Specific Behavior of the Propagating Macromolecules in the Bis(π-crotylnickel iodide)-Catalyzed Polymerization of Butadiene

L. A. Churlyaeva, V. I. Valuev, T. S. Dmitrieva, M. I. Lobach, V. N. Sokolov, R. A. Shlyachter, and V. A. Kormer*

S. V. Lebedev Synthetic Rubber Research Institute, Leningrad, 198035 USSR.

Received July 15, 1975

ABSTRACT: The polymerization of butadiene by ^{14}C-labeled bis(π-crotylnickel iodide) in benzene solution has been studied. It is shown that chain propagation occurs through a "living" chain mechanism. In the initial polymerization stages, polymers with narrow MWD are formed which contain two radioactive groups per molecule. With increasing polymerization degree the portion of double-labeled polymers decreases and that of single-labeled polymers increases. These changes in the composition of growing chains lead to binodal MWD and to some growth of the polydispersity index ($\bar{M}_w/\bar{M}_n$). From the experimental results obtained it is concluded that binodal MWD of 1,4-*trans*-poly(butadiene) is due to the change in the association degree of "living" macromolecules in the course of polymerization.

Since the discovery of the possibility to carry out *trans*-1,4-polymerization of butadiene using bis(π-allylnickel iodide)[1,2] the regularities of this reaction have been studied by some authors.[3-9] Investigations conducted in our institute by means of ^{1}H NMR and radiochemical techniques[10-13] have shown that polymerization in the presence of bis(π-crotylnickel iodide) occurs by successive insertions of monomer molecules at metal–carbon bonds having π-allylic character, with all the initiator molecules participating in the polymer chain propagation. In ^{1}H NMR spectra of the system bis(π-perdeuteriocrotylnickel iodide)–butadiene there were no signals from protons of the methyl groups of π-crotylnickel iodide or its adducts with butadiene whose formation should be taken into account in case the hydride transfer to monomer takes place.

trans-1,4-Poly(butadienes) prepared in the presence of ^{14}C-labeled bis(π-crotylnickel iodide) contained after termination of polymerization approximately two radioactive labels per macromolecule.[13] Based on the π-allylic structure of active sites it was proposed that the appearance of double-labeled polymers is due to the recombinational mechanism of termination of growing chains.

In the present paper, the proposed concepts of the mechanism of butadiene polymerization by bis(π-allylnickel iodide) are extended and data obtained earlier are refined by studying MWD and radioactivity distribution in the chains of butadiene polymers prepared using bis(π-crotyl-^{14}C-nickel iodide).

Experimental Section

Preparation of the Catalyst and *trans*-1,4-Poly(butadiene-^{14}C). Bis(π-crotylnickel iodide) was prepared by reaction of crotyl-^{14}C iodide with nickel carbonyl[14] in benzene solution.

Polymerization was carried out in a 3.0 l. stainless steel autoclave at 40°. The initial concentration of butadiene and bis(π-crotyl-^{14}C-nickel iodide) was 3.6 and 4.35×10^{-2} *M*, respectively. The amount of butadiene fed into the autoclave was 4.8 mol. Benzene was used as a solvent.

In the course of polymerization, polymer samples were taken which were precipitated from solution by acidified methanol. The polymer was washed several times with methanol, then precipitated three times from benzene and dried in a vacuum at the room temperature.

Analysis of *trans*-1,4-Poly(butadiene-^{14}C). The number-average molecular weights of polymers and their fractions were determined in benzene using a Ray ebulliometer fitted with a 15-joint thermocouple.

The fractionation of polymers by molecular weights was performed by means of a stepwise extraction on a column with an inert packing composed of quartz glass (particle size 0.1–0.3 mm);[15] the packing volume in the column was 90 cm^3 and the liquid-phase volume was 50 ml. Ethanol was used as a precipitating agent and benzene as a solvent. The amount of the latter in the eluating mixture was changed discretely; the volume of fractions taken was 50 ml. Solvents were removed in a vacuum and the polymers were dried to a constant weight. Then the molecular weight and specific radioactivity were measured.

The radioactivity (^{14}C) of polymers and their fractions and also of crotyl-^{14}C iodide was measured on a Beckman 250 liquid scintillation β-spectrometer. The number of radioactive crotyl groups in the polymer was calculated as the ratio of the number-average molecular weight to the equivalent weight ($\bar{M}_{eq}$):

$$n = \bar{M}_n/\bar{M}_{eq}$$

where $\bar{M}_{eq}$ is the weight of a polymer chain per radioactive crotyl group:

$$\bar{M}_{eq} = A_{mol}/a_{sp}$$

where A_{mol} is the molar activity of crotyl-^{14}C iodide (imp/min mol); a_{sp} is the polymer specific activity (imp/min g).

Molar fractions of polymers with various numbers of radioactive crotyl groups ($n = 0, 1, 2, 3$) were calculated from results of determination of "n" in polymer fractions, the assumption being made that fractions with fractional number of "n" contain only two adjacent (by the number of "n") types of molecules.

The MWD of polymer samples differing in conversion was measured by means of gel permeation chromatography using a Waters 200 GPC chromatograph. A set of four columns of 60-, 500-, 1 000-, and 10 000-Å porosity (cross-linked poly(styrene)) was used. Toluene was utilized as a solvent. Gel permeation chromatograph was calibrated by maximum molecular weights $\bar{M}_{peak} = (\bar{M}_n \cdot \bar{M}_w)^{1/2}$, where $\bar{M}_n$ and $\bar{M}_w$ are number-average and weight-average molecular weights measured in carrying out column fractionation by a stepwise extraction from a thin film.

Results

The polymerization of butadiene in the presence of bis(π-crotylnickel iodide) proceeds with a constant rate up to conversions of about 40% (Figure 1, curve 1). A subsequent decrease in the reaction rate is due to a decrease in the monomer concentration, as evidenced by proportionality in the dependence of the logarithm of the ratio of initial butadiene concentration (M_0) to its concentration at any given moment (M_t) on the polymerization rate (Figure 1, curve 2). With increasing degree of conversion a growth of number-average and weight-average molecular weights is observed along with some broadening of MWD of resulting *trans*-1,4-poly(butadienes). All the fractions of polymers obtained at different conversions contain radioactive crotyl ligands of the starting bis(π-crotyl-^{14}C-nickel iodide) (Table I). With increasing molecular weights of poly(buta-

Table I
Fractionation Data for *trans*-1,4-Poly(butadienes) Obtained at Different Conversions

Sample no.	Conversion, %	Fraction	Wt % of fraction	M % of fraction	$\bar{M}_n$	$K = \bar{M}_w/\bar{M}_n$	No. n^a
1	14				950	1.04	2.0
		1	6.8	10.1	640		1.5
		2	22.5	25.5	840		1.9
		3	59.4	58.0	960		2.1
		4	11.3	6.4	1680		2.4
2	42				1600	1.07	1.8
		1	17.8	27.3	1050		1.1
		2	60.0	56.7	1700		2.0
		3	13.9	10.7	2100		2.2
		4	8.3	5.3	2550		2.5
3	59				1980	1.11	1.7
		1	11.3	19.5	1150		1.1
		2	7.9	10.2	1550		1.4
		3	14.2	16.5	1700		1.5
		4	48.6	42.6	2270		1.9
		5	12.2	8.4	2900		2.4
		6	5.8	2.8	4000		3.1
4	74				2140	1.15	1.5
		1	8.4	17.8	1010		0.9
		2	19.7	26.3	1600		1.1
		3	23.2	22.8	2170		1.5
		4	47.2	32.3	3090		2.1
		5	1.5	0.8	3840		2.7

[a] The number of crotyl groups.

Table II
Change of "n" as a Function of Conversion

"n"	Conversion, % 14	42	59	74
0				1
1	5	27	33	49
2	91	66	61	47
3	4	7	6	3

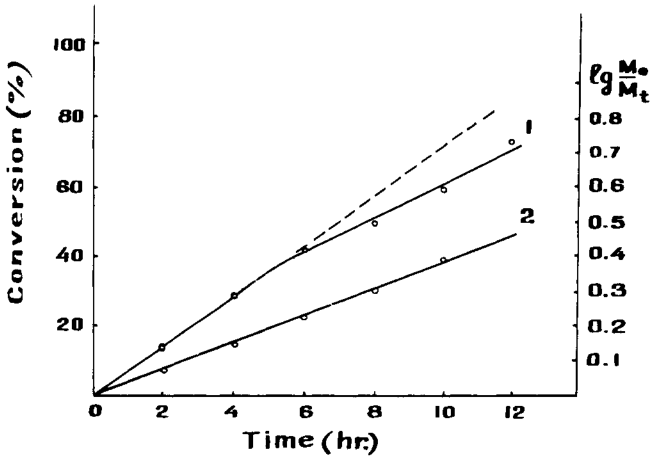


Figure 1. Kinetic curves of butadiene polymerization in the presence of bis(π-crotyl-^{14}C-nickel iodide).

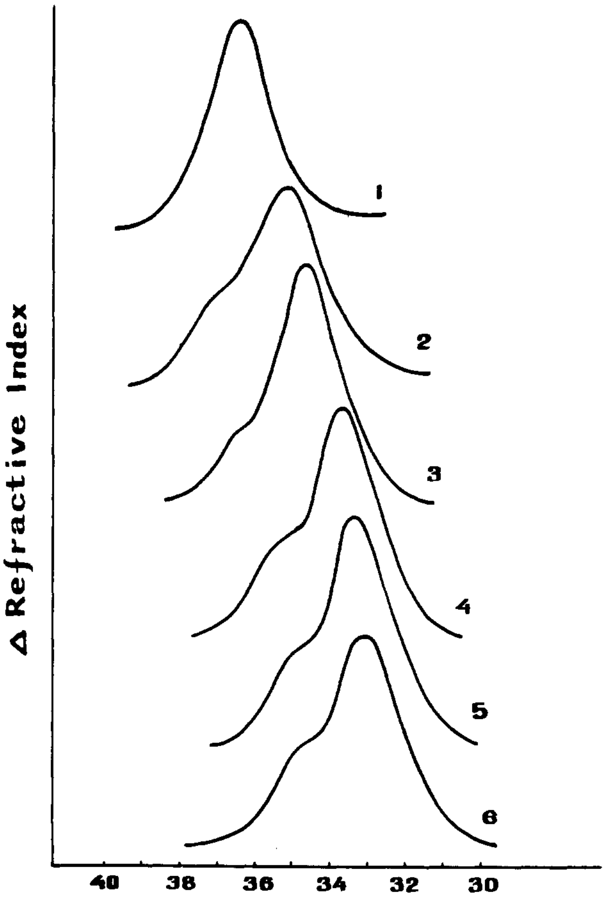


Figure 2. Gel permeation chromatograms of polymers obtained at different conversions: 1–14%; 2–28%; 3–42%; 4–50%; 5–59%; 6–74%.

diene) fractions the number of crotyl groups bound to the polymer chain in each sample is increased. The molar portion of single-labeled polymer chains increases and that of double-labeled polymer chains decreases with increasing conversion (Table II). From gel permeation chromatographs of samples (Figure 2) it can be concluded that beginning with a definite degree of conversion the deactivated reaction products contain two types of homogeneous polymers differing in polymerization degree. With increasing conversion the molecular weight distribution becomes somewhat broader, a binodal distribution arises, and the portion of low molecular weight fraction increases, both MWD peaks shifting toward higher molecular weights. Some of the trends mentioned above have already been reported.[8,9]

Discussion

The polymerization of butadiene by bis(π-crotylnickel iodide) under conditions studied (the catalyst/monomer

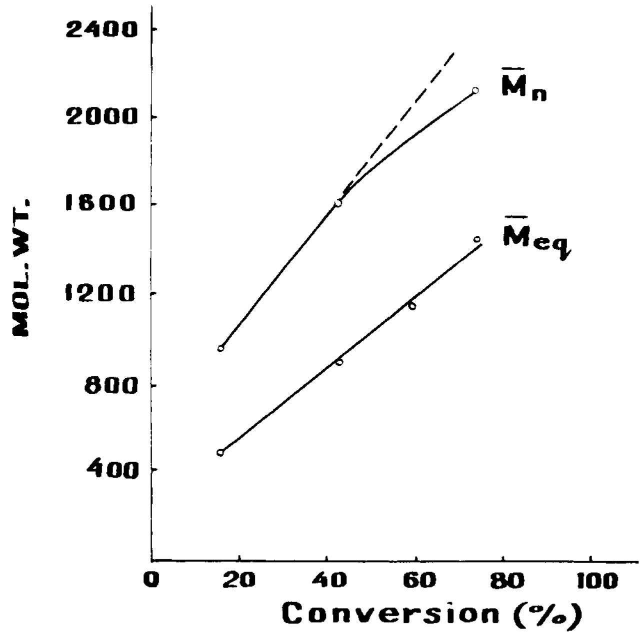


Figure 3. Dependence of number-average ($\bar{M}_n$) and equivalent ($\bar{M}_{eq}$) molecular weight on conversion.

ratio, temperature, degree of conversion) is characterized by the fact that the reactions limiting the polymer chain propagation practically do not occur. This is evidenced not only by ^{1}H NMR spectra data[11] but also by the data reported in the present paper. First, all the polymer chains are radioactive. At the conversion of 74% the content of nonradioactive chains does not exceed 1–2% (Table II). Second, with increasing conversion a linear growth of the equivalent weight ($\bar{M}_{eq}$) is observed (Figure 3). The concept of the equivalent weight, that is of the polymer chain weight per radioactive crotyl group, is to our mind very important for the interpretation of experimental data. The fact is that in the system under investigation a regular decrease in the content of double-labeled molecules and a growth in the content of single-labeled molecules is observed (Table II). The number-average molecular weight ($\bar{M}_n$) of single-labeled polymer chains is always lower than that of double-labeled ones (Table I). So it is quite natural that a deviation of $\bar{M}_n$ from a linear dependence is observed with increasing conversion (Figure 3). On the basis of changes in $\bar{M}_n$ alone, with $\bar{M}_{eq}$ being not taken into consideration, one can come to an erroneous conclusion that transfer reactions do occur in the system.

In the polymerization of butadiene with bis(π-crotylnickel iodide) the difference between initiation and termination constants is very small.[10] This fact together with the data on variations in the MWD and radioactivity distribution along the polymer chains allow the conclusion to be made that in the reaction under investigation a specific mechanism of molecular weight and MWD control is operative that is not characteristic of known processes in which termination and transfer reactions do not play any significant role.

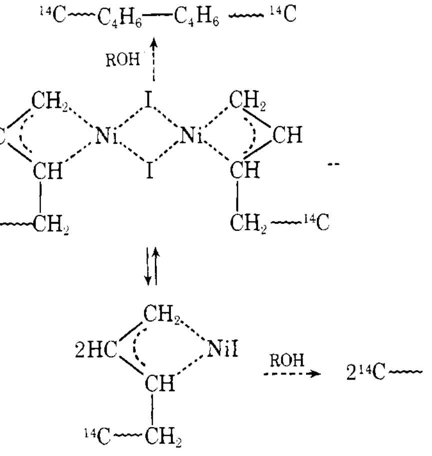
The π-allylnickel complexes readily enter into reactions leading to the coupling of allylic ligands. Bis(π-allyl)nickel is known to give diallyl in the presence of electron donors.[16] The reaction of allyl halides with nickel carbonyl in the alcohol medium which proceeds with the formation of intermediate bis(π-allylnickel halides)[17] is a good preparative method of synthesis of diallyl and its homologues.[18] In our studies we have found that on treatment of bis(π-crotylnickel iodide) with air-saturated methanol or ethanol the main products formed are also the products of crotyl ligand coupling: octadiene-2,6 and its isomers 3-methylheptadiene-1,5 and 3,4-dimethylhexadiene-1,5 (in the ratio approximately 55:20:1). As it follows from experiments the coupling of allylic ligands occurs as a rule with dimeric forms of allylnickel halides; monomeric complexes of this type give products containing one allylic group.[13]

Table III
Dependence of Average Molecular Weight of Single- and Double-Labeled Polymers on Conversion

Conversion, %	$\bar{M}_n$ Single-labeled polymers	$\bar{M}_n$ Double-labeled polymers
14	470	920
42	890	1700
59	1140	2300
74	1450	2900

Taking into account the π-allylic character of active sites in the polymerization of butadiene with bis(π-crotylnickel iodide) we believe that the mode of changes in molecular weight and MWD of *trans*-1,4-poly(butadiene) is strongly dependent on the recombination of "living" π-allylic macromolecules taking place during their deactivation with methanol when the polymer is precipitated from solution.

According to our viewpoint, variations in the content of polymer chains containing two and one radioactive groups in poly(butadienes) differing in polymerization degree are due to the change in the equilibrium concentration of associated and monomeric forms of "living" macromolecules. It is believed that deactivation of monomeric chains will result in polymers having one ^{14}C-label; deactivation of dimeric chains is accompanied by their coupling (two ^{14}C labels):



The fact that the dissociation dimer ⇄ monomer is an equilibrium process is confirmed by molecular weight of polymers with two radioactive crotyl groups being twice as much as that of polymers containing one crotyl group (Table III).

From data given in Tables I and II it may be concluded that at low polymerization degrees the "living" allylic chains exist mostly in the dimeric form; at the polymerization degrees of about 40, one-half of the chains are already dissociated. The dissociation should favor the interaction between hydrocarbon chains (for example, physical knots, etc.), this interaction increasing with a growing chain length. A decrease in the association degree of poly(butadienyl)lithium with variation in the chain length has been reported.[19]

The above considerations that the MWD of poly(butadienes) prepared with the use of bis(π-crotylnickel iodide) is strongly dependent on the transformations of "living" chains during their deactivation offer a good explanation of our experimental results as well as of those obtained by other authors[8,9] on the variation of MWD with conversion.

In the case of low polymerization degrees, with "living" chains being associated and hence mainly undergoing recombination in the course of deactivation, the MWD of poly(butadienes) formed is uninodal (Figure 2, curve 1) and is characterized by very high monodispersity (K = 1.04, Table I). The high homogeneity of *trans*-1,4-poly(butadienes) supports the conclusion that reactions which limit the chain growth do not occur and that the difference in the rate of addition of the first and subsequent butadiene units is very small.

With increasing degree of conversion the dissociation of dimeric "living" chains is observed and monomeric forms enter into deactivation along with dimers; as a result, the MWD becomes binodal. Each peak of summerized distribution represents an independent narrow symmetric distribution. In principle, at high degrees of conversion when the dimers of "living" chains are dissociated for the most part, the MWD should again become unimodal, as it was observed in ref 8.

The difference between gel permeation chromatograms of *trans*-1,4-poly(butadienes) recorded by us and those given in ref 8 (disappearance of binodal distribution in the latter case and its appearance in our chromatograms with increasing conversion) is apparent and can be explained by our studies of the process of polymer formation with the polymerization degree not higher than 40 while in ref 8 the lowest polymerization degree of *trans*-1,4-poly(butadiene) was about 50, hence, the chromatograms complement each other nicely.

Formally, the polymerization of butadiene with bis(π-crotylnickel iodide) resembles the polymerization in the presence of bifunctional initiators giving "living" chains with two growing chains in media containing some or no impurities which prevent macromolecules from growing at one end. The variations of MWD in these systems[20,21] are very much like those observed in the present study.

The investigation performed is a good illustration of great possibilities offered by combination of radiochemical and MWD studies in clarifying the fine specific features of polymerizations carried out in the presence of organometallic catalysts.

References and Notes

(1) V. A. Kormer, B. D. Babitskii, M. I. Lobach, and N. N. Chesnokova, *Int. Symp. Macromol. Chem., Prepr.*, 413 (1965); *J. Polym. Sci., Part C*, 4351 (1969).
(2) L. Porry, G. Natta, and M. C. Gallazzi, *Int. Symp. Macromol. Chem., Prepr.*, 494 (1965); *J. Polym. Sci., Part C*, 2525 (1967).
(3) V. A. Kormer, B. D. Babitskii, and M. I. Lobach, *Adv. Chem. Ser.*, **No. 91**, 306 (1969).
(4) V. A. Kormer, R. S. Lyastch, B. D. Babitskii, G. V. L'vova, M. I. Lobach, and T. Ya. Tchepurnaya, *Dokl. Akad. Nauk SSSR*, **180**, 665 (1968).
(5) J. F. Harrod and L. R. Wallace, *Macromolecules*, **2**, 449 (1969).
(6) A. I. Lazutkina, L. Ya. Alt, T. L. Matveeva, A. M. Lazutkin, and Yu. I. Ermakov, *Kinet. Catal. (Engl. Transl.)*, **12**, 1162 (1971).
(7) J. F. Harrod and L. R. Wallace, *Macromolecules*, **5**, 682 (1972).
(8) J. F. Harrod and L. R. Wallace, *Macromolecules*, **5**, 685 (1972).
(9) G. Henrici-Olivé, S. Olivé, and S. Schmidt, *J. Organomet. Chem.*, **39**, 201 (1972).
(10) M. I. Lobach, V. A. Kormer, I. Yu. Tseretely, G. P. Kondratenkov, B. D. Babitskii, and V. I. Klepikova, *Dokl. Akad. Nauk SSSR*, **196**, 114 (1971).
(11) M. I. Lobach, V. A. Kormer, I. Yu. Tseretely, G. P. Kondratenkov, B. D. Babitskii, and V. I. Klepikova, *J. Polym. Sci., Polym. Lett. Ed.*, **9**, 71 (1971).
(12) V. I. Klepikova, G. P. Kondratenkov, V. A. Kormer, M. I. Lobach, and L. A. Churlyaeva, *J. Polym. Sci., Polym. Lett. Ed.*, **11**, 193 (1973).
(13) B. D. Babitskii, V. A. Kormer, M. I. Lobach, I. Ya. Poddubnyi, and V. N. Sokolov, *Dokl. Akad. Nauk SSSR*, **180**, 420 (1968).
(14) E. O. Fischer and G. Bürger, *Z. Naturforsch., B*, **16**, 77 (1961).
(15) V. I. Valuev, R. A. Shlyachter, and N. P. Apuchtina, *Vysokomol. Soedin., Ser. B*, **10**, 147 (1968).
(16) G. Wilke and B. Bogdanovič, *Angew. Chem.*, **73**, 756 (1961).
(17) E. J. Corey, M. F. Semmelhack, and L. S. Hegedus, *J. Am. Chem. Soc.*, **90**, 2416 (1968).
(18) I. D. Webb and G. T. Borcherdt, *J. Am. Chem. Soc.*, **73**, 2654 (1951).
(19) H. S. Makowski and M. Lynn, *J. Macromol. Chem.*, **1**, 443 (1966).
(20) R. V. Figini, *Makromol. Chem.*, **44–46**, 497 (1961).
(21) F. M. Brower and H. W. McCormick, *J. Polym. Sci., Part A*, **1**, 1749 (1963).

Kinetics and Mechanism of the Initial Stages in the Bis(π-crotylnickel iodide)-Catalyzed Polymerization of Butadiene

V. I. Klepikova, G. B. Erusalimskii, M. I. Lobach, L. A. Churlyaeva, and V. A. Kormer*

S. V. Lebedev Synthetic Rubber Research Institute, Leningrad, 198035 USSR.
Received July 15, 1975

ABSTRACT: Using the ^1H NMR technique a kinetic study has been made of the active centers formation and initial stages of polymer chain propagation in the polymerization of 1,1,4,4-tetradeuteriobutadiene with bis(π-crotyl-d_6-nickel iodide). The fact that the orders of these reactions are close to unity is explained by dimeric forms of the catalyst complexes taking part in the reactions.

Studies on transformations of 1,3-dienes under the action of bis(π-crotylnickel halides) made it possible to establish some regularities which contribute to fundamental understanding of the mechanism of ionic coordination polymerization. Of the observed phenomena the most interesting are the following: the dependence of the catalyst stereoselectivity in the formation of cis-1,4 and trans-1,4 structures on the nature of halogen atom bound to nickel[1–3] and the ability of iodide complexes to initiate the formation of *trans*-1,4-poly(dienes) in an aqueous medium[3,4] which is not observed with other organometallic catalysts except for the butadiene polymerization by Rh(III) salts.[5]

Investigation of the reaction between butadiene and bis(π-crotylnickel iodide) in the medium containing Lewis bases showed that by their effect on the polymerization the Lewis bases can be subdivided into two clearly defined