Model Butadiene Polymerizations. III. An Investigation of 1:2, 1:3, and 1:10 Ratios of *sec*-Butyllithium to Butadiene

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ABSTRACT: Transition probabilities have been obtained for a series of butadiene oligomers which were observed to conform to second-order Markov statistics. The transition probabilities were sensitive to changes in the reaction temperature, alkyllithium concentration, and medium polarity, and were useful in mechanistic considerations of the oligomerization process. More polar reaction media, whether obtained through addition of tetrahydrofuran or alkyllithium concentration, resulted in an increase in 1,2 addition. Polarization of the alkenyllithium terminal unit is suggested as a major requisite for 1,2 addition. Hydrolysis of the alkenyllithium terminal groups resulted in 1,4 addition as the predominant configuration independently of the preferred mode of addition.

Alkyllithium-initiated polymerization of butadiene propagates through addition of monomer nnits to a terminal alkenyllithium unit. A resonance-stabilized allylic lithium complex has been proposed for the alkenyllithium unit on the basis of product distributions and nuclear magnetic resonance studies.[1] Further evidence is presented in this study on hydrogenated butadiene oligomers that demonstrates that the configuration of the butadiene terminal unit is not fixed until after addition of a new monomer unit. A series of butadiene oligomer samples have been characterized under various experimental conditions known to affect polymer macrostructure.[2] Markov chain transition probabilities were determined for each oligomer sample in order to gauge the effects of reaction conditions on the oligomer molecular structure.

Experimental Section

Oligomerizations of Butadiene. Stock solutions of *sec*-butyllithium in cyclohexane were prepared for later use in the oligomer syntheses. Aliquots were taken and transferred to dry, nitrogen filled 7-oz. beverage bottles with perforated crown caps over self-sealing liners. A chilled (−10°) quantity of butadiene was then added and the mixtures were placed in a constant-temperature bath and tumbled for desired lengths of time. Reaction times, temperatures, and reactant concentrations are given in Table I. Upon removal from the constant-temperature bath, each sample was allowed to cool to room temperature and deionized water was added to hydrolyze the alkenyllithium end units. The samples were then ready for hydrogenation and determination of the oligomer distribution.

Analysis of the Oligomer Distributions. The oligomer samples were hydrogenated and gas chromatograms obtained of each sample according to the procedures described earlier.[3] Markov chain transition probabilities were calculated from relative concentrations of various oligomers again as described in ref 3. In addition, an analysis of several of the unhydrogenated oligomers for *trans*-3-methyl-2-heptene, *cis*-3-methyl-2-heptene, and 3-methyl-1-heptene was obtained by gas chromatography.[1] The results, reported only as per cent 1,4, are given in the first column of Table II. Relative 1,4 concentrations for each monomer unit in the C_{12}, C_{16}, and C_{20} hydrogenated oligomers are also included in Table II for each of the samples.

Results and Discussion

From an earlier investigation of alkyllithium-initiated butadiene oligomers, the distributions obtained under various experimental conditions were observed uniformly to conform to second-order Markov statistics.[3] The present study involves a number of oligomer samples which permit reproducibility or consistency of the Markov chain order to be investigated. In testing the oligomer distributions for conformity to Markov chain statistics, the mole fractions of the isomeric distributions of C_{16}, C_{20}, and C_{24} oligomers were defined in terms of second-order transition probabilities for both propagating and initiating steps.[3] These transition probabilities are given in Table I for each oligomer sample and are coded by the subscripts, 3, 2, 1, and 0 which represent, respectively, the terminal sequences, 1,2-1,2; 1,2-1,4; 1,4-1,2; and 1,4-1,4. The transition probability P_{13} thus defines the probability of addition of a butadiene monomer to an ultimate 1,4-1,2 sequence to produce a new ultimate 1,2-1,2 sequence. Similarly the initiating probability P_3^{II} represents the probability of obtaining the sequence, *sec*-butyl-1,2-1,2 after initiation and so forth. The fact that the oligomerization process generally does not conform to first-order statistics is clearly illustrated by the observed differences for P_{33}, P_{13} and P_{20}, P_{00}, respectively.[3,4] The standard errors of estimates, from a nonlinear regression analysis of the experimental glpc areas defined algebraically in terms of the Markov transition probabilities, were uniformly within experimental error and are included in Table I. Samples 2-A, 2-B and 3-B, 3-C were duplicates, respectively, and the agreement is gratifying since the reproducibility depends upon both the glpc measurements and control of experimental variables in preparation of the oligomer samples.

Four experimental variables were examined in the present study of oligomer distributions, *i.e.*, temperature, alkyllithium concentration, monomer to initiator ratio, and tetrahydrofuran concentration. Generally,

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

(2) H. L. Hsieh, *J. Polym. Sci., Part A*, **3**, 181 (1965).

(3) J. C. Randall and R. S. Silas, *ibid.*, **3**, 491 (1970).

(4) H. L. Frisch, C. L. Mallows, F. Heatley, and F. A. Bove *ibid.*, **1**, 533 (1968).

TABLE I
REACTION CONDITIONS, TRANSITION PROBABILITIES FOR VARIOUS OLIGOMER DISTRIBUTIONS IN CYCLOHEXANE

Sample	[*sec*-Butyllithium]/[butadiene]	[RLi]	[THF]	*T*, °C	Reaction time, min	P_{33}[a]	P_{13}	P_{20}	P_{00}	P_3^{II}	P_2^{II}	P_1^{II}	P_0^{II}	Standard error of estimates
1-A	1:2	1.6	0	70	90	0.21	0.39	0.67	0.55	0.15	0.21	0.37	0.27	0.0130
1-B	1:2	1.6	0.8	70	90	0.26	0.25	0.49	0.53	0.17	0.38	0.34	0.11	0.0311
1-C	1:2	1.6	0	25	360	0.64	0.70	0.36	0.23	0.44	0.15	0.35	0.06	0.0153
1-D	1:2	1.4	1.4	70	60	0.72	0.72	0.32	0.11	0.53	0.24	0.22	0.01	0.0168
1-E	1:2	0.4	0	70	90	0.34	0.32	0.75	0.69	0.07	0.19	0.26	0.48	0.0114
1-F	1:2	0.4	0	25	360	0.27	0.52	0.67	0.42	0.23	0.27	0.33	0.17	0.0229
2-A	1:3	1.6	0	70	45	0.29	0.44	0.68	0.51	0.18	0.21	0.39	0.22	0.0068
2-B	1:3	1.6	0	70	90	0.26	0.40	0.67	0.56	0.16	0.21	0.39	0.24	0.0124
2-C	1:3	1.6	0	25	360	0.56	0.71	0.49	0.45	0.47	0.16	0.32	0.05	0.0046
2-D	1:3	0.4	0	70	90	0.06	0.27	0.83	0.69	0.07	0.22	0.28	0.43	0.0108
2-E	1:3	0.4	0	25	360	0.20	0.47	0.70	0.47	0.21	0.27	0.32	0.20	0.0236
3-A	1:10	1.6	0	70	2	0.33	0.51	0.64	0.36	0.21	0.23	0.35	0.21	0.0190
3-B	1:10	0.4	0	70	4	0.01	0.32	0.87	0.67	0.08	0.25	0.26	0.41	0.0217
3-C	1:10	0.4	0	70	4	0.06	0.34	0.80	0.61	0.09	0.23	0.28	0.40	0.0154

[a] The transition probabilities were obtained from nonlinear regression analyses of the oligomer distributions defined algebraically in terms of the Markov chain transition probabilities. Standard errors of estimates are given in the last column for each oligomer distribution.

TABLE II
SEQUENTIAL DISTRIBUTIONS OF 1,4-BUTADIENE UNITS IN C_8, C_{12}, C_{16}, AND C_{20} *sec*-BUTYLLITHIUM INITIATED BUTADIENE OLIGOMERS

	Percentage of 1,4 units[a]							
Sample no.	C_8[b]	αC_{12}[a]	αC_{16}	αC_{20}	βC_{16}	βC_{20}	γC_{20}	Overall[c] (for propagation)
1-A	92	59	65	64	50	48	63	62
1-B	85	38	48	45	50	49	63	60
1-C	92	27	42	41	21	21	33	33
1-D		16	23	23	27	25	29	28
1-E	63	73	74	74	69	67	70	70
1-F		44	53	50	44	44	58	56
2-A	88	48	62	61	43	43	60	60
2-B		52	64	63	45	45	63	62
2-C		21	37	37	21	21	40	42
2-D		69	72	71	65	65	72	74
2-E		43	54	52	46	47	62	59
3-A		45	57	56	43	44	54	53
3-B		66	69	67	64	66	75	73
3-C		64	70	68	64	63	70	69

[a] The butadiene units are labeled α, β, γ for first, second, and third units, respectively. [b] The percentage 1,4 for the C_8's were obtained from the 3-methylheptene distribution after hydrolysis. [c] The final or overall compositions were calculated from eq 1 (see text) and is for propagation steps only.

the changes in 1, 4, and 1,2, addition, as indicated by the transition probabilities, were in directions that were expected from the reaction conditions. The addition of tetrahydrofuran increased 1,2 addition, which was also related to the alkyllithium concentration. The increase of 1,2 addition with a decrease in temperature was observed in a previous study of butadiene oligomers by Makowski, *et al.*[5] The most important aspect of a determination of transition probabilities is that specific structural changes can be identified as a function of reaction variables. An increasing 1,4 content with the degree of polymerization observed by Makowski and coworkers was reproduced on a smaller scale in this study. It was instructive to compare the per cent 1,4 units for each degree of addition of butadiene for various hydrogenated oligomers up to a degree of polymerization of 4. Given in Table II are the per cent 1,4 units after each butadiene addition and the total calculated for the related polymers. The first butadiene unit after the initiator unit is denoted by α, the second by β, and the third by γ. The 1,4 percentages for the C_{12} and C_{16} oligomers were determined directly from the glpc relative areas. The C_{20} 1,4 relative percentages were calculated using the transition probabilities listed in Table I while the final polymer 1,4 compositions were calculated from eq 1 derived by Price.[6] A penultimate effect that was

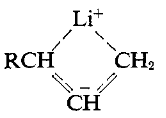
(5) H. S. Makowski, M. Lynn, and A. N. Bogard, *J. Macromol. Sci., Chem.*, 2 (4), 665 (1968).

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

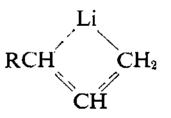
$$N_{1,4}/N_{1,2} = \frac{1 + [P_{20}/(1 - P_{00})]}{1 + [P_{13}/(1 - P_{33})]} \qquad (1)$$

indicated from the observed oligomer distributions is demonstrated here also by the observation that it is not until the γ unit that the 1,4 percentages correspond to that calculated for a butadiene polymer. The close correspondence of the 1,4 percentage compared to that calculated overall, which assumes that the reaction conditions remain constant, indicates that any changes in composition with degree of polymerization are a direct result of the sensitivity of the polymerization process to changes in reaction conditions. Undoubtedly depletion of the alkyllithium initiator and subsequent polymer growth favor 1,4 addition. Thus a comparison of 1,4 and 1,2 contents between butadiene oligomers and polymers cannot be meaningful unless effects of the initiator unit and reaction conditions have been taken into account. The 1,4 percentages calculated from the transition probabilities *via* eq 1 are for propagation steps only and are valid for comparison with reaction conditions.

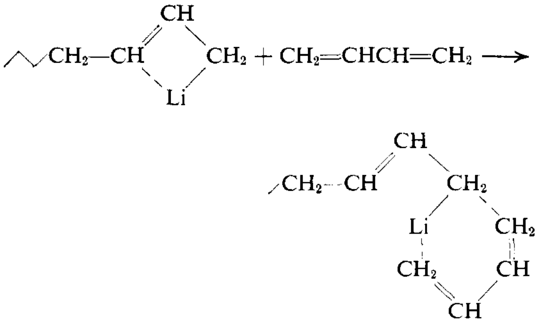
The 1,4 percentages for the α and β units for the C_{16} and C_{20} oligomers were uniformly in close agreement for the various oligomer samples. Agreement among the C_{12} α units was not so close. The 1,4 composition of the α units was generally higher than that for the β units and reflects a preference of 1,4 addition to *sec*-butyllithium that was observed in a previous study of the octenyllithium adducts.[1] The relatively poor agreement of the α units of the C_{12}'s when compared to the C_{16}'s and C_{20}'s appears outside experimental error from the reproducibility of the observation. The reasons for such a result remain unclear since late formers are expected to be higher in 1,4 content. A depletion of alkyllithium would favor 1,4 addition in the initiating steps as illustrated by the P_0^{II} transition probabilities for samples 1-E and 1-A, 2-D and 2-A, and 3-B and 3-A. Makowski, *et al.*, have interpreted the changes in polymer composition with degree of polymerization as a result of decreasing association of the alkenyllithium ultimate units. The alkenyllithium adduct is significantly affected by medium polarity as indicated by nmr studies of various alkenyllithium compounds in tetrahydrofuran.[7] A completely delocalized adduct



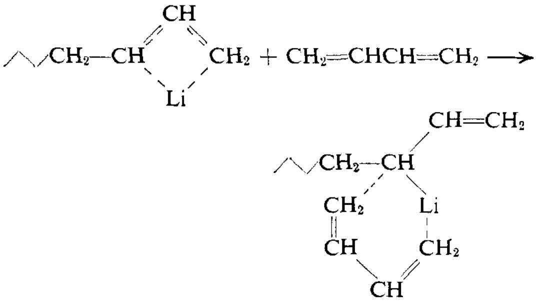
appears likely under polar conditions, whereas in a nonpolar solvent, the lithium atom is more strongly bonded to the 1 position than the 3 position as indicated by nmr[7]



A partially delocalized alkenyllithium adduct that has an electronic structure depending upon environment will result in a changing polymer composition with changing reaction conditions. The effects of reaction conditions on polymer structure are clearly indicated by the transition probabilities in Table I. The transition probabilities, P_{33}, P_{13}, P_{21}, and P_{01} generally increase with medium polarity either through addition of THF or an increase in alkyllithium concentration. Association effects likely account, to some extent, for the oligomer distributions prepared with high concentrations of initiator, but surprisingly similar results were obtained for samples 2-D and 3B, C in spite of a monomer to initiator change of 3:1 to 10:1. Second, an increase in 1,2 addition is achieved through addition of tetrahydrofuran or an increase in alkyllithium concentration; thus the medium polarity and subsequent effects upon the alkenyllithium adduct appear to be a major factor in determining polymer microstructure. Monomer addition under nonpolar conditions, which yields predominantly the 1,4 addition product, is expected with a nondelocalized alkenyllithium adduct (eq 2). Similarly, conditions that favored change delocalization would result in a higher 1,2 content (eq 3). For 1,2 addition, polarization of the alkenyllithium complex would be necessary and possibly could be achieved through the approach of the incoming monomer unit; thus the process should be favored by a polar medium but also subject to steric interferences. In Table I the probabilities for a 1,2 configuration when the ultimate and penultimate units were both 1,4, *i.e.*, P_{01}, were usually the highest of the four probabilities for 1,2 addition. Interestingly, the lowest probabilities for 1,2 addition occurred quite generally when the penultimate units were 1,2 independently of the ultimate unit configurations. The general favorability for 1,4 addition in a reasonably nonpolar medium is best illustrated by samples 3-B and 3-C where the probabilities for 1,4 addition P_{32}, P_{12}, P_{20}, and P_{00} were 0.94–0.99, 0.66–0.68, 0.80–0.87, and 0.61–0.67, respectively.



(2)



(3)

Further support for an alkenyllithium ultimate unit that could produce either *cis,trans* or vinyl monomer configurations was obtained after examination of the hydrolysis product distributions among the methyl-

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(7) See ref 1 (part I of this series) and the references therein.

heptenes in several of the oligomer samples. The C_{12} and C_{16} olefin oligomers gave gas chromatograms that appeared far too complex for specific oligomer identifications; thus only the C_8 distributions were investigated. As observed in the octenyllithium adducts,[1] hydrolysis yields primarily the 1,4 addition product irrespective of the incipient modes of butadiene addition as indicated by a comparison of the 1,4 percentages between α units for the C_8 and that of the C_{12}, C_{16}, and C_{20} oligomers. The C_8 1,4 content in Table II includes both *cis* and *trans* isomers as measured directly from the gas chromatograms of the various octenes. The most striking example of a change in the α configuration with hydrolysis was in sample 1-C. The 1,4 percentage among the octenes was 92 whereas the C_{12}, C_{16}, and C_{20} oligomers contained only 20–40% 1,4 configurations among the α units.

Conclusions

The observation that the oligomer distributions conformed to the Markov chain statistics proved very useful since glpc assignments could be made as a direct consequence[3] and each step of the oligomerization process subsequently characterized. The transition probabilities can be used to calculate "final polymer" compositions under carefully controlled reaction conditions, thus allowing the reaction conditions to be directly related to the incipient polymer microstructure. The sensitivity of the polymer microstructure to changes in reaction conditions precludes a similar but meaningful study of butadiene polymers. The second-order effects of the oligomerization processes were clearly indicated by a comparison of the compositions of the first monomer unit for the C_{12}, C_{16}, and C_{20} oligomers; however, the penultimate and ultimate effects upon the oligomer microstructure are small by comparison with experimental variables.

A polymerization mechanism involving butadiene addition to an alkenyllithium ion pair does not appear favorable in view of the nmr studies of the octenyllithium adducts and the product distributions *vs.* reaction conditions. There can be little doubt, however, that a two-step process is necessary before a reacting monomer unit assumes a particular configuration: (1) addition to form an alkenyllithium adduct which (2) assumes a configuration only after removal of the lithium atom through either a propagation or termination step.

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Computer Simulation of the Polymerization of Styrene. The Mechanism of Thermal Initiation and the Importance of Primary Radical Termination[1]

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ABSTRACT: We here report a computer simulation of the polymerization of styrene at 60°. Both the spontaneously initiated "thermal" polymerization and initiation by azobisisobutyronitrile and benzoyl peroxide have been studied by the use of the REMECH program of DeTar.[18] The primary aim of this study is to elucidate the mechanism of the thermal polymerization of styrene and to test the mechanism proposed by Mayo.[8] The Mayo mechanism postulates the reversible formation of a Diels–Alder dimer, AH, between two styrene molecules and the reaction of AH with a third sytrene molecule to form radicals. Values of k_{ith}, k_p, and k_t are known from the literature as are R_{ith}, R_{Pth}, and $\bar{P}_n$. (Rate constants are defined in Schemes I–III.) We have assigned values to K_{DA}, k_{fDA}, k_{rDA}, k_{MIH}, and k_{trAH}; the concentration of AH as a function of conversion was calculated by the program. We have reassigned a more reasonable value to k_{trM} and our treatment explains why the experimentally measured value for the apparent transfer constant of monomer is unreasonable. Our study also makes some predictions about the thermal mechanism. The program also allows the measurement of the importance of primary radical termination (PRT) in initiated polymerization. Primary radical termination is the reaction in which initiator radicals terminate growing chains rather than adding to monomer to initiate chain growth. We have evaluated k_{PRT} and the fraction of the chain ends formed by PRT for styrene.

A number of systems are known in which free radicals are produced at greatly enhanced rates from the interaction of normal organic molecules. This fascinating phenomenon, called molecule-induced homolysis, has been reviewed[3] and, at least in some cases, is well understood. The self-initiated "thermal" polymerization of styrene is perhaps the earliest known example of this phenomenon, and its mechanism still is not known with certainty.

Carefully and exhaustively purified styrene undergoes

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(1) (a) Reactions of Radicals. XXXIII. (b) We wish to acknowledge partial support of this work by the U. S. Army Research Office (Durham).

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(3) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, pp 119–124.