

Characterization of polybutadiene produced with $\text{CoBr}_2(\text{PPh}_3)_2$ -based catalysts

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(Received: January 11, 1995)

SUMMARY:

Polymerization of 1,3-butadiene was conducted with the $\text{CoBr}_2(\text{PPh}_3)_2$ (Ph: phenyl)-methylaluminoxane (MAO) and MgCl_2 -supported $\text{CoBr}_2(\text{PPh}_3)_2$ - $\text{Al}(\text{CH}_3)_3$ catalyst systems. The microstructure of polybutadiene was analyzed in detail by ^{13}C NMR spectroscopy after hydrogenation, which indicated that the distribution of the 1,2 and 1,4 units in polybutadiene is more random when the homogeneous $\text{CoBr}_2(\text{PPh}_3)_2$ -MAO catalyst was used. The microstructure of these polymers was compared with that obtained using BuLi as catalyst.

Introduction

The structure of polybutadiene is regulated by chemo-, regio- and stereospecificities of the catalyst system used. Most of the catalyst systems based on transition metals like $\text{Ti}^{(1)}$ or $\text{Ni}^{(2)}$ give *cis*- or *trans*-1,4-polybutadiene. On the other hand, *syndiotactic*-1,2-polybutadiene is obtained with some $\text{Co}^{(3)}$ or $\text{Ti}^{(4)}$ catalyst systems. We have already reported that the catalyst systems composed of $\text{CoBr}_2(\text{PPh}_3)_3$ and an alkyl-aluminium produce polybutadienes with a wide range of 1,2 and *cis*-1,4 units depending upon the polymerization conditions^{5,6}. It is difficult, however, to determine the sequence distribution of each unit directly from the analysis of polybutadiene. Therefore, the polybutadiene was hydrogenated and the resulting hydrogenated polybutadiene was analyzed by ^{13}C NMR spectroscopy in detail⁷. For reference, polybutadiene with a similar content of 1,2 units was synthesized by anionic polymerization using BuLi as catalyst and analyzed after hydrogenation.

Experimental part

Materials

Toluene (commercially obtained extra pure grade) was further purified by refluxing over CaH_2 for 12 h followed by fractional distillation and stored over 4 Å molecular sieves. Extra pure grade $\text{RhCl}(\text{PPh}_3)_3$ was purchased from Kanto Chemical Co., and used without further purification. Triphenylphosphine (PPh_3) (commercially obtained from Tokyo

Kasei Co. Ltd.) was used after recrystallization from ethanol. Polybutadienes were synthesized with the following catalyst systems.

- Run 1⁵⁾: $\text{CoBr}_2(\text{PPh}_3)_2$ -MAO;
 run 2⁶⁾: $\text{CoBr}_2(\text{PPh}_3)_2/\text{MgCl}_2\text{-Al}(\text{CH}_3)_3$ ($\text{Co}/\text{MgCl}_2 = 0,20 \text{ wt.-%}$);
 run 3⁶⁾: $\text{CoBr}_2(\text{PPh}_3)_2/\text{MgCl}_2/\text{SiPh}_2(\text{OCH}_3)_3\text{-Al}(\text{CH}_3)_3$ ($\text{Co}/\text{MgCl}_2 = 0,031 \text{ wt.-%}$, $\text{Si}/\text{Co} = 4$);
 run 4: $\text{CoBr}_2(\text{PPh}_3)_2/\text{MgCl}_2/\text{SiPh}_2(\text{OCH}_3)_3/\text{PPh}_3\text{-Al}(\text{CH}_3)_3$ ($\text{Co}/\text{MgCl}_2 = 0,031 \text{ wt.-%}$, $\text{Si}/\text{Co} = 4$, $\text{PPh}_3/\text{Co} = 5$);
 runs 5–7⁸⁾: BuLi.

Hydrogenation of polybutadiene

Hydrogenation of polybutadiene was conducted according to the literature⁹⁾ as follows: polybutadiene (0,5 g), $\text{RhCl}(\text{PPh}_3)_3$ (20 μmol) and PPh_3 (0,38 mmol) together with 25 cm^3 of toluene were placed in a 50 cm^3 stainless steel autoclave equipped with a magnetic stirrer. The mixture was kept stirring at 100 °C under a pressure of hydrogen at 50 kg/cm^2 . The reaction was stopped by adding a large amount of ethanol and the precipitates were adequately washed with ethanol and dried *l.-vac.* at 60 °C.

Analytical procedures

The content of 1,2 units was estimated from the relative intensities of vinyl ($\delta = 4,9 \text{ ppm}$) and vinylenes ($\delta = 5,5 \text{ ppm}$) protons in the ^1H NMR spectrum of polybutadiene. ^1H NMR was measured at room temperature with a JEOL EX-90 spectrophotometer operating at 89,5 MHz. The steric triad of 1,2 sequences was calculated from the peaks of the vinyl carbons (around $\delta = 114 \text{ ppm}$) in the ^{13}C NMR spectrum¹⁰⁾. The ^{13}C NMR spectrum was obtained in CDCl_3 at room temperature with a JEOL EX-400 spectrophotometer operating at 100 MHz. The ^{13}C NMR spectrum of hydrogenated polybutadiene was also measured in CDCl_3 at room temperature. Chemical shift of each peak was estimated using the center peak of CDCl_3 ($\delta = 77,0 \text{ ppm}$) as reference. The ^{13}C NMR spectrum of hydrogenated polybutadiene insoluble in CDCl_3 (run 1) was measured in a mixture of C_6D_6 and 1,2,4-trichlorobenzene (vol. ratio 1:9) at 120 °C with hexamethyldisiloxane as internal reference ($\delta = 2 \text{ ppm}$). The content of *trans*-1,4 units was estimated from the peak of *trans* double bond deformations at 967 cm^{-1} in the IR (JASCO FT/IR-3) spectrum¹¹⁾. Differential scanning calorimetry measurements were made on a SII DSC220C at a heating rate of 10 °C/min.

Results and discussion

As previously reported^{5,6)}, polybutadienes obtained with Co-based catalysts are composed of 1,2 and *cis*-1,4 units. Whereas, those obtained with BuLi were found to be composed of 1,2 and *trans*-1,4 units. The contents of 1,2 units in the polybutadienes obtained in the present study ranged from about 60% to 95%. The stereoregularities of the 1,2 sequences of polybutadienes produced with Co-based catalysts and BuLi were *syndiotactic* ($[\text{rr}] \approx 60\%$) and *atactic*, respectively.

The thermal properties of hydrogenated polybutadienes obtained with Co-based catalysts are shown in Tab. 1, indicating that the melting points of the hydrogenated polymers are much lower than that of ordinary linear polyethylene. The melting point as well as the heat of fusion decreased and finally disappeared with increasing 1,2

Tab. 1. Thermal properties of hydrogenated polybutadienes^{a)}

Run	1,2 Cont. ^{b)} in %	T_m °C	ΔH J/g
1	64	108,5	45,4
2	84	88,3 (strong) 85,6 (weak)	23,9
3 ^{c)}	89	—	—
4 ^{c)}	92	—	—

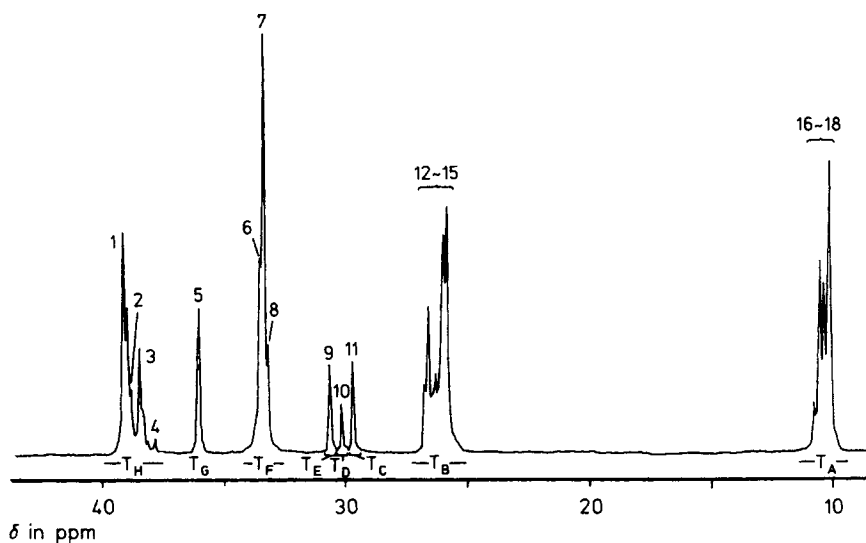
a) T_m : melting temperature; ΔH : heat of fusion.

b) Estimated by ^1H NMR spectroscopy.

c) T_m was not observed.













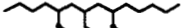



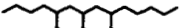
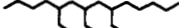
content, which suggests that both the 1,2 and *cis*-1,4 units are randomly distributed in the polybutadienes.

A typical ^{13}C NMR spectrum of hydrogenated polybutadiene together with the calculated ¹²⁾ and observed chemical shifts (run 4) are shown in Fig. 1 and Tab. 2.

Fig. 1. ^{13}C NMR spectrum of hydrogenated polybutadiene (run 4)

If the 1,2 units are assumed to be inserted regioselectively, the contents of 1,2 ([V]) and *cis*-(*trans*-)1,4([C]) units can be determined from the relative intensities of the peaks defined in Fig. 1 and Tab. 2 ($T_A - T_H$) as follows:

Tab. 2. Observed and calculated chemical shifts of hydrogenated polybutadiene (run 4)

Peak	Region	Chemical shift in ppm		Assignment
		obsd. ^{a)}	calcd. ¹²⁾	
1	T _H	39,29	38,98	
2		38,91	39,12	
3		38,54	38,73	
4		37,90	38,48	
5	T _G	36,09	37,05	
6	T _F	33,57	34,98	
7		33,41	34,47	
8		33,26	34,22	
9	T _E	30,69	30,46	
10	T _D	30,23	30,21	
11	T _C	29,79	29,96	
12	T _B	26,02 ^{b)}	27,52	
13			27,41	
14			27,66	
15			27,16	
16	T _A	10,55 ^{b)}	11,36	
17			11,36	
18			11,36	

^{a)} Top peak.^{b)} Center of peaks.

$$[V] = k \cdot [T_A]$$

$$[C] = k \cdot \{[T_E] + [T_D] + ([T_C] - \frac{3}{2} [T_D])/4\}$$

$$= k \cdot \{[T_E] + \frac{5}{8} [T_D] + \frac{1}{4} [T_C]\}$$

$$[1,2] = 100 \cdot [V]/([V] + [C])(\%)$$

$$[VV] = k \cdot ([T_H] + [T_A] - [T_B])/2$$

$$[CC] = k \cdot \{([T_C] - \frac{3}{2} [T_D])/2 + [T_D]/2\} = k \cdot \left(\frac{1}{2} [T_C] - \frac{1}{4} [T_D] \right)$$

$$[VC] = k \cdot (2 [T_E] + [T_D])$$

Supposing that the present polybutadienes are copolymers of 1,2 and 1,4 units produced via the first Markovian process, the reactivity ratios of 1,2 ($r_{(1,2)}$) and 1,4 ($r_{(1,4)}$) additions can be estimated from the diad sequences using the following equations:

$$r_{(1,2)} = [VV]/(0,5 \cdot [VC]) \quad r_{(1,4)} = [CC]/(0,5 \cdot [VC])$$

The reactivity ratios thus estimated are shown in Tab. 3. The value of $r_{(1,2)} \cdot r_{(1,4)}$ for the polymer obtained with the homogeneous Co-catalyst (run 1) is estimated to be unity, whereas those for the polymers obtained with the heterogeneous Co-catalysts

Tab. 3. Sequence distributions and reactivity ratios of polybutadiene

Run	1,2 Content in %		[VV]	[VC]	[CC]	$r_{(1,2)}$	$r_{(1,4)}$	$r_{(1,2)} \cdot r_{(1,4)}$
	¹ H NMR	¹³ C NMR						
1	64	67	0,435	0,447	0,117	1,9	0,52	1,0
2	84	85	0,669	0,284	0,047	4,7	0,33	1,6
3	89	87	0,730	0,223	0,046	6,5	0,41	2,7
4	92	88	0,727	0,233	0,037	6,2	0,31	2,0
5 ^{a)}	67	72	0,384	0,500	0,116	1,5	0,46	0,7
6 ^{a)}	85	85	0,673	0,302	0,023	4,5	0,16	0,7
7 ^{a)}	92	95	0,897	0,100	0,003	18	0,05	0,9

^{a)} Composed of 1,2 and *trans*-1,4 units.

(runs 2, 3 and 4) are larger than unity. Those for the polymers produced with BuLi (runs 5, 6 and 7) are smaller than unity. Therefore, polybutadiene obtained with the homogeneous CoBr₂(PPh₃)₃-MAO catalyst is a random copolymer of 1,2 and *cis*-1,4 units, whereas those obtained with the heterogeneous MgCl₂-supported CoBr₂(PPh₃)₃ catalysts are slightly blocky. Polybutadiene obtained with BuLi might have an alternating character.

In conclusion, it was found that the distributions of 1,2 and 1,4 units in 1,2 rich polybutadienes could be more or less controlled by the polymerization catalysts.

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