Model Butadiene Polymerizations. II. Monomer Distributions in Butadiene Oligomers

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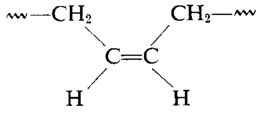
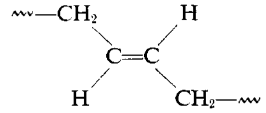
ABSTRACT: Butadiene oligomers, prepared by *sec*-butyllithium initiation, were hydrogenated and characterized according to carbon number and sequences of 1,4 and 1,2 units by gas chromatography. Peak assignments in the gas chromatogram of the C_8, C_{12}, and some of the C_{16} and C_{20} oligomers were made initially by carbon number and number of branches per isomer. Complete assignments for all oligomers through the C_{24}'s were made after testing the oligomerization process for conformity to Markov chain statistics. Close conformity was demonstrated by the fact that correct relative peak intensities for various C_{16}, C_{20}, and C_{24} isomers were obtained independently from the same set of transition probabilities. The Markov chain analysis did not give a unique assignment; however, a unique assignment was obtained following a glpc-mass spectroscopy investigation. Evidence is presented that indicated the oligomerization process was second order.

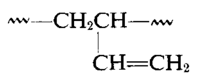
The alkyllithium initiation of butadiene may result in any one of the following configurations for the polymer unit



cis-1,4 addition



trans-1,4 addition



$$\sim CH_2\underset{\displaystyle CH{=}CH_2}{\underset{|}{C}}H\text{—}\sim$$

1,2-vinyl addition (*d* or *l*)

The physical properties of the polymer will depend upon the distribution of monomer units among the configurations shown above as well as the sequences of the various configurations.[2a] Infrared techniques have been developed which allow a determination of total *cis*, *trans*, and vinyl content in butadiene polymers.[2b] The total 1,4 *vs.* 1,2 concentrations have also been determined in a straightforward approach by nuclear magnetic resonance.[3] Of additional interest would be a determination of the sequences of 1,4 and 1,2 units in butadiene polymers.

No means for determining directly the sequence distributions of monomer units in high molecular weight butadiene polymers is yet available. An indirect approach may be possible if the polymerization process conforms to Markov chain statistics. We have investigated hydrogenated butadiene oligomers by gas chromatography and determined the applicability of Markov chain statistics. The use of Markov chain theory in the analysis of the oligomer gas chromatograms has considerable merit and a method is reported here that allows assignments to be made independently of whether the oligomerization process follows first- or second-order Markov statistics.

Experimental Section

The hydrogenated butadiene oligomer samples are labeled A–F and were initially prepared under conditions that would give different relative amounts of 1,4 and 1,2 addition.[4] Hydrogenation prior to the gas chromatography investigation was accomplished by placing 5 ml of each sample in sealed tubes under 30 psi hydrogen and a platinum oxide catalyst with stirring for a period of 2 hr. The completeness of the hydrogenation reaction was evident in both glpc and glpc–mass spectroscopy scans since only an insignificant amount of olefins could be detected.

A Perkin-Elmer Model 880 gas chromatograph equipped with a flame ionization detector was used for the oligomer analysis. The column consisted of 15 ft of $^1/_8$ in. i.d. copper tubing packed with 12% OV-1 liquid substrate on 80–100 mesh Chromosorb P. The temperature was programmed from 100 to 325° at a rate of 8°/min. Other information pertinent to the gas chromatography analysis is: inlet sample splitter ratio 10:1; inlet temperature 250°; inlet pressure 55 psig; and the detector temperature 175°. The peak areas were determined by the triangulation method. The glpc–mass spectroscopy results were obtained from a Perkin-Elmer F-11 chromatograph coupled to a CEC 21-130 mass spectrometer.

Results and Discussion

The addition of 1,3-butadiene to *sec*-butyllithium when butadiene is in excess (2:1, 3:1) gives oligomers which differ in carbon number by increments of four and possess degrees of branching that are determined by the modes of addition. The oligomer samples investigated differed substantially in relative concentrations of 1,4 and 1,2 monomer units as reflected by the gas chromatograms of the hydrogenated oligomers which contained significant differences in intensities among samples A–F for peaks with similar retention times. The gas chromatogram of sample A is reproduced in Figure 1. With the exception of intensity

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(1) Deceased.

(2) (a) J. N. Short, G. Kraus, R. P. Zelinski, and F. E. Naylor, *Rubber Chem. Technol.*, 32 (2), 614 (1959); (2) (b) R. S. Silas, J. Yates, and V. Thornton, *Anal. Chem.*, **31**, 529 (1959).

(3) W. L. Senn, Jr., *Anal. Chim. Acta*, **29**, 505 (1963).

(4) J. C. Randall, F. E. Naylor, and H. L. Hsieh, *Macromolecules*, 3, 497 (1970).

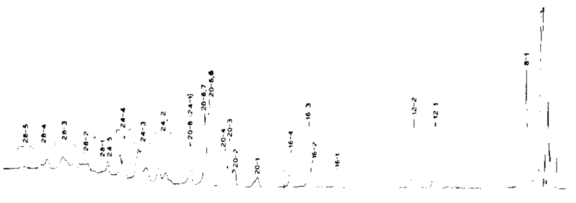

Figure 1. Gas chromatogram of oligomers from reaction of *sec*-butyllithium with 1,3-butadiene.

TABLE I

TENTATIVE GAS CHROMATOGRAPHY ASSISGNMENTS BY CARBON NUMBERS AND NUMBERS OF BRANCHES[a]

8–1	I–T	
12–1	I–1,2–T	
12–2	I–1,4–T	
16–1	$I\text{–}(1,2)_2\text{–}T$	
16–2 16–3	$I\text{–}(1,2)_1\text{–}(1,4)_1\text{–}T$	(2)
16–4	$I\text{–}(1,4)_2\text{–}T$	
20–1	$I\text{–}(1,2)_3\text{–}T$	
20–2 20–3 20–4	$I\text{–}(1,2)_2\,(1,4)_1\text{–}T$	(3)
20–5,6 20–6,7	$I\text{–}(1,2)_1\,(1,4)_2\text{–}T$	(3)
20–8	$I\text{–}(1,4)_3\text{–}T$	
24–1	$I\text{–}(1,2)_4\text{–}T$	
24–2	$I\text{–}(1,2)_3\,(1,4)_1\text{–}T$	(4)
24–3	$I\text{–}(1,2)_2\,(1,4)_2\text{–}T$	(6)
24–4	$I\text{–}(1,2)_1\,(1,4)_3\text{–}T$	(4)
24–4	$I\text{–}(1,4)_4\text{–}T$	

[a] I denotes the *sec*-butyl initiator unit; T denotes the "*n*-butyl" terminal unit, see text. The number of isomers for each collective assignment are given in parentheses.

differences, the gas chromatogram is typical of the oligomer samples.

Tentative gas chromatography assignments for the oligomers were made initially by inspection. An elution order was assumed that considered the total number of isomers possible for each carbon number arranged according to the number of branches. Each oligomer has one methyl branch from the *sec*-butyl initiator unit and a number of ethyl branches determined by the number of 1,2 units. Reverse of 2,1 addition was not considered since to our knowledge it has not been reported and appears improbable from the mechanistic considerations in part I of this series.[5] The preclusion of 2,1 addition was justified by the observation that only one C_8, 3-methylheptane, was present among the hydrogenated oligomers. In addition, a larger number of isomers than observed would be expected for the higher oligomers if there were 2,1 addition. An important consequence of hydrogenation is that the terminal unit will always be "*n*-butyl" after 1,4 and 1,2 addition as shown. Thus the total

$$\begin{array}{l} \sim\!\sim CH_2CH{=}CHCH_3 \\ \quad \text{1,4-terminal unit} \\ \sim\!\sim CH_2CH_2CH{=}CH_2 \\ \quad \text{1,2-terminal unit} \end{array} \xrightarrow{H_2} \sim\!\sim CH_2CH_2CH_2CH_3$$

numbers of isomers possible for each carbon number are substantially reduced and, more importantly, any sequence change related to termination is automatically removed from the analysis. Sequence changes brought about by termination can only be resolved in the unhydrogenated oligomers. The total number of isomers expected for each oligomer is therefore 2^{n-1} where "*n*" is the number of added butadiene units for a particular oligomer. The only C_8 is 3-methylheptane, likewise 3-methyl-5-ethylnonane and 3-methylundecane are the only C_{12}'s, and so forth. The observed number of gas chromatography peaks correspond well with the number of isomers predicted for each oligomer through the C_{20}'s. Considerable overlap is encountered among the C_{24}'s, but even the C_{24} oligomers can be grouped according to the longest carbon chain into a pentadecane, four heptadecanes, six nonadecanes, four heneicosanes, and a tricosane. Tentative peak assignments, 8–1, 12–1, 12–2, etc., are given in Figure 1 according to carbon number. Stereoisomers are possible with 1,2 addition and may account for the broadness of some of the early peaks for each carbon number. The last peak of each series should be a singlet unless there is overlap with the next higher homolog. In the glpc scans of samples which contained substantial quantities of oligomers producing peak 24–1, a distinct shoulder was present on peak 20–8. With overlap indicated for 20–8 and 24–1, five groups of C_{24}'s can be discerned. Overlap within the set of C_{20} oligomers also appears likely for either the fifth or sixth peak of the series, and are labeled, respectively, 20–5,6 and 20–6,7. Peak 20–5,6 was likely the two-component peak as indicated by a comparison of line widths at half-height with "20–6,7," however, we were unable to resolve either peak. Structural assignments for 8–1, 12–1, 12–2, etc., are given in Table I which corresponds to assignments according to carbon number and the numbers of branches. Collective assignments are made for those peaks which result from isomers with the same number of branches. For example, 16–2 can be assigned to either 3-methyl-5-ethyltridecane or 3-methyl-9-ethyltridecane. A similar situation exists for 20–2, 20–3, and 20–4 and 20–5,6; 20–6,7. No attempts were made for specific assignments in the C_{24}'s or even group assignments in the C_{28}'s. A sufficient number of tentative assignments have been made to check the conformity of the oligomer distribution to Markov chain statistics.

Assignments by Markov Chain Analysis. The hydrogenated butadiene oligomers can be easily defined in terms of Markov chain theory by letting "0" represent a 1,4 unit and "1" a 1,2 unit with the chains growing conceptually from left to right as described in ref 6. We will follow the basic notation of ref 6 with modifications only as necessary. For a first-order Markov chain, transition probabilities for a two-unit sequence are given as follows.

P_{11}, probability for a monomer unit to add 1,2 to a preceding 1,2 unit

P_{10}, probability for a monomer unit to add 1,4 to a preceding 1,2 unit

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(5) F. E. Naylor, H. L. Hsieh, and J. C. Randall, *Macromolecules*, 3, 486 (1970).

(6) F. P. Price, *J. Chem. Phys.*, 36, 209 (1962).

P_{01}, probability for a monomer unit to add 1,2 to a preceding 1,4 unit
P_{00}, probability for a monomer unit to add 1,4 to a preceding 1,4 unit

A second-order Markov chain takes into account the penultimate unit configuration and has the transition probabilities

P_{33}, probability for a monomer unit to add 1,2 to preceding 1,2–1,2 units
P_{32}, probability for a monomer unit to add 1,4 to preceding 1,2–1,2 units
P_{21}, probability for a monomer unit to add 1,2 to preceding 1,2–1,4 units
P_{20}, probability for a monomer unit to add 1,4 to preceding 1,2–1,4 units
P_{13}, probability for a monomer unit to add 1,2 to preceding 1,4–1,2 units
P_{12}, probability for a monomer unit to add 1,4 to preceding 1,4–1,2 units
P_{01}, probability for a monomer unit to add 1,2 to preceding 1,4–1,4 units
P_{00}, probability for a monomer unit to add 1,4 to preceding 1,4–1,4 units

For conciseness, the second-order transition probabilities have been written in decimal numbers corresponding to the polymer binary notation;[6] *i.e.*, $P_{11,10} = P_{32}$.

The sequences of butadiene units in the various oligomers can now be defined by either first- or second-order Markov chains; however, if the oligomers are to be defined completely, two more sets of transition probabilities are needed.

P_1^{I}, probability for a monomer unit to add 1,2 to *sec*-butyllithium
P_0^{I}, probability for a monomer unit to add 1,4 to *sec*-butyllithium

For second-order chains

P_3^{II}, probability for two consecutive monomer units to add 1,2–1,2 to *sec*-butyllithium
P_2^{II}, probability for two consecutive monomer units to add 1,2–1,4 to *sec*-butyllithium
P_1^{II}, probability for two consecutive monomer units to add 1,4–1,2 to *sec*-butyllithium
P_0^{II}, probability for two consecutive monomer units to add 1,4–1,4 to *sec*-butyllithium

TABLE II
BUTADIENE OLIGOMERS DEFINED IN TERMS OF MARKOV CHAIN TRANSITION PROBABILITIES

		First order	Second order
C_{12}	I–1,2–T	P_1^{I}	
	I–1,4–T	P_0^{I}	
C_{16}	I–1,2–1,2–T	$P_1^{I}P_{11}$	P_3^{II}
	I–1,2–1,4–T	$P_1^{I}P_{10}$	P_2^{II}
	I–1,4–1,2–T	$P_0^{I}P_{01}$	P_1^{II}
	I–1,4–1,4–T	$P_0^{I}P_{00}$	P_0^{II}
C_{20}	I–1,2–1,2–1,2–T	$P_1^{I}P_{11}P_{11}$	$P_3^{II}P_{33}$
	I–1,2–1,2–1,4–T	$P_1^{I}P_{11}P_{10}$	$P_3^{II}P_{32}$
	I–1,2–1,4–1,2–T	$P_1^{I}P_{10}P_{01}$	$P_2^{II}P_{21}$
	I–1,4–1,2–1,2–T	$P_0^{I}P_{01}P_{11}$	$P_1^{II}P_{13}$
	I–1,2–1,4–1,4–T	$P_1^{I}P_{10}P_{00}$	$P_2^{II}P_{20}$
	I–1,4–1,2–1,4–T	$P_0^{I}P_{01}P_{10}$	$P_1^{II}P_{12}$
	I–1,4–1,4–1,2–T	$P_0^{I}P_{00}P_{01}$	$P_0^{II}P_{01}$
	I–1,4–1,4–1,4–T	$P_0^{I}P_{00}P_{00}$	$P_0^{II}P_{00}$

Definitions for the C_{12}, C_{16}, and C_{20} *sec*-butyllithium–butadiene oligomers are given in Table II in terms of both first- and second-order Markov chain transition probabilities. Hydrogenation eliminates any necessity for defining the terminal unit which has a probability of one. Unequivocal glpc assignments can lead to a determination of the applicability of Markov chain theory, the subsequent order, and the resulting transition probabilities. Reference compounds would be useful; however, assignments can be made if the addition of butadiene to an alkenyllithium chain end conforms to a Markoffian process since the following relationships exist for the C_{16} and C_{20} oligomers for either first- or second-order Markov chains

$$X_{16}(\text{I–1,2–1,2–T}) = X_{20}(\text{I–1,2–1,2–1,2–T}) + X_{20}(\text{I–1,2–1,2–1,4–T}) \quad (1)$$

$$X_{16}(\text{I–1,2–1,4–T}) = X_{20}(\text{I–1,2–1,4–1,2–T}) + X_{20}(\text{I–1,2–1,4–1,4–T}) \quad (2)$$

$$X_{16}(\text{I–1,4–1,2–T}) = X_{20}(\text{I–1,4–1,2–1,2–T}) + X_{20}(\text{I–1,4–1,2–1,4–T}) \quad (3)$$

$$X_{16}(\text{I–1,4–1,4–T}) = X_{20}(\text{I–1,4–1,4–1,2–T}) + X_{20}(\text{I–1,4–1,4–1,4–T}) \quad (4)$$

The X's represent respective mole fractions. The relationships follow from

First order

$$P_{00} + P_{01} = 1 \quad (5)$$

$$P_{10} + P_{11} = 1 \quad (6)$$

Second order

$$P_{00} + P_{01} = 1 \quad (7)$$

$$P_{12} + P_{13} = 1 \quad (8)$$

$$P_{20} + P_{21} = 1 \quad (9)$$

$$P_{32} + P_{33} = 1 \quad (10)$$

since addition of butadiene must occur by either 1,4 or 1,2.

Equations 1–4 will be hereafter referred to as the "sum rule" equations. Since the glpc response factors for alkanes with the same carbon number are similar,[7] the relative areas can be used as mole fractions and both sides of the sum rule equations can be checked for equalities after each possible assignment. If an assignment with consistently low deviations from the sum rule equations can be found for varied oligomer distributions, the conformity to Markov chain theory could be examined further through a calculation of C_{24} relative intensities with the resulting transition probabilities. Unfortunately, overlap among oligomers in the gas chromatogram necessitates a combination of

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(7) R. Kaiser, "Gas Phase Chromatography," Butterworths, London, 1963, p 117.

TABLE III
ASSIGNMENTS I, II, AND CALCULATED
SECOND-ORDER TRANSITION PROBABILITIES

Structure	Assignment I	Assignment II
I–1,2–1,2–T	16–1	16–1
I–1,2–1,4–T	16–2	16–3
I–1,4–1,2–T	16–3	16–2
I–1,4–1,4–T	16–4	16–4
I–1,2–1,2–1,2–T	20–1	20–1
I–1,4–1,2–1,2–T	20–3	20–2
I–1,2–1,4–1,2–T	20–2	20–3
I–1,2–1,2–1,4–T	20–4	20–4
I–1,2–1,4–1,4–T	20–5,6	20–7
I–1,4–1,4–1,2–T		20–5,6
I–1,4–1,2–1,4–T	20–7	
I–1,4–1,4–1,4–T	20–8	20–8

Sample	P_3^{II}	P_2^{II}	P_1^{II}	P_0^{II}	P_{33}	P_{13}	P_{20}	P_{00}
	Transition Probabilities (Assignment I)							
A[a]	0.18	0.21	0.39	0.22	0.29	0.44	0.68	0.51
B	0.07	0.19	0.26	0.48	0.34	0.32	0.75	0.65
C	0.44	0.15	0.35	0.06	0.64	0.70	0.36	0.23
D	0.15	0.21	0.37	0.28	0.21	0.39	0.67	0.55
E	0.47	0.16	0.32	0.05	0.56	0.71	0.49	0.45
F[a]	0.16	0.21	0.39	0.23	0.26	0.40	0.62	0.56

[a] Duplicate determinations on separate runs.

appropriate sum rule equations which reduces the number of independent equations and the opportunity for a unique assignment. The tentative assignments in Table I were evaluated using the sum rule equations and all possible specific assignments where only collective assignments could be made previously, including the assignment of a pair of structures to 20–5,6 and a single structure of 20–6,7 and likewise the reverse assignment. It also became necessary in several of the samples to evaluate the extent of overlap between 20–8 and 24–1. Resolution was obtained with the appropriate sum rule equations for the C_{20} and C_{24} oligomers, the details of which are given in the Appendix. Depending upon the assignments to 20–5,6 and 20–6,7, it was necessary to combine the sum rule equations (2) + (3) or (3) + (4) or (2) + (4) as directed by the assignment. A computer program was written which considered all these assignments and subsequent permutations of eq 2, 3, and 4. There were a total of 72 sets and each was evaluated by its deviation from the equalities specified by the three independent sum rule equations. The absolute values of the deviations from each of the sum rule equations were combined and printed out with each assignment. The 72 assignments could be divided into 36 pairs since an interchange of assignments for 16–2, 16–3, and the C_{20} derivatives thereof led to the same result. A number of pairs of assignments gave low deviations from the sum rule equations in a particular sample; however, only one pair gave consistently a low deviation for samples A–F. The assignments, labeled I and II, both indicated that overlap occurred for 20–5,6 and are given in Table III. Assignment I was used in a nonlinear least squares analysis to obtain the second-order Markov chain transition probabilities which were used, in turn, to calculate predicted relative areas. The C_{16} and C_{20} predicted relative areas for assignments I and II are the same as discussed previously; however, the transition probabilities for assignment II can be obtained by simply interchanging eq 11–14.

$$P_{21}(\mathrm{I}) = P_{13}(\mathrm{II}), \text{ etc.} \tag{11}$$

$$P_{13}(\mathrm{I}) = P_{21}(\mathrm{II}), \text{ etc.} \tag{12}$$

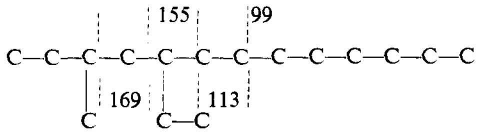
$$P_2^{II}(\mathrm{I}) = P_1^{II}(\mathrm{II}) \tag{13}$$

$$P_1^{II}(\mathrm{I}) = P_2^{II}(\mathrm{II}) \tag{14}$$

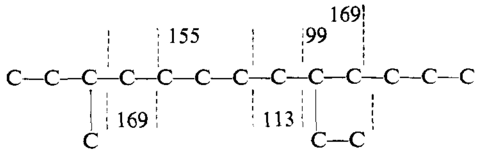
The remainder of the transition probabilities are the same for both assignments. The observed and predicted values from the nonlinear regression analysis are given in Table IV for assignments I and II. The relative areas are reported to the nearest 0.01 mol fraction which is the estimated experimental error. The resulting transition probabilities were also rounded to two significant figures and are included in Table IV. The C_{24} glpc assignments were grouped by the numbers of 1,2 units as given in Table I. Relative areas were calculated from the transition probabilities that were obtained from analysis of the C_{16} and C_{20} oligomers and are listed in Table V with the observed values. The agreement among observed and predicted relative areas overall is gratifying and demonstrates the conformity to Markov chain statistics in support of glpc assignments, I, II. If sufficient differences has existed for the transition probabilities interchanged in assignments I and II, one possibly could have distinguished the two assignments through a comparison of the predicted and observed C_{24} relative areas. Both assignments, however, gave nearly the same predicted areas as evident from the results listed in Table V.

The true assignment can be selected if glpc peaks 16–2 and 16–3 can be independently assigned since the only differences in assignment, I and II result from this interchange. The glpc–mass cracking patterns were obtained for 16–2 and 16–3. The fragment ratio 155:169 was higher for 16–2 than 16–3. A second

(16–2)



(16–3)



fragment ratio 99:113, was lower for 16–2. Both observations are consistent with the above structural assignments for 16–2 and 16–3. The isomer 3-methyl-5-ethyltridecane (16–2) would be expected to give abundant 113, 155, and 169 fragments. The alternative, 3-methyl-9-ethyltridecane (16–3), should give abundant 99 and 169 fragments with only low amounts of 155 and 113 since these fragments require cracking between unbranched carbon atoms. An inspection of the remaining fragment intensity ratios, *i.e.*, branched to unbranched, were consistent with the given structures.

With assignment I now estsblished, it is of further interest to determine the Markov chain order of the

TABLE IV

OBSERVED AND PREDICTED VALUES OF RELATIVE GLPC AREAS FOLLOWING A NONLINEAR REGRESSION ANALYSIS BASED ON SECOND-ORDER MARKOV CHAIN THEORY

	Sample											
	A		B		C		D		E		F	
Glpc peak	Obsd	Pred	Obsd	Pred	Obsd	Pred	Obsd	Pred	Obsd	Pred	Obsd	Pred
16–1	0.18	0.18	0.06	0.07	0.43	0.44	0.14	0.15	0.47	0.47	0.15	0.16
16–2	0.21	0.21	0.20	0.19	0.15	0.15	0.21	0.21	0.16	0.16	0.21	0.21
16–3	0.40	0.39	0.25	0.26	0.36	0.35	0.37	0.37	0.32	0.32	0.40	0.39
16–4	0.22	0.22	0.49	0.52	0.06	0.06	0.28	0.28	0.05	0.05	0.23	0.23
20–1	0.06	0.05	0.03	0.02	0.30	0.28	0.04	0.03	0.26	0.26	0.05	0.04
20–2	0.07	0.07	0.04	0.05	0.09	0.09	0.06	0.07	0.08	0.08	0.07	0.07
20–3	0.17	0.18	0.08	0.08	0.23	0.24	0.14	0.14	0.22	0.23	0.15	0.16
20–4	0.13	0.13	0.06	0.05	0.17	0.16	0.13	0.12	0.21	0.21	0.13	0.12
20–5,6	0.25	0.25	0.28	0.29	0.10	0.10	0.26	0.27	0.11	0.11	0.24	0.24
20–7	0.21	0.22	0.18	0.18	0.09	0.10	0.22	0.22	0.09	0.09	0.23	0.24
20–8	0.11	0.11	0.32	0.33	0.01	0.01	0.15	0.15	0.02	0.02	0.13	0.13

TABLE V

OBSERVED RELATIVE GLPC AREAS FOR C_{24} OLIGOMERS AND PREDICTED VALUES FROM MARKOV CHAIN THEORY

	Sample																	
	A			B			C			D			E			F		
Glpc		Pred			Pred			Pred			Pred			Pred			Pred	
peak	Obsd	I	II	Obsd	I	II	Obsd	I	II	Obsd	I	II	Obsd	I	II	Obsd	I	II
24–1		0.02	0.02		0.01	0.01	0.02	0.18	0.18		0.01	0.01	0.15	0.15	0.15	0.02	0.01	0.01
24–2	0.16	0.16	0.17	0.02	0.07	0.07	0.42	0.43	0.43	0.15	0.12	0.13	0.44	0.41	0.42	0.26	0.15	0.16
24–3	0.45	0.43	0.44	0.32	0.26	0.26	0.30	0.32	0.32	0.43	0.42	0.42	0.29	0.33	0.33	0.32	0.42	0.42
24–4	0.32	0.34	0.32	0.40	0.43	0.43	0.07	0.07	0.07	0.33	0.37	0.36	0.05	0.10	0.09	0.32	0.34	0.33
24–5	0.07	0.06	0.06	0.26	0.23	0.23		0.00	0.00	0.09	0.08	0.08	0.07	0.01	0.01	0.07	0.07	0.07

TABLE VI

OBSERVED AND PREDICTED VALUES OF RELATIVE GLPC AREAS FOLLOWING A NONLINEAR REGRESSION ANALYSIS BASED ON FIRST-ORDER MARKOV CHAIN THEORY

	Sample											
	A		B		C		D		E		F	
Glpc peak	Obsd	Pred	Obsd	Pred	Obsd	Pred	Obsd	Pred	Obsd	Pred	Obsd	Pred
12–1	0.52	0.43	0.27	0.27	0.73	0.63	0.41	0.37	0.79	0.67	0.49	0.40
16–1	0.18	0.20	0.06	0.08	0.43	0.45	0.14	0.15	0.47	0.46	0.15	0.17
16–2	0.21	0.23	0.20	0.19	0.15	0.18	0.21	0.22	0.16	0.21	0.21	0.23
16–3	0.40	0.35	0.25	0.24	0.36	0.26	0.37	0.32	0.32	0.30	0.40	0.32
16–4	0.22	0.22	0.49	0.49	0.06	0.12	0.28	0.31	0.05	0.03	0.24	0.28
20–1	0.06	0.09	0.03	0.02	0.30	0.32	0.04	0.06	0.26	0.32	0.05	0.07
20–2	0.07	0.14	0.04	0.06	0.09	0.13	0.06	0.11	0.09	0.19	0.07	0.12
20–3	0.17	0.16	0.08	0.07	0.23	0.18	0.14	0.13	0.22	0.21	0.15	0.14
20–4	0.13	0.11	0.06	0.05	0.17	0.13	0.13	0.09	0.21	0.14	0.13	0.10
20–5,6	0.25	0.22	0.28	0.29	0.10	0.14	0.26	0.26	0.11	0.05	0.24	0.26
20–7	0.21	0.19	0.18	0.17	0.09	0.07	0.22	0.19	0.09	0.09	0.23	0.19
20–8	0.11	0.08	0.32	0.33	0.01	0.04	0.15	0.15	0.03	0.00	0.13	0.13

oligomerization process. If the process were first order, a second-order analysis should result in equalities between the following sets of transition probabilities

$$P_{00} = P_{20} \qquad (15)$$

$$P_{33} = P_{13} \qquad (16)$$

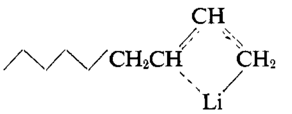
That this was not the case was clearly illustrated by the transition probabilities in Table III. However, to test more completely the possibility of a first-order fit, the first-order probability products given in Table I were used in a nonlinear least squares analysis of the relative intensities of the C_{12}'s, C_{16}'s, and C_{20}'s. The observed and predicted values, on this basis, are given in Table VI. Many of the differences between predicted and observed values are outside experimental error. Sample B gave the best first-order fit as expected since P_{33}, P_{13} and P_{20}, P_{00} were nearly the same in the second-order calculation. With more parameters, a better second-order fit is expected; however, the standard error for the second-order fit is within the experimental error of the glpc area measurements whereas the first-order fit is not. The standard errors for both first- and second-order calculations are given in Table VII. The close conformity to second-order statistics strongly suggests that this is the case. In either event, the tentative glpc assignments in Table II are substantiated, as well as the preclusion of 2,1 addition.

The applicability of Markov chain theory to the butadiene oligomerization process presents a unique

TABLE VII
STANDARD ERRORS OF ESTIMATES FOR PREDICTED *vs.* OBSERVED GLPC RELATIVE AREAS ON A BASIS OF FIRST-ORDER AND SECOND-ORDER MARKOV CHAIN THEORY

Sample	Second order	First order
A	0.0068	0.0489
B	0.0114	0.0124
C	0.0153	0.0617
D	0.0130	0.0336
E	0.0046	0.0678
F	0.0124	0.0493

approach for making glpc assignments. Second, the oligomer distribution is completely characterized. The observation that the butadiene polymerization process is second order is not too surprising in light of similar findings with poly(methyl methacrylate).[8] The penultimate effect in the butadiene oligomerization is small, but the existence of such an effect affords interesting questions concerning butadiene polymerizations. The alkenyllithium active end has been reported to possess an unfixed configuration possibly as shown[5]



The configuration of the ultimate unit is determined at the moment of further addition of butadiene. In a second-order Markov process, the final configuration would depend not only upon the manner in which the reacting unit approaches but also upon the configuration sequence of the two preceding units. Whether such an effect is steric in origin or the result of a complex is open to speculation.

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Appendix

Resolution of the overlap between 24–1 and 20–8 was important in sample C only since the intensity of peak 24–1 could be neglected in samples A, B, and D. The relative area of peak 20–8 is given by

$$A_{20-8}\Big/\sum_{n=1}^{8}A_{20-n}$$

and similarly for 24–1

$$A_{24-1}\Big/\sum_{n=1}^{5}A_{24-1}$$

where "*A*" represents the absolute measured area for a given peak. From the "sum rule" relationships for the C_{16}'s, C_{20}'s, and C_{24}'s, we find that

$$\left(A_{24-1}\Big/\sum_{n=1}^{5}A_{24-n}\right)\Big/\left(A_{20-1}\Big/\sum_{n=1}^{8}A_{20-n}\right) = \left(A_{20-1}\Big/\sum_{n=1}^{8}A_{20-n}\right)\Big/\left(A_{16-1}\Big/\sum_{n=1}^{4}A_{16-n}\right) \quad \text{(A1)}$$

if we denote the following experimentally obtained values by

$$A_{24-1} = X = \sum_{n=1}^{5}A_{24-n} + \sum_{n=1}^{8}A_{20-n} = C \quad \text{(A2)}$$

$$\sum_{n=1}^{5}A_{24-n} - A_{24-1} = D \quad \text{(A3)}$$

$$A_{20-1} = F \quad \text{(A4)}$$

and

$$A_{16-1}\Big/\sum_{n=1}^{4}A_{16-n} = G \quad \text{(A5)}$$

After solving eq A1 in terms of *X*, we obtain

$$GX^3 - 2G(C - D)X^2 + \{G(C - D)^2 - F^2\}X - F^2D = 0 \quad \text{(A6)}$$

For sample C

$$C = 2927$$

$$D = 488$$

$$F = 685$$

$$G = 0.43$$

For these values, eq A6 has the roots

$$X = A_{24-1} = 3554.72 \quad \text{(I)}$$

$$1199.46 \quad \text{(II)}$$

$$124.89 \quad \text{(III)}$$

Only the third root, ~125, has any physical significance. The relative fractions for 20–8 and 24–1 are 0.20 and 0.01, respectively.

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[8] H. L. Frisch, C. L. Mallows, F. Heatley, and F. A. Bovey, *Macromolecules*, **1**, 533 (1968).