and IR spectroscopies.

EXPERIMENTAL

Materials

2,3-Dimethylbutadiene was synthesized by the dehydration of pinacol as described by Allen.⁵ The monomer was fractionally distilled, and the fraction of 69.5°C (760 mm) was collected. The purified DMB was dried over lithium aluminum

hydride and distilled *in vacuo* before use.

n-Butyllithium (*n*-BuLi) was prepared in *n*-heptane according to the method of Ziegler⁶ from *n*-butyl chloride and metallic lithium.

Na and K dispersions were prepared in *n*-heptane. Tetrahydrofuran (THF), which had previously been refluxed over metallic sodium and then over lithium aluminum hydride, was distilled onto Na-K alloy and naphthalene. From the green solution the solvent was transferred to a reaction vessel on a vacuum line just before use.

Benzene and *n*-heptane were purified by the usual method and were stored over sodium. Before use, each of the solvents was transferred to a flask containing a small amount of *n*-BuLi in *n*-heptane and then redistilled under high vacuum.

Diethyl ether purified in the usual manner was distilled onto lithium aluminum hydride. The solvent was then transferred to a reaction vessel on the vacuum line just before use.

Polymerization

A solvent was first transferred using the vacuum line to a glass ampoule which had been evacuated and heated with a gas burner. Then the monomer and an initiator were added with hypodermic syringes to the ampoule, which was held in a thermostat, under an atmosphere of dry nitrogen. The ampoule was sealed and the reaction was allowed to proceed. After the polymerization was terminated by adding a small amount of methanol, the reaction mixture was poured into a large amount of methanol which contained *N*-phenyl-2-naphthylamine as a polymer antioxidant. The precipitated polymer was filtered, washed with methanol and dried. The obtained polymer was stored at -20°C .⁷

Measurement

The NMR spectrum of the polymer was measured at 60°C with a JNM-4H-100 spectrometer at 100 MHz by using carbon tetrachloride or benzene as a solvent. The concentration of the sample was *ca.* 10% (w/v) and tetramethylsilane was used as an internal standard. The content of the microstructure of the polymer was determined from the ratio of the olefinic protons in the 1,2-unit to the others.

The infrared spectrum of the polymer was obtained with a JASCO IR-S spectrometer with a thin film cast on a rock salt plate from a solution in methylene chloride.

The solution viscosity of the polymer was

determined in toluene at 30.0°C , the concentration of the polymer being 0.5 g/dl.

RESULTS

The polymerization of DMB was carried out with *n*-BuLi in THF. The results are shown in Table I. The rate of polymerization and the content of the 1,4-unit decreased, as the polymerization temperature decreased. At -78°C the polymer produced had a high 1,2-content, but above -30°C the 1,2- and 1,4-content became almost 1:1. The solution viscosity of the polymer decreased with decreasing yield, while the softening point of the polymer rose with an increase in the 1,2-unit. The microstructure of the polymer was not affected either by the substitution of the solvent with ether or by the addition of *N,N,N',N'*-tetramethylethylenediamine in THF at 30°C . After polymerization was carried out at -20°C , the reaction mixture was stood for three days at 30°C , but the polymer was almost the same as that obtained at -20°C .

Table II shows the results of the polymerization in *n*-heptane and benzene at 30 – 50°C . At lower temperatures the rate of polymerization was extremely low. Contrary to the polymerization in THF the polymers obtained were rich in the 1,4-unit. As the temperature of polymerization was raised, the content of the

Table I. Polymerization of 2,3-dimethylbutadiene in THF^a

No.	Temp, $^{\circ}\text{C}$	Time, day	Yield, %	1,4-Content, %	1,2-Content, %	η_{sp}/c , dl/g	SP ^b , $^{\circ}\text{C}$
01	50	1	96.6	58	42	0.20	58–66
02	30	1	99.6	56	44	0.20	62–72
03 ^c	30	10	58.8	56	44	0.11	—
04	0	1	99.3	52	48	0.19	68–77
05 ^d	0	1	98.4	52	48	0.28	—
06 ^e	0	1	90.1	52	48	0.21	—
07 ^f	-20 – -30	4+3	99.7	48	52	—	—
08	-20	4	99.8	46	54	—	—
09	-30	1	51.9	46	54	0.11	70–79
10	-45	2	38.3	31	69	0.10	79–88
11	-78	22	18.9	14	86	0.08	88–97

^a Monomer, 0.53–0.58 g; solvent, THF 10 ml; initiator, *n*-BuLi 0.064 mmol. ^b Softening point of polymer. ^c Solvent, diethyl ether. ^d *n*-BuLi, 0.032 mmol. ^e Solvent, THF 9.0 ml and *N,N,N',N'*-tetramethylethylenediamine 1.0 ml. ^f The reaction was carried out first for 4 day at -20°C and then at 30°C for 3 day.

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Table II. Polymerization of 2,3-dimethylbutadiene in hydrocarbon solvent^a

No.	Temp, °C	Additive, mmol		Yield, %	1,4-Content, %	1,2-Content, %	η_{sp}/c , dl/g
12	50	—	—	98.8	69	31	0.47
13 ^b	40	—	—	98.0	82	18	—
14	30	—	—	91.7	80	20	0.18
15 ^c	30	—	—	87.9	82	18	0.10
16 ^d	30	—	—	94.6	87	13	0.19
17	30	H ₂ O	0.064	30.0	83	17	—
18	30	THF	0.128	99.1	54	46	0.19
19	30	THF	1.280	94.2	55	45	0.18
20	30	THF	0.247	99.8	50	50	0.16

^a Monomer, 0.54–0.56 g; solvent, benzene 10 ml; initiator, *n*-BuLi 0.064 mmol; time, 6 day. ^b Solvent, *n*-heptane; time 5 day. ^c *n*-BuLi, 0.128 mmol. ^d *n*-BuLi, 0.032 mmol.

Table III. Polymerization of 2,3-dimethylbutadiene with various initiators^a

No.	Initiator, mmol	Solvent		Temp, °C	Time, day	Yield, %	1,4-Content, %	1,2-Content, %	η_{sp}/c , dl/g
21	<i>n</i> -BuLi	0.032	THF	0	1	98.4	52	48	0.28
22	Na-dispersion	0.161	THF	0	1	98.8	55	45	0.23
23	K-dispersion	0.114	THF	0	1	98.6	55	45	0.34
24	<i>n</i> -BuLi	0.032	Benzene	30	2	16.9	83	17	—
25	EtLi	0.030	Benzene	30	6	95.0	86	14	0.25
26	K-dispersion	0.057	Benzene	30	6	81.0	58	42	0.15

^a Monomer, 0.55–0.58 g; solvent, 10 ml.

1,4-unit decreased slightly. Even with the addition of an equimolar amount of water to *n*-BuLi, a considerable amount of polymer was obtained. It seemed that the reaction of *n*-BuLi and water was not complete, and the polymer was produced with the *n*-BuLi remaining unchanged. The existence of LiOH formed by the reaction did not affect the microstructure of the polymer. The effect of THF on the polymerization in benzene solution was also investigated (Table II). It was found that when only two moles of THF per *n*-BuLi were added, the polymerization at 30°C produced a polymer having almost the same microstructure as that of the polymer formed in THF at 30°C. No effect of the initiator concentration on the microstructure of the polymer was found either in benzene or THF.

The results of the polymerization of DMB with *n*-BuLi, Na and K dispersions as initiators are shown in Table III. The initiator did not seem to affect the microstructure of the produced

polymer in THF, but showed remarkable influences in benzene. A K dispersion gave a polymer similar to that obtained in THF: almost equal contents of 1,2- and 1,4-units, even in benzene.

The NMR spectra of four PDMBs having different microstructures are shown in Figure 1. Each proton, which belongs to the two configurations of the monomeric unit, 1,2- and 1,4-structure, was marked as follows

Here, the 1,4-structure was presented in *trans* form for convenience sake. However, the *cis*

Figure 1. NMR spectra of poly(2,3-dimethylbutadiene) (at 60°C, 100 MHz): A, B, and C, measured in CCl₄; D, measured in benzene.

and *trans* isomers could not be distinguished in the present work. The spectra were assigned as shown in Figure 1 from the chemical shifts and the area intensities of the peaks, referring to the spectrum of polyisoprene.⁸ It is obvious that the peaks appearing at 4.5–5.0 ppm can be assigned to the olefinic protons *c* in the 1,2-unit. As stated in the previous section the content of the 1,2-unit and accordingly that of the 1,4-unit were determined from the intensity ratio of the peaks *c* against the total one. The contents of the microstructures in the polymers, the spectra of which are illustrated in Figure 1, were as follows

Polymer	A	B	C	D
1,2-content, %	13	50	86	50
1,4-content, %	87	50	14	50

Table IV. The chemical shifts of the protons in the polymers measured in CCl₄ and in benzene at 60°C

		Polymer A,		Polymer C,	
		In CCl ₄ ppm	In C ₆ H ₆ ppm	In CCl ₄ ppm	In C ₆ H ₆ ppm
1,2-structure	<i>a</i>	0.99	1.14	1.18	1.41
	<i>b</i>	—	—	1.80	1.91
	<i>c</i>	4.74	4.90	4.70	4.88
	<i>d</i>	1.76	1.82	1.74	1.84
1,4-structure	<i>e</i>	2.00	2.23	2.14 ^a	2.27
	<i>f</i>	1.64	1.78	1.55	1.73
	<i>g</i>	2.00	2.23	— ^b	—

where A, B, C, and D correspond to No. 16, 20, 11, and 20, respectively, in Tables I and II. The spectrum of D, the same polymer with B, was inserted in order to demonstrate the solvent effect on the chemical shift.

It was found from detailed observations of these spectra that the chemical shifts of the methyl and methylene protons were not constant and changed with the variation of the microstructure of the polymer. The chemical shifts of the protons in A and C measured in carbon tetrachloride and in benzene at 60°C are listed in Table IV. We may postulate that the differences in the chemical shifts between polymers A and C are caused by the differences in the configurations of the monomeric units at both sides of the unit concerned. Since the polymer A has 87% of 1,4-unit, not only almost all of the 1,2-unit but also a major part of the 1,4-unit in the polymer should lie between 1,4-units. On the other hand, in the polymer C having 14% of 1,4-unit, most of the 1,2-unit as well as the 1,4-unit must be held between 1,2-units. Therefore, the chemical shifts of each polymer A and C shown in Table IV may be considered to be those of the monomeric units between 1,4-units and those of the units between 1,2-units, respectively. There must be monomeric units lying between 1,2- and 1,4-unit, but they may be so few in polymers A and C that the resonances of their protons

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Figure 2. IR spectra of poly(2,3-dimethylbutadiene): I, polymer prepared in THF by *n*-BuLi at -78°C ; 1,4-content, 14.5%; 1,2-content, 85.5% and II, polymer prepared in benzene by *n*-BuLi at 50°C ; 1,4-content, 69.0%; 1,2-content, 31.0%.

are hidden in the peaks of the monomeric units described above. When we focus the methyl protons *a* attached to the main chain in the 1,2-unit, their resonances appear at 0.99 ppm in polymer A and at 1.18 ppm in polymer C. Then, it must be noted that polymer B shows a sharp peak of methyl protons *a* at 0.99 ppm, in spite of 50% of 1,4-unit. It is suggested that the 1,2-unit in this polymer is put between 1,4-units; that is, both the units are arranged alternately.

Figure 2 shows the infrared spectra of two PDMBs, one (I) rich in the 1,2- and the other (II) rich in the 1,4-structure. The strong absorption of the olefinic methylene in the 1,2-unit was observed at 890 cm^{-1} in the spectrum of the polymer I, while in that of the polymer II two absorptions were found at 1200 and 1155 cm^{-1} , which were reported to be due to the *cis*-1,4- and *trans*-1,4-structure in PDMB.⁷

DISCUSSION

Similar to butadiene² and isoprene,³ 2,3-dimethylbutadiene forms a polymer rich in the 1,4-unit by polymerization with *n*-BuLi in a nonpolar medium. It also tends to produce PDMB having a high 1,2-content in polar systems, such as with *n*-BuLi in THF and with K dispersion in a hydrocarbon solvent. However, its behavior is very different from those of butadiene and isoprene in polymerizations in polar systems. DMB gives a high 1,2-polymer

in THF only at very low temperature. However, above -30°C the content of the 1,2-unit reaches only about 50%, which is very low compared with those of polybutadiene and polyisoprene produced under the same conditions. It must also be noted that the polymerization of DMB at 30°C with *n*-BuLi in diethyl ether, and even in benzene containing only a very small quantity of THF, gives a polymer having the same microstructure as that of the polymer produced in THF at the same temperature.

The effect of temperature on the microstructure of PDMB produced in THF is illustrated in Figure 3, where $k_{1,4}$ and $k_{1,2}$ are the rate constants of the propagation reactions leading to the 1,4- and 1,2-structure, respectively, and hence $k_{1,4}/k_{1,2}$ shows the ratio of these two units in the polymer. From the plots in Figure 3 the following equation,

$$RT \ln (k_{1,4}/k_{1,2}) = -(\Delta H_{1,4} - \Delta H_{1,2}) + T(\Delta S_{1,4} - \Delta S_{1,2}) \quad (1)$$

indicates that:

above -30°C ,

$$\Delta H_{1,4} - \Delta H_{1,2} = 980\text{ cal/mol}$$

$$\Delta S_{1,4} - \Delta S_{1,2} = 3.7\text{ e.u.}$$

and below -30°C

$$\Delta H_{1,4} - \Delta H_{1,2} = 3230\text{ cal/mol}$$

$$\Delta S_{1,4} - \Delta S_{1,2} = 12.8\text{ e.u.}$$

These data showed that the over-all activation

Figure 3. Microstructure of poly(2,3-dimethylbutadiene) vs. polymerization temperature; with *n*-BuLi in THF.

energy leading to the 1,2-structure was smaller than that leading to the 1,4-structure in THF, and that there may be a change in the mechanism of the polymerization at about -30°C . The steric hindrance in the 1,2-structure must be responsible for the relatively low content of this unit in PDMB produced in THF at higher temperatures. The monomeric unit of PDMB in the 1,2-structure is considered to be sterically very similar to that of poly(α -methylstyrene). α -Methylstyrene can be polymerized at low temperature, but cannot form a high polymer above room temperature owing to the low ceiling temperature of this monomer.⁹

Since the polymerization of DMB at -78°C in THF gave a polymer having a very high 1,2-content, this anionic polymerization in THF must substantially favor the propagation leading to the 1,2-structure. At higher temperatures, however, the continuous arrangement of 1,2-units may become impossible due to the steric hindrance

as stated above. Contrary to α -methylstyrene, DMB is able to avoid steric hindrance by growing through the 1,4-structure resulting in the insertion of the 1,4-unit into the sequence of 1,2-units in the polymer. With the elevation of the polymerization temperature the intervals of the insertion of the 1,4-unit become shorter and shorter, and finally the content of the 1,4-unit in the polymer comes to exceed that of the 1,2-unit above -30°C . Therefore, in the polymer produced at -30°C – 0°C the 1,2- and 1,4-units, which are contained equally, must be arranged alternately. This is consistent with the observation in the NMR spectrum of the polymer. As mentioned above the changes in the thermodynamic data were found at about -30°C , where the polymer may have almost no more continuous arrangements of 1,2-units. The alternating copolymer of DMB and α -MeSt was obtained with anionic initiators in THF at 60°C , where DMB was incorporated only in the 1,4-form.¹⁰

In polyisoprene the *cis*-1,4- and *trans*-1,4-structure can be distinguished by the NMR spectrum, but the chemical shifts of each monomeric unit seem to be not so apparently influenced by the structures of the neighboring

monomeric units.⁸ On the contrary, it is characteristic that the chemical shifts of the monomeric unit of PDMB are remarkably affected by the structures of the units at both sides. This must be attributed to the crowded protons in this polymer. The protons are so closely packed that the situation may cause variations in the chemical shifts with the differences in the neighboring monomeric units.

The preference of the 1,4-structure in the polymerization of DMB with *n*-BuLi in hydrocarbon solvent may be caused for the same reason as those in similar polymerizations of butadiene and isoprene.¹¹⁻¹³

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