Macromolecules

Volume 2, Number 5 September–October 1969

# Kinetics of π-Crotylnickel Iodide Catalyzed Butadiene Polymerization

**J. F. Harrod and L. R. Wallace**[1]

*Chemistry Department, McGill University, Montreal, Canada.* *Received June 12, 1969*

ABSTRACT: The polymerization of 1,3-butadiene by π-crotylnickel iodide was studied in a constant-pressure system under pseudo-zero-order reaction conditions. The rate law is given in the Results. In the initial stages of polymerization the molecular weight of the polymer increased with conversion and the dispersion of molecular weight was very narrow. With increasing conversion the number of polymer molecules per catalyst molecule increased, as did the polydispersity of the polymer. A polymerization mechanism involving rapid initiation by a monomeric allylnickel iodide, slow propagation, and a slow transfer process (probably hydride transfer) is proposed.

Polymerization of unsaturated monomers by transition organometallic catalysts has had an enormous impact on the development of transition organometallic chemistry. However, this impact has been largely in the area of new synthetic chemistry rather than in the area of increased understanding of the detailed mechanisms of initiation, propagation, termination, and transfer processes involved in actual polymerization reactions. The extreme sensitivity of transition organometallic catalysts to trace impurities, and the intrinsic instability of many, has precluded such an extensive investigation of mechanism by kinetic means as was so successfully applied to free-radical reactions and, more recently, carbanionic reactions.

A great deal of attention has been paid to the polymerization and oligomerization of butadiene by complexes of nickel. The work of Wilke and his colleagues on the cyclotrimerization, cyclodimerization, and polymerization of butadiene is already a classic example of the success that may be achieved by the synthetic approach to understanding mechanism.[2,3]

The implication of π-allyl intermediates in these cyclization reactions has led to numerous investigations of stable π-allyl complexes as catalysts for polymerization of butadiene to high molecular weight linear polymers, both by Wilke and numerous Russian and other groups.[2–16]

Our interest in this subject was aroused by reports that π-crotylnickel halides are effective catalysts for polymerization of butadiene under mild conditions.[4,5,11] Moreover, these catalysts exhibit a remarkable stereoselectivity, the iodide giving a polymer of predominantly *trans*-1,4 structure, whilst the chloride gives a polymer of predominantly *cis*-1,4 structure. Under the same conditions, π-allylnickel halides give similar results, low molecular weight polymers being obtained.[4,16]

π-Crotylnickel iodide (**1**) is an example of a first row transition organometallic which exhibits both considerable chemical stability and catalytic activity at the same time. This combination of properties led us to investigate the kinetics of butadiene polymerization by this catalyst, in the expectation that impurity problems would not be as severe as those so often encountered with transition metal alkyl catalysts. The results of this study are the subject of the present report.

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(1) National Research Council of Canada Scholar.

(2) (a) G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinrucke, D. Walter, and H. Zimmermann, *Angew. Chem. Intern. Ed. Engl.*, 5 (2), 151 (1966); (b) G. Wilke, *ibid.*, 2 (3), 105 (1963).

(3) G. Wilke, B. Bogdanovic, P. Heimbach, M. Kroner, and W. Muller, Advances in Chemistry Series, No. 34, American Chemical Society, Washington, D. C., 1962, p 137.

(4) B. D. Babitskii, B. A. Dolgoplosk, V. A. Kormer, M. I. Lobach, E. A. Tinyakova, and V. A. Yakovlev, *Izv. Akad. Nauk SSSR*, 1507 (1965).

(5) B. D. Babitskii, B. A. Dolgoplosk, V. A. Kormer, M. I. Lobach, E. I. Tinyakova, and V. A. Yakovlev, *ibid.*, **161**, 583 (1965).

(6) P. A. Vinogradov, B. A. Dolgoplosk, V. N. Zgonnik, O. P. Parengo, E. I. Tinyakova, and B. S. Turov, *ibid.*, **163**, 1147 (1965).

(7) T. K. Vydrina, E. I. Tinyakova, and B. A. Dolgoplosk, *ibid.*, **183** (3), 591 (1968).

(8) B. D. Babitskii, V. A. Kormer, M. I. Lobach, I. Ya. Poddubnyi, and V. N. Sokolov, *ibid.*, **180** (2), 420 (1968).

(9) V. A. Kormer, R. S. Lyasch, B. D. Babitskii, G. V. L'vova, M. I. Lobach, and T. Ya. Chepurnaya, *ibid.*, **180** (3), 665 (1968).

(10) E. Mushina, T. K. Vydrina, E. V. Sakharova, E. I. Tinyakova, and B. A. Dolgoplosk, *ibid.*, 177 (2), 361 (1967).

(11) B. D. Babitskii, B. A. Dolgoplosk, V. A. Kormer, M. I. Lobach, E. I. Tinyakova, N. N. Chesnokova, and V. A. Yakovlev, *Vysokomol. Soedin.*, **6**, 2202 (1964).

(12) T. Matsumoto and J. Furukawa, *J. Polym. Sci., Part B*, 5, 935 (1967).

(13) B. A. Dolgoplosk, E. I. Tinyakova, P. A. Vinogradov, O. P. Parengo, and B. S. Turov, *ibid.*, *Part C*, **16**, 3685 (1968).

(14) E. I. Tinyakova, A. V. Alferov, T. G. Golenko, B. A. Dolgoplosk, I. A. Oreshkin, O. K. Sharaev, G. N. Cherneko, and V. A. Yakovlev, *ibid.*, *Part C*, **16**, 2625 (1967).

(15) O. K. Sharaev, A. V. Alferov, E. I. Tinyakova, and B. A. Dolgoplosk, *Vysokomol. Soedin.*, *Ser. A*, **9** (3), 633 (1967).

(16) L. Porri, G. Natta, and M. C. Gallazzi, *J. Polym. Sci.*, *Part C*, **16**, 2525 (1967).

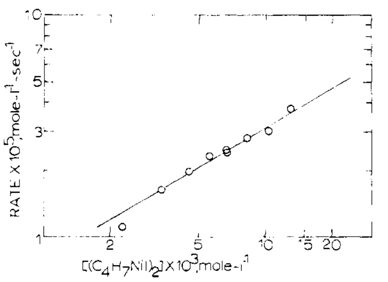

Figure 1. Polymerization rate as a function of catalyst concentration.

## Experimental Section

$\pi$-Crotylnickel iodide was prepared by Wilke's[2a] method (reaction of crotyl iodide with bis(cyclooctadiene)nickel(0)[17] in diethyl ether). Stock solutions of the catalyst were made up in dry benzene and reserved for the polymerization experiments.

Polymerizations were run in a 30-ml dimpled reaction flask immersed in a thermostated water bath controlled to ±0.02°, and shaken at a rate of about 2 cps to ensure rapid equilibration between the gas and liquid phases. The uptake of butadiene was manually monitered at constant pressure and temperature by a gas buret apparatus equipped with an oil manometer for sensitive detection of pressure changes. During polymerizations lasting several hours an automated gas buret was employed. A nitrogen-driven mercury piston was used to compensate for gas uptake. The nitrogen flow into the piston was regulated by a solenoid valve, operated by a pressure-sensitive, mercury-switch-activated relay. In any given run, the monomer concentration never varied more than $\pm 0.01\ M$ from the original concentration. When a measurement of the reaction rate was being determined, the monomer concentration was kept constant to $\pm 0.002\ M$.

In a typical experiment, sodium-dried, outgassed benzene was saturated with butadiene to a given pressure, or monomer concentration. Once equilibrium had been attained, catalyst was injected into the reaction flask through a rubber septum by means of a 1.0-ml hypodermic syringe.

As reaction proceeded, periodic gas-uptake measurements were made. The gas uptake was linear with time after a short induction period (*ca.* 15 min.) had elapsed. Reactions were terminated by precipitation of the polymer in methanol containing a small amount of hydrochloric acid. The polymer was purified by reprecipitation from benzene and dried at room temperature under high vacuum. The molecular weight of the polymer increased slowly during storage in air and after several days, the polymer was no longer totally soluble in tetrahydrofuran. This problem was completely eliminated by storing the products under high vacuum in the absence of light.

The stereoregularity of the polymer produced was determined by the method of Hampton,[18] and in all cases, the products were at least 95% *trans*-1,4 with approximately equal amounts of *cis*-1,4 and vinyl-1,2 structure in accord with the work of Babitskii.[4]

Molecular weights and molecular weight distributions were determined on a Model 200 Waters Associates gel permeation chromatograph. Tetrahydrofuran (THF) was used as solvent at a flow rate of 1 ml/min and the instrument was operated at ambient, or 33°. A solution of 0.5 mg of polymer in the THF was injected onto the column during a 15-sec interval. Column banks of polystyrene beads of 100, 400, $10^3$ and $10^4$ Å, or $10^3$, $10^4$, and $10^5$ Å, were used. A plot of log [equivalent chain length] *vs.* elution count for standard monodisperse polystyrenes and polypropylene glycols supplied by Waters Associates served as the calibration curve and was used for the calculation of molecular weights. Chromatograms were analyzed at one-fifth count intervals. Molecular weights and molecular weight distributions obtained on the two column banks were in good agreement.

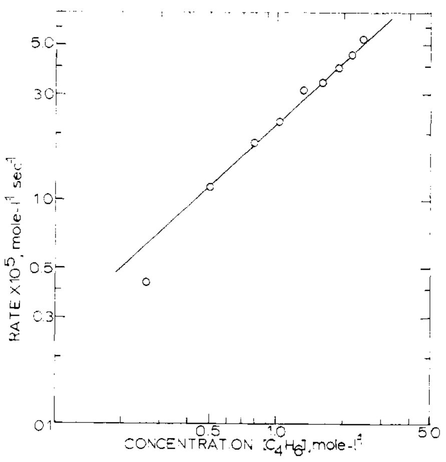

Figure 2. Polymerization rate as a function of monomer concentration.

## Results

**Kinetics of the Reaction.** Under our experimental conditions (constant monomer concentration, catalyst concentration, and temperature), butadiene was polymerized by **1** in benzene solution with a pseudo-zero-order uptake of monomer. The uptake of monomer remained linear over long periods of time, indicating that polymerization was taking place under steady-state conditions. However, over exceptionally long reaction times a slight decline in rate was observed (5% in 24 hr, 25% in 48 hr at 50°), and this decline in rate was attributed to a loss of catalyst, manifest by the appearance of a trace of black residue on the walls of the reaction vessel in the course of such runs.

With a given sample of **1** it was possible to reproduce rates to within ±2% and the reproducibility of rates using different preparations of **1** was better than ±5%.

The dependence of the reaction rate on catalyst concentration is shown in Figure 1. A good fit is obtained for a half-order dependence on catalyst and the small intercept is readily explained by the assumption that *ca.* 10% of the first aliquot of catalyst is destroyed by impurities in the monomer solution. The first-order dependence of rate on monomer concentration is shown in Figure 2.

A good Arrhenius plot was obtained in the range of 40–70°, yielding values of $\Delta H^{\ddagger} = 14.5$ kcal/mol and $\Delta S^{\ddagger} = -21.5$ eu. The over-all rate expression is thus

$$-\frac{d[C_4H_6]}{dt} = \frac{kT}{h}\exp\left[\frac{14{,}500}{RT} - \frac{21.5}{R}\right] \times [C_4H_6][(C_4H_7NiI)_2]^{1/2}$$

The rate constant at 50° was $2.08 \pm 0.04 \times 10^{-4}\ M^{-1/2}$.

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(17) B. Bogdanovic, M. Kroner, and G. Wilke, *Liebigs Ann. Chem.*, **699**, 1 (1966).

(18) R. R. Hampton, *Anal. Chem.*, **21** (8), 923 (1949).

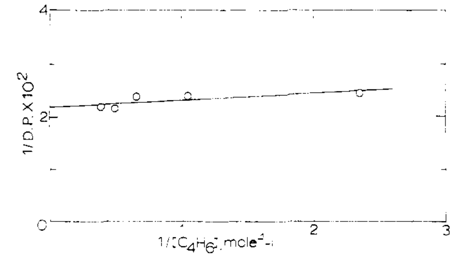


Figure 3. Reciprocal of degree of polymerization as a function of reciprocal of monomer concentration.

These results are in accord with those of Vasil'eva,[19] who studied the polymerization of butadiene by $\pi$-allylnickel halides. For polymerization catalyzed by allylnickel iodide, values of $\Delta H^{\ddagger} = 15.6$ kcal/mol and rate constant at 50° = $1.28 \times 10^{-4}$ $M^{-1/2}$ were found.

**Molecular Weights of the Polymers.** The molecular weights of polymers produced under our experimental conditions were generally quite low and almost independent of monomer concentration. Figure 3 shows the molecular weights of a series of polymers produced at different monomer concentrations, but constant catalyst concentration and conversion. The molecular weight showed a strong, though not linear, dependence on conversion, as illustrated in Figure 4. Table I shows the near independence of molecular weight with polymerization temperature over the range of 40–70°. Such behavior is indicative of a transfer process having about the same activation energy as the propagation reaction.[20]

**The Molecular Weight Distributions.** Molecular weights and distributions were determined by standard gel permeation chromatography (gpc) techniques. Because of the difficulty of obtaining well-characterized samples of polybutadiene in the molecular weight range of interest, absolute calibration of the instrument was not possible. The "$Q$" value method[21] was not considered to be reliable for absolute molecular weight determinations, but was assumed to be valid for comparative molecular weight studies. It should be pointed out that in the single instance where we compared a gpc number average molecular weight with a Mechrolab vapor pressure osmometer value for the same polymer, quite good agreement was achieved. Values of 2340 were obtained for the former and 2713 for the latter.

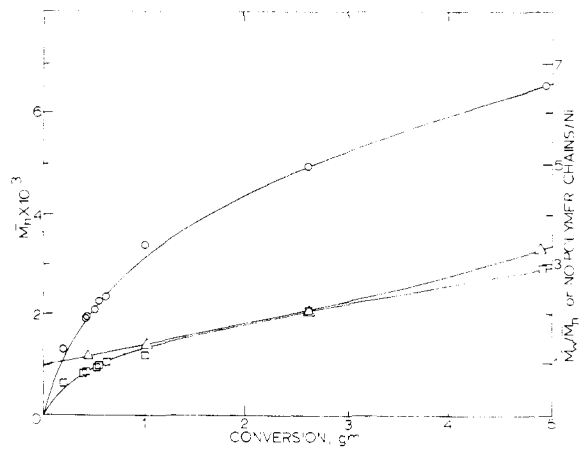


Figure 4. Molecular weight (○), $\overline{M}_w/\overline{M}_n$ (△), number of polymer molecules per nickel atom (□) as a function of conversion.

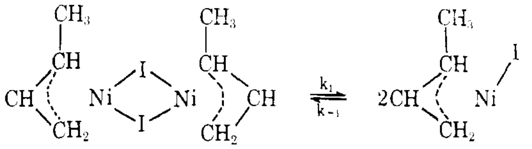
TABLE I

| $T$, °K | $\overline{M}_n$ | $\overline{M}_w$ | $\overline{M}_w/\overline{M}_n$ | Conversion, g |
|---|---|---|---|---|
| 313 | 4024 | 5646 | 1.40 | 1.0158 |
| 323 | 3813 | 5393 | 1.41 | 1.0075 |
| 333 | 4021 | 5689 | 1.41 | 1.0458 |
| 343 | 3866 | 5350 | 1.38 | 1.0410 |

All of the gpc distribution curves indicated that the polymer contained two overlapping distributions of comparable size. At lower molecular weights (<2500) the distribution was very narrow ($\overline{M}_w/\overline{M}_n \simeq 1.2$), but as the molecular weight increased, so did the dispersion as shown in Figure 4. We have obtained similar chromatograms from mixtures of two monodisperse polystyrenes of molecular weight similar to that of our polybutadienes (see Figure 5).

## Discussion

The kinetics of the polymerization reaction described above are surprisingly simple. The half-order dependence on catalyst concentration suggests that the dimer is inactive and that the first step in the reaction is a dissociative equilibrium where $k_1 \ll k_{-1}$. Such a dissociative equilibrium was originally proposed by Vasil'eva[19] to explain the half-order catalyst dependence and first-order monomer dependence in polymerization of butadiene by $\pi$-allylnickel halides. A dissociative reaction such as eq 1 is unlikely to be spontaneous and it most probably involves monomer. A mechanism giving the experimentally observed kinetics would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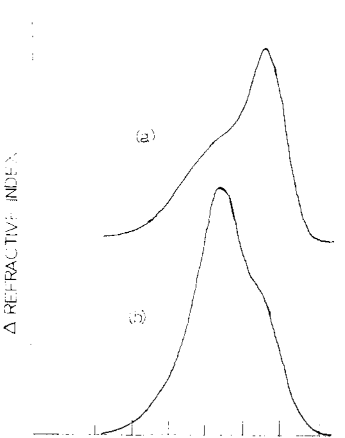

Figure 5. Gel permeation chromatograms of (a) mixed polystyrenes of $\overline{M}_n$ = 4600 and 9700, (b) typical polymer produced by $\pi$-crotylnickel iodide catalysis.

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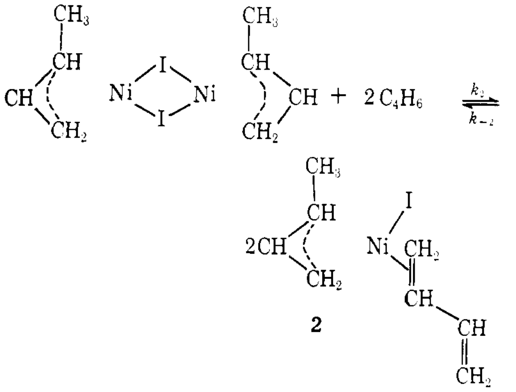
(19) A. M. Lazutkin, V. A. Vashkevich, S. S. Medvedev, and V. N. Vasil'eva, *Dokl. Akad. Nauk SSSR*, **175** (4), 859 (1967).

(20) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 145.

(21) Waters Associates Instruction Manual on GPC No. 2-2064, Framingham, Mass.

involve a rapid dissociative equilibrium (eq 2), with propagation occurring *via* a slow insertion of coordinated butadiene into the π-crotyl–metal bond (eq 3).



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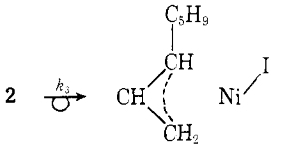


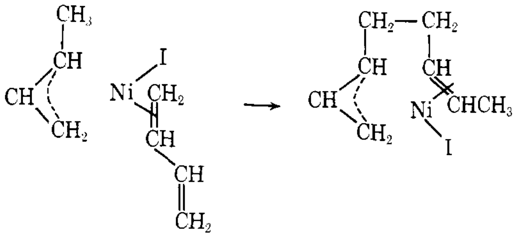
(3)

3

If **3** undergoes dimerization, or reacts with monomer to give an analog of **2**, at a rate much greater than $k_3$, the following rate law applies.

$$-\frac{d[C_4H_6]}{dt} = k_3\left(\frac{k_2}{k_{-2}}\right)^{1/2}[(C_4H_7NiI)_2]^{1/2}[C_4H_6] \qquad (4)$$

It is unlikely that the insertion step (eq 3) occurs spontaneously to give a species as coordinately unsaturated as **3**. It is quite conceivable that a double bond displaced from the Ni in eq 3 actually fulfills a coordinating role, thus



(5)

The observed very narrow molecular weight distribution in the early stages of growth under steady-state conditions indicates that initiation is rapid compared to propagation. In fact, the short induction period generally observed probably corresponds to the initial insertion step, the crotyl species being somewhat less reactive than the $C_8H_{13}$ species. The scheme also requires an inactive dimer–active monomer equilibrium analogous to eq 2 even after the allylic ligand has begun to propagate.

In the early stages of growth, the reaction has the characteristics of a rapidly initiated "living polymerization" (*i.e.*, very narrow molecular weight distribution and roughly one polymer molecule per catalyst unit). At later stages, a clear deviation from this behavior (*i.e.*, broadening distribution and increase in the number of polymer molecules per catalyst unit) is apparent, suggesting the existence of a transfer process with a significant rate compared to the rate of propagation. Although we have no direct evidence to support it, a hydride transfer to butadiene such as that which occurs in the Co(I)-catalyzed dimerization of butadiene to methylheptatriene seems the most probable transfer mechanism.[22-24]

Hydride transfer to butadiene within a complex structurally analogous to **2** would yield a transfer rate with a rate law of the same form as the propagation rate law (eq 4). Assuming that this is the only process by which polymer chains are terminated then the number average degree of polymerization ($\overline{\mathrm{D.P.}}$) is given by eq 6, where $k_{tr}$ is the true transfer rate constant

$$\frac{1}{\overline{\mathrm{D.P.}}} = \frac{2[(C_4H_7NiI)_2]^{1/2}}{k_3(k_2/k_{-2})^{1/2}[C_4H_6]t} + \frac{k_{tr}}{k_3} \qquad (6)$$

and $t$ is the time for which the reaction has proceeded. The occurrence of the factor $t$ in the denominator of eq 6 explains the very narrow molecular weight distribution obtained during the initial stages of the polymerization.

According to eq 6, a plot of $1/\overline{\mathrm{D.P.}}$ *vs.* $1/[C_4H_6]$ at constant catalyst concentration and constant conversion should yield a straight line with zero slope (since the constant conversion criterion makes $[C_4H_6]t$ a constant) and an intercept of $k_{tr}/k_3$. Such a plot is shown in Figure 3. The intercept value corresponds to $k_3/k_{tr} \simeq 50$. The slight positive slope to the best-fit line shown in Figure 3, within the limits of experimental error, is not significantly different from zero.

These results indicate that propagation occurs as a slow step-growth addition process accompanied by a transfer step which is slow compared to the time scale of the experiment, but fast enough relative to the propagation rate to act as a molecular weight limiting process. Under these conditions the molecular weight only asymptotically approaches a constant value. We are in fact observing, on a very much expanded time scale, the same kind of nonsteady molecular weight condition as exists in the first milliseconds of a free radical initiated vinyl polymerization.

We have as yet arrived at no satisfactory explanation for the double distribution in the molecular weight of the polymers obtained in this work. The only reasonable inference is that there are two distinct catalytic species present in the system with slightly different values for $k_3$. In order to obtain two separate distributions these species should not interconvert within the lifetime of a propagating polymer chain. Since the over-all rate law is invariant over a fairly wide range of experimental conditions it must be concluded that the rate laws for the two catalytic species are the same. One possible explanation could be the existence of two isomeric forms of the catalyst, *e.g.*, the growing chain may be *cis* or *trans* to the halide ion, or the chain may adopt a *syn* or *anti* configuration with respect to the allyl group. Although one would intuitively expect a rather rapid interconversion between such isomers, we are presently seeking experimental evidence in support of such a hypothesis.

**Acknowledgment.** The authors would like to acknowledge financial support for this work under a grant from the National Research Council of Canada.

(22) G. Allegra, F. Lo Guidice, G. Natta, U. Giannini, G. Fagherazzi, and P. Pino, *Chem. Commun.*, 1263 (1967).

(23) G. Natta, U. Giannini, P. Pino, and A. Cassata, *Chem. Ind.* (Milan), **47**, 524 (1965).

(24) T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifuji, and S. Ikeda, *J. Organometal. Chem.*, **6**, 572 (1966).