Babitskii, and V. I. Klepikova, *Dokl. Akad. Nauk SSSR*, **196**, 114 (1971).
(16) V. A. Vasiliev, V. I. Klepikova, G. P. Kondratenkov, V. A. Kormer, and M. I. Lobach, *Dokl. Akad. SSSR*, **206**, 347 (1972).
(17) 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).
(18) V. I. Klepikova, V. A. Vasiliev, G. P. Kondratenkov, M. I. Lobach, and V. A. Kormer, *Dokl. Akad. Nauk SSSR*, **211**, 1111 (1973).
(19) V. I. Klepikova, M. I. Lobach, and V. A. Kormer, *Dokl. Akad. Nauk SSSR*, **217**, 352 (1974).
(20) V. A. Kormer, M. I. Lobach, V. I. Kelpikova, and B. D. Babitskii, *J. Polym. Sci., Polym. Lett. Ed.*, **14**, 317 (1976).
(21) V. A. Vasiliev, N. A. Kalinicheva, V. A. Kormer, M. I. Lobach, and V. I. Klepikova, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 2489 (1973).
(22) P. Bourdauducq and F. Dawans, *J. Polym. Sci., Part A-1*, **10**, 2527 (1972).
(23) R. Warin, Ph. Teyssie, P. Bourdauducq, and F. Dawans, *J. Polym. Sci., Polym. Lett. Ed.*, **11**, 177 (1973).
(24) J. M. Thomassin, E. Walckiers, R. Warin, and Ph. Teyssie, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 1147 (1975).
(25) D. Craig and R. B. Fowler, *J. Org. Chem.*, **26**, 713 (1961).
(26) A. C. Cope, G. A. Berchtold, and D. L. Ross, *J. Am. Chem. Soc.*, **83**, 3859 (1961).
(27) E. O. Fisher and G. Bürger, *Z. Naturforsch., B*, **16**, 77 (1961).
(28) V. I. Klepikova, G. B. Erusalimskii, M. I. Lobach, L. A. Churlyaeva, and V. A. Kormer, *Macromolecules*, **9**, 217 (1976).
(29) L. A. Churlyaeva, V. I. Valuev, T. S. Dmitrieva, M. I. Lobach, V. N. Sokolov, R. A. Shlyachter, and V. A. Kormer, *Macromolecules*, **9**, 214 (1976).
(30) J. W. Faller, M. E. Tully, and K. J. Laffey, *J. Organomet. Chem.*, **37**, 193 (1972).
(31) J. W. Faller, M. E. Thomsen, and M. J. Mattina, *J. Am. Chem. Soc.*, **93**, 2642 (1971).
(32) J. W. Faller and K. J. Laffey, *Organomet. Chem. Synth.*, **1**, 471 (1972).
(33) L. A. Churlyaeva, M. I. Lobach, G. P. Kondratenkov, and V. A. Kormer, *J. Organomet. Chem.*, **39**, C23 (1972).

Polymerization of Butadiene by η^3-Crotylbis(triethylphosphite)nickel(II) Hexafluorophosphite

John F. Harrod* and Alexandre Navarre

Department of Chemistry, McGill University, Montreal, Canada, H3C 3G1.
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ABSTRACT: By a combination of kinetic and molecular weight studies the title reaction was shown to be complicated by decomposition of the initially active catalyst, **1**, into more active transient species, **2**, and finally into a stable species, **3**, with an activity comparable to that of **1**. Molecular weight distributions, measured by gel permeation chromatography, showed that **1** and **3** and part of **2** produce low molecular weight *trans*-1,4-polybutadiene ($\overline{M}_n \sim 5000$) similar to that produced by allylnickel iodides. Part of the more reactive transient species, **4**, produces a polymer fraction of much higher molecular weight ($\overline{M}_n \sim 100\,000$). Such high molecular weight fractions were absent from polymer produced by catalyst solutions that had been preheated to 90 °C for several hours. The heating of **1** in the absence of butadiene appears to convert it to **3**. At 90 °C the complex **1** reacts with added triethylphosphite to produce diethyl ether. The transitory nature of the inhibiting effect of added triethylphosphite on the polymerization rate is attributed to the removal of the phosphite by the latter reaction.

The stereospecific polymerization of 1,3-dienes by transition organometallic catalysts has been the subject of intensive investigation for over 20 years, and at the synthetic level this work has been very fruitful. In fact almost any desired stereo or positional microstructure for simple 1,3-dienes can be achieved by choice of the appropriate catalyst.[1,2] The evolution of understanding, at a detailed mechanistic level, of the processes governing stereoselectivity and degree of polymerization has been much slower.

One of the major barriers to success in this problem is the difficulty in finding systems which are valid models for active polymerization catalysts yet have the necessary chemical and physical properties to allow direct observation of the insertion process. This difficulty is exemplified by the fact that insertion reactions of allylpalladium complexes can be investigated in great mechanistic detail[3] but they are relatively poor models for polymerization catalysts since they show neither great versatility, nor activity for diene polymerization. On the other hand, allylnickel complexes show considerable versatility and activity in polymerization, but their greater reactivity and lower stability make application of the methodology used in allylpalladium chemistry to probe the details of the insertion mechanism difficult or impossible to apply.

The allylnickel halide system held early promise that the riddle of stereoselectivity would be easily solved.[4–6] The allylnickel halides are relatively stable and polymerize butadiene by a fairly uncomplicated mechanism. Most striking however is the great effect the minor structural change of replacing chloride with iodide has on the stereoselectivity.[5] The early promise of this model has not been realized, in spite of some ingenious experimentation,[7,8] mainly because it is impossible to observe the primary insertion product of the reaction. The active species in these systems are monometallic but the bulk of the nickel sites are in the form of resting dimer and it is these species which are observed by physical methods such as NMR.[7,8] Similar hopes and problems were characteristic of studies on the allylnickel acetate and haloacetate catalysts.[9]

In the present paper we present results of a study of the polymerization of butadiene by η^3-crotylbis(triethylphosphite)nickel(II) hexafluorophosphate, **1**. This compound has been extensively studied as a catalyst for the codimerization of ethylene/butadiene.[10] In a footnote it was reported that this catalyst produced a white waxy solid, presumed to be polybutadiene, when heated with butadiene.[10] This observation was confirmed in our laboratory and the product was shown to be *trans*-1,4-polybutadiene (>95%). The complex, **1**, seemed very attractive as a possible model for studying the stereochemistry of diene insertion under polymerization conditions. It is monomeric, easy to synthesize and purify, and gives the appearance of being quite stable in the absence of oxygen.

Results

Selection of Solvent. The choice of a solvent for the polymerization of butadiene by **1** was restricted by three factors.

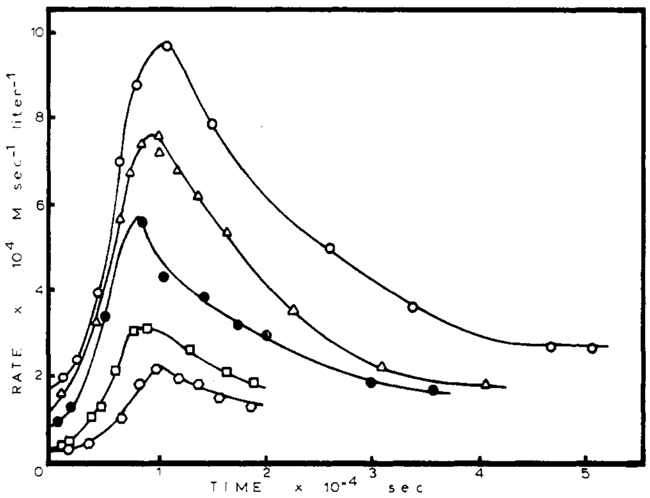


Figure 1. Influence of catalyst concentration on the rate of polymerization in anisole. P_{total} = 800 Torr; T = 90 °C; catalyst concentration is: 50 mM (○); 30 mM (△); 20 mM (●); 7.5 mM (□); 5 mM (○).

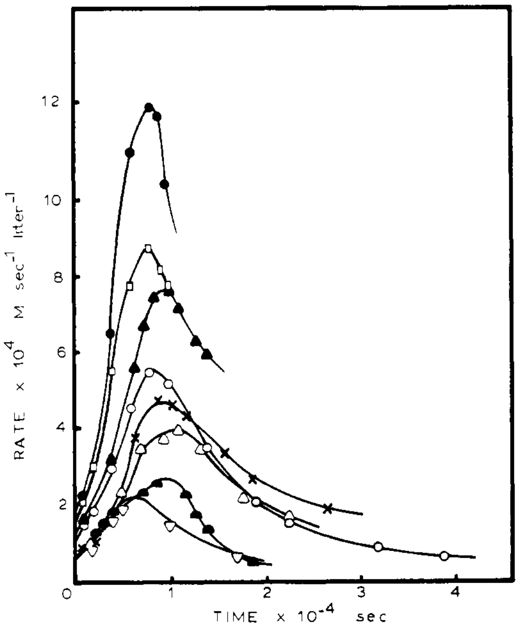


Figure 2. Influence of monomer concentration on the rate of polymerization in anisole. T = 90 °C; catalyst concentration = 30 mM; monomer concentration is 0.29 M (▽); 0.37 M (◓); 0.45 M (△); 0.49 M (×); 0.53 M (○); 0.57 M (▲); 0.73 M (□); 0.89 M (●).

The first was the need for a solvent which was simultaneously good for the ionic catalyst and for the relatively nonpolar polymer. The second was the requirement of a high boiling point, since preliminary studies revealed that useful polymerization rates were only realized at temperatures above 80 °C. The third was the need for chemical inertness toward the highly reactive catalyst.

A number of solvents were investigated. Several high boiling alcohols, including benzyl alcohol and 2-ethoxyethanol, were rejected because they were shown to undergo transesterification with the phosphite ligands. Alkyl benzenes, such as toluene and xylene, were rejected because of low catalyst solubility and a tendency of the catalyst to slowly decompose. Several high boiling aliphatic ethers such as bis(2-methoxyethyl) ether were rejected because of low polymer solubility.

Both anisole and chlorobenzene appeared to fulfill all of the conditions for a suitable solvent outlined above. Anisole was chosen as the preferred solvent since nickel(0) complexes are known to undergo oxidative addition with aryl halides.[13] Although the solvents described in the preceding paragraph were not suitable for a detailed study, the polymerization rate profile in each was qualitatively the same as that observed in anisole and described in detail below.

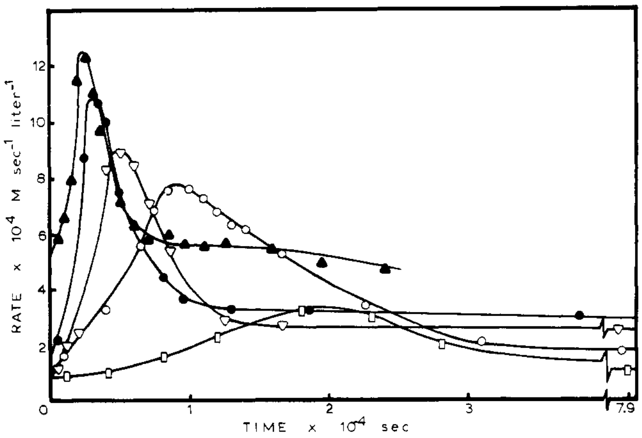


Figure 3. Influence of temperature on polymerization rate in anisole. Catalyst concentration = 30 mM; P_{total} = 800 Torr; T °C is: 120 (▲); 110 (●); 100 (▽); 90 (○); 80 (□).

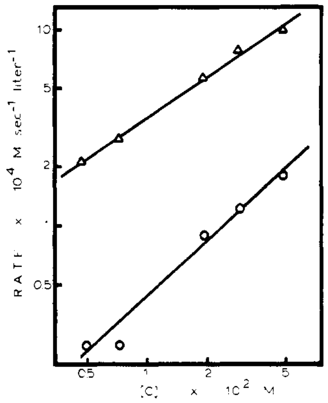


Figure 4. Plots of initial (○) and maximum rates vs. catalyst concentration (data from Figure 2).

Effect of Experimental Parameters on Reaction Rate. The behavior of reaction rate with time was quite complicated, but showed the same pattern over a very wide range of reaction conditions. The rate profiles shown in Figures 1, 2, and 3 were typical. The rate profile for the reaction is characterized by the following features: (a) a finite initial rate, (b) an acceleration to a maximum rate, consistently at ca. 10 000 s at 90 °C, (c) a deceleration from the maximum and an assymptotic approach to a constant rate slightly higher than the initial rate.

The effects of varying catalyst concentration ([C]), monomer concentration ([M]), and temperature are shown in Figures 1, 2, and 3, respectively. In the series of experiments at different temperatures and constant [C] it was not possible to hold [M] constant, since the apparatus was not usable at pressures significantly greater than 800 Torr.

A log–log plot of rate vs. [C], for both the initial and maximum rates, is shown in Figure 4. Best fit straight lines through the data points have slopes of 0.9 ± 0.1 and 0.7 ± 0.1 for the initial and maximum rate data, respectively. Similar plots of rate vs. [M] are shown in Figure 5. The initial rate data are very scattered, especially at low monomer concentration; al-

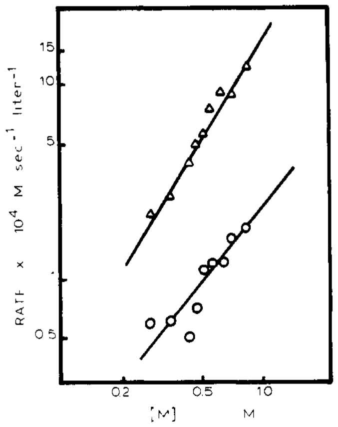


Figure 5. Plots of initial (○) and maximum rates vs. monomer concentration (data from Figure 3).

though the best fit line has a slope of roughly unity, the deviation is very large. At the maximum rate the data are more consistent and give a best slope of 1.7 ± 0.2.

The effect of temperature is illustrated in Figure 3. The effect of decreasing [M] with increasing temperature is overridden by the intrinsic rise in activity throughout the rate profile. The most significant feature of the curves in Figure 3 is the progressive shift of the rate maximum to shorter times with increasing temperature.

No attempt was made to explore the effects of experimental parameters on the rate in the plateau region since very long times and high conversions were required to reach a constant rate. It was very difficult to control adventitious factors such as thermal decomposition of the catalyst, contamination by leakage of air or trace impurities in the monomer, and effects due to the large amount of polymer present in the solution in the plateau region.

Effect of Preheating the Catalyst. In the course of the above experiments it became obvious that the results were to some degree dependent on the history of the catalyst. In particular it was found that preheating the catalyst solution in the absence of monomer had a profound effect on the rate profile, as illustrated in Figure 6. The main effects of preheating were an increase in the initial rate and a diminution of the maximum rate. At extremely long times of preheating the rate profile seems to approach a condition of constant rate at a value characteristic of the plateau region.

Effect of Adding Free Triethylphosphite. A common feature of coordination catalysis is inhibition by the addition of strongly binding ligands. For example, the polymerization of butadiene by bis(η^3-allyl-μ-halonickel(II)) is strongly inhibited by addition of triphenylphosphine beyond a 1:1 molar ratio of P:Ni. Addition of excess triethylphosphite to the present catalyst system exhibited the expected inhibition, particularly if addition was in excess of a 1:1 molar ratio. Rather surprisingly, the system exhibited a capacity to recover from this inhibition and the reaction rate, after being initially suppressed by the added phosphite, returns asymptotically to the value it would have had if the phosphite had not been added.

The Molecular Weights and Microstructures of the Polymers. A study of the evolution of the polymer molecular weights and molecular weight distributions proved very useful in evaluating the mechanism of polymerization in the case of the bis(η^3-crotyl-μ-iodonickel) catalyzed reaction.[11] The great complexity of the present system precludes as detailed an analysis of the molecular weight data as was possible with the iodide catalyst, but nevertheless the molecular weight properties exhibit some interesting features. The evolution of $\overline{M}_n$ and $\overline{M}_w$ for a typical reaction is illustrated in Figure 7. The value of $\overline{M}_n$ increases in the early stages of reaction but reaches a constant value fairly quickly. This behavior parallels that observed using crotylnickel iodide as a catalyst.[11] The arrival at constant $\overline{M}_n$ was much faster in the present case and the lower limiting value of $\overline{M}_n$ indicates a faster transfer rate (k_t) relative to propagation rate (k_p). The polydispersity index ($\overline{M}_w/\overline{M}_n$) continued to rise throughout the reaction due to a continuing increase in $\overline{M}_w$. The evolution of the molecular weight distribution with increasing conversion is illustrated in Figure 8. In the early stages of the reaction the distribution was bimodal and quite narrow. Corresponding to the rise in reaction rate there is a broadening of the distribution, a loss of resolution, and a shift in the center of the distribution to higher molecular weight. At very long reaction times, corresponding to the approach to constant reaction rate, the distributions are very broad and show multimodal structure.

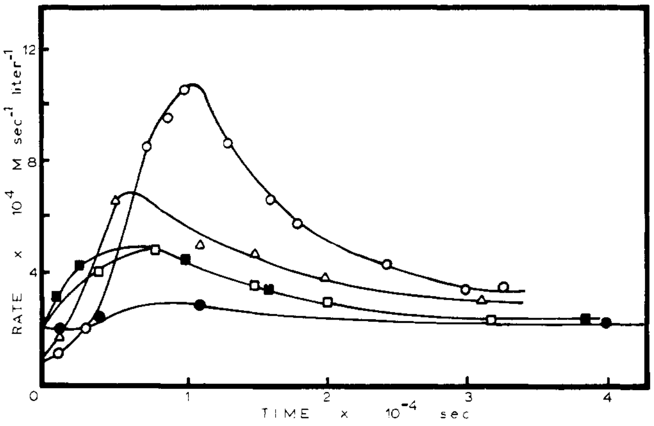


Figure 6. Influence of the time of preheating the catalyst solution on the polymerization rate profile. Catalyst concentration 30 = mM; P_{total} = 800 Torr; T = 90 °C. Preheating time (s): 300 (○); 5000 (△); 10 000 (■, □); 30 000 (●).

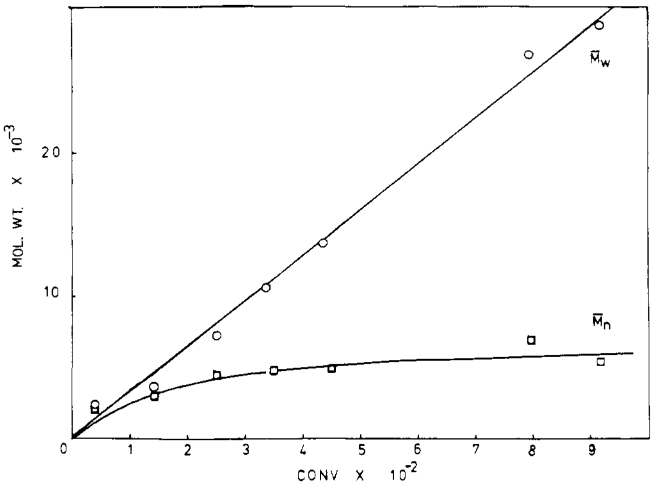


Figure 7. Evolution of $\overline{M}_n$ and $\overline{M}_w$ with conversion, expressed as moles of monomer consumed per mole of catalyst. (Reaction conditions as for Figure 1.)

A set of experiments analogous to those illustrated in Figure 8 was performed using a catalyst solution which had been preheated in the absence of monomer for 50 000 s at 90 °C and the results are shown in Figure 9. Such a catalyst showed almost constant activity, similar to that of the lowest curve of Figure 6. The major difference in the polymer produced by the preheated catalyst was the absence of high molecular weight components (M > 50 000 daltons).

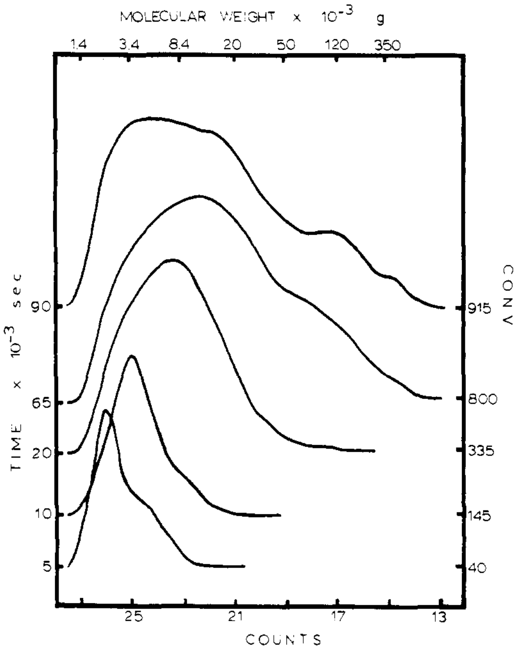


Figure 8. Gel permeation chromatograms illustrating the evolution of molecular weight distribution with conversion. Polymerization conditions as for Figure 1. The figures on the ordinates represent the polymerization time and conversion for each sample.

The microstructures of the polymers produced in the present work were investigated by both IR[14] and ^{13}C NMR methods.[15] The structures were characterized by high trans-1,4 contents (>95%) and were more or less invariant with conversion or temperature in the ranges studied. The ^{13}C NMR spectra showed that the polymers have highly regular structures; any asperities, such as conjugated double bonds or cross-links, if present at all, were at levels of less than 1%.

The Thermal Stability of the Catalyst. The polymerization studies described above clearly indicate that the catalyst undergoes a series of slow chemical transformations in the course of the polymerization reaction. Experiments were performed to investigate thermal reactions of the catalyst on heating in the absence of monomer but otherwise under typical polymerization conditions.

The proton NMR spectra of solutions of the catalyst in anisole and chlorobenzene were normal, showing all of the anticipated resonances for the phosphite and crotyl groups.[10] Heating these solutions for times up to 9 h caused no readily interpretable changes beyond a loss of resolution, a change in peak shape of the $-CH_2-O-$ resonance, and a loss of resolution and intensity of the crotyl resonances. During the heating period the solutions changed from orange-yellow to pale yellow.

An NMR study of the reaction of the catalyst with excess triethylphosphite in anisole and chlorobenzene proved to be more informative. Although the same behavior was observed in both solvents, and results were much clearer in chlorobenzene due to the absence of interfering solvent resonances. The changes in the NMR spectrum of a 1:1 solution of **1** and triethylphosphite in chlorobenzene on heating to 90 °C for various times are illustrated in Figure 10. The initial spectrum corresponds to that of the η^3-crotyltris(triethylphosphite)-nickel(II) cation,[10] characterized by a pseudo-quintet for the $-O-CH_2-$ resonance (τ 6.45) and crotyl group resonances at τ 5.3 (H_a), 7.1 (H_d), and 8.2 (H_c). Heating the solution to 90 °C resulted in a rapid disappearance of the crotyl resonances of the tris(phosphite) complex and the appearance of the crotyl resonances characteristic of the bis(phosphite) complex (τ 5.0 (H_a), 7.6 (H_c), 8.2 (syn-CH_3)). More remarkable was the appearance of a well-resolved quartet at 6.9, clearly the methylene resonance of a new, simple ethoxy compound. Addition of diethyl ether to the reaction mixture resulted in enhancement of the quartet and of three of the peaks in the region of 9.0, leaving little doubt that the reaction product was ether.

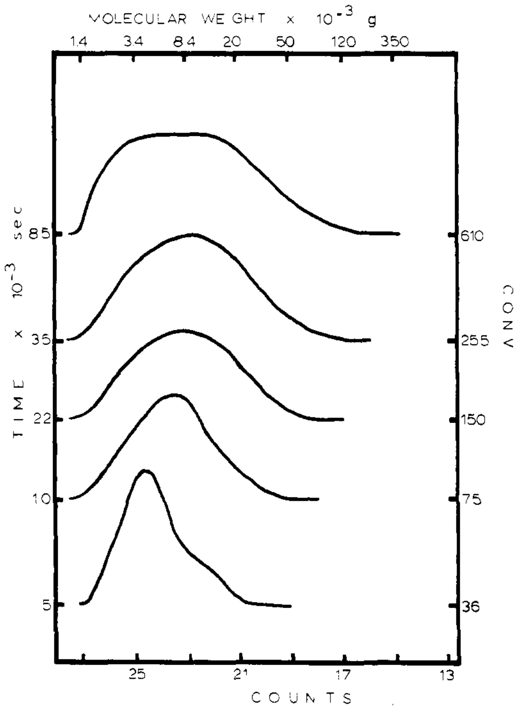


Figure 9. Evolution of molecular weight distribution for a polymer produced with a catalyst preheated for 50 000 s. Polymerization conditions as for Figure 1.

Discussion

The results described above clearly show that the complex **1** is active for the polymerization of butadiene but that it is chemically unstable at temperatures where polymerization proceeds at a reasonable rate. The specific nature of the instability depends on the presence or absence of butadiene or excess phosphite ligand.

In the presence of butadiene **1** is transformed under polymerizing conditions to a species of considerably greater activity than **1** (species **2**); this species is also unstable and is further transformed to one or more species of lower activity. Since no significant change in microstructure of the polymer was detected throughout the course of the reaction it may be concluded that all of the species involved manifest a high selectivity for trans-1,4 enchainment.

The molecular weight distributions shown in Figure 8 have some interesting features. The earliest sample, taken when the system must have contained both the initial and more active species in substantial amounts, has a bimodal distribution. The relative size of the peaks is opposite to that reported for the earliest samples of polymers produced with an allylnickel iodide catalyst.[11] However, both the shape of the distribution and the molecular weight parameters bear a close similarity to those for polymers produced with the latter catalyst at moderate conversions.[11] The fact that the polydispersity of the earliest sample shown in Figure 8 is only 1.2, even though at least two polymerizing species of very different reactivity were present, suggests that the molecular weight properties of the polymers produced are very similar. This in turn points to the probability that the species **2**, in addition

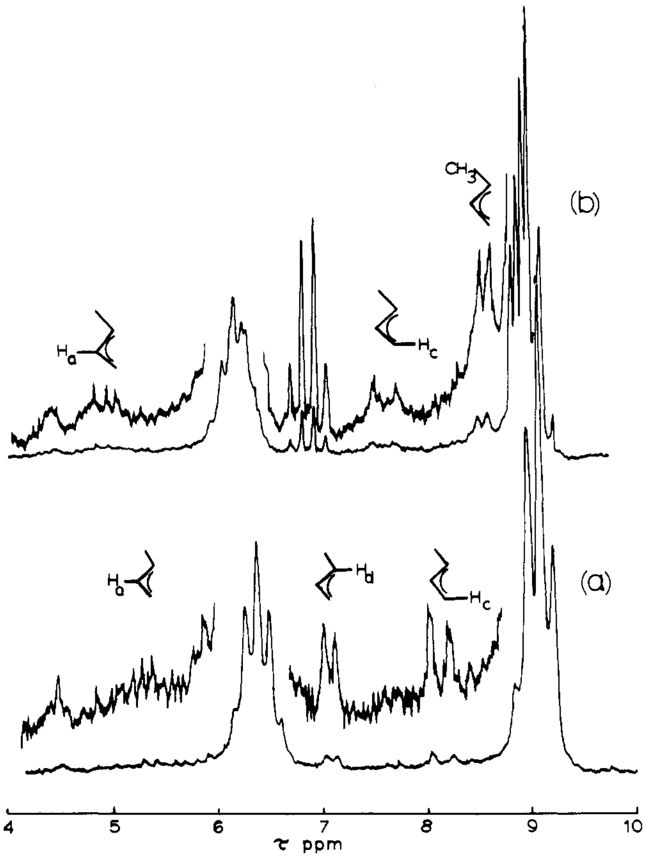


Figure 10. ^{1}H NMR spectra of a mixture of triethylphosphite and η^3-crotylbis(triethylphosphite)nickel(II) hexafluorophosphate (1:1 molar ratio) in chlorobenzene: (a) after mixing at 30 °C; (b) after heating for 1 hr at 90 °C. The high gain scan in (a) shows the crotyl resonances of the trisphosphite complex and that in (b) the crotyl resonances of the bisphosphite complex.

to having a much higher propagation activity than **1**, also has a proportionately higher rate of transfer. The molecular weight distributions in the present case were found to be almost independent of both [C] and [M] at constant conversion, indicating the same rate laws for propagation and termination for each respective catalytic species (DP = k_p/k_t). The same behavior was previously noted for the allylnickel halides.[11]

Beyond the rate maximum and at high conversions the present system produces a polymer fraction of unusually high molecular weight. This observation is of particular interest since nickel-based catalysts in general do not produce *trans*-1,4-polybutadienes of sufficiently high molecular weight to be of commercial interest. This problem is compounded by a complete ignorance of the factors which influence propagation relative to transfer in this type of system. The present data suggest that there is a species present which has a much higher k_p/k_t than is typical for simple organonickel catalysts. This species is not likely to be simply a decay product of **2** (species **3**), since the higher molecular weight fractions ($M \approx 10^5$) could not be produced by a stepwise polymerization at the polymerization rate characteristic of the constant rate region ($\sim 2 \times 10^{-4}$ M s^{-1}) and in the maximum reaction time ($\sim 10^5$ s) if all the nickel is still active. Such a molecular weight could be realized by a species with a propagation rate as large as that of **2**. The molecular weight data may be explained in terms of four catalytic species. **1** and **2** are responsible for production of the large low molecular weight component and have k_p and k_t which both differ by about an order of magnitude; **3** has a propagation rate roughly the same as **1** and an unknown contribution to the molecular weight distribution and **4** has a propagation rate considerably greater than **1** or **3** and a much larger k_p/k_t.

The results with a preheated catalyst are most simply interpreted by assuming that heating the catalyst in the absence of butadiene converts **1** to **3** and that **1** and **3** have very similar properties. This leads to the conclusion that **2** and **4** depend on reaction with butadiene for their formation and accounts for the absence of the high molecular weight fractions in polymer produced with extensively preheated catalyst.

Interpretation of Rate Behavior. To a first approximation we may model the present system upon the consecutive conversion of **1** into **2** and **2** into **3**, with each species being active toward butadiene polymerization. Although **1** can also convert directly to **3**, in the presence of butadiene we shall assume the direct path to be slower than the consecutive route via **2**. The model is illustrated in Scheme I.

Scheme I

$$1 + C_4C_6 \xrightarrow{k_1} 2 \xrightarrow{k_2} 3$$

Assuming that the steps are all first order, or pseudo-first order, in nickel species and are of the same order in other reactants, the standard consecutive first-order reaction treatment may be applied[12] and we obtain:

$$[1]_t = [1]_0 e^{-k_1 t} \tag{1}$$

and

$$[2]_t = \frac{[1]_0 k_1}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t}) \tag{2}$$

therefore

$$\left[\frac{[1]}{[2]}\right]_t = \frac{k_2 - k_1}{k_1}\left[\frac{e^{-k_1 t}}{e^{-k_1 t} - e^{-k_2 t}}\right]. \tag{3}$$

Equation 3 shows that the ratio of **1**:**2** at any time is independent of the initial concentration of **1**. Furthermore, at the time of maximum polymerization rate, t_M, the value of [**2**] reaches a maximum and d[**2**]/dt = 0. This turning point yields the relationship:

$$[[1]/[2]]_{t_M} = k_2/k_1 \tag{4}$$

Combining (3) and (4) yields:

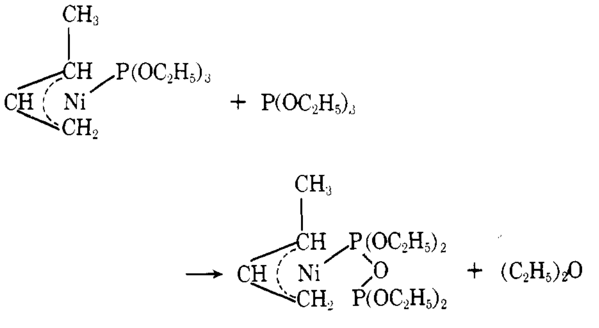
$$t_M = \frac{\ln k_1 - \ln k_2}{k_1 - k_2} \tag{5}$$

Equation 5 predicts the following: (a) the value of t_M is independent of $[1]_0$ and $[C_4H_6]_0$; (b) if k_1 and k_2 have different energies of activation t_M will vary with temperature. If k_1 increases relative to k_2 with increasing temperature, an increase in temperature will reduce t_M. Although it is obviously crude the above model agrees well with the general features of the rate profiles shown in Figures 1, 2, and 3 except that it fails to account for the clearly autocatalytic feature for the transformation of **1** into **2**. Attempts to introduce an autocatalytic component into the first step lead to mathematical intractibility in the kinetic analysis.

There is an indication that the overall orders in catalyst and monomer are different at $t = 0$ and $t = t_M$. Although the data are badly scattered at $t = 0$, there is no indication that the orders in monomer and catalyst concentrations are significantly different from unity. At t_M the order in monomer appears to be significantly greater, and the order in catalyst significantly less, than unity. The higher apparent order in monomer may reflect a contribution from the involvement of monomer in the conversion of **1** to **2**, as well as in the propagation step of the polymerization reaction. The lower order in catalyst suggests that the species **2** may be a polymerization inactive dimer in equilibrium with an active monomeric complex, a situation similar to that found with the allylnickel halides.

Chemical identities of **2** and **3** or **4** have not thus far been determined. The poor quality ^1H NMR spectra obtained from heated samples of **1** did not allow any kind of assignment of product spectra. However, the spectra in the ethyl regions were good enough to exclude catalyzed Arbusov rearrangement of the phosphite ligands as a mode of reaction.

The formation of ether by reaction of **1** with excess phosphite does not seem to play an important part in the decomposition of **1** in the absence of butadiene but does result in the conversion of the tris(phosphite) complex into the bis(phosphite) complex. In the presence of butadiene the ether forming reaction may occur even with the bis(phosphite) complex but attempts to study that reaction have so far been unsuccessful. Since the ether most probably results from an unusual metal induced elimination to produce a pyrophosphite, according to (6) this reaction is under further investigation, as are the other decomposition reactions of **1** described in this work.



(6)

(nonreacting ligands omitted)

Experimental Section

All solvents used in this work were obtained by refluxing reagent grade materials with calcium hydride for 24 h, distilling, and using only the middle half. Research grade butadiene (99.8% minimum purity) was obtained from Matheson Canada Ltd.

The general procedures for polymerization, recovery of polymer, and measurement of molecular weight properties were the same as those previously described for allylnickel halide catalysts.[11]

η^3-Crotylbis(triethylphosphite)nickel(II) hexafluorophosphate was prepared according to the method of Tolman.[10] The product was purified by several recrystallizations from cold oxygen-free methanol. For a series of polymerization reactions a concentrated stock solution of the catalyst was prepared and stored under vacuum at −20 °C. Samples were taken by warming the stock solution to room temperature under nitrogen and transferring aliquots by gas-tight hypodermic syringe to the reaction vessel. Except for the experiments where the catalyst was deliberately preheated in the absence of monomer, the reactions were all performed by addition of catalyst aliquots to a pre-equilibrated solution of butadiene at the reaction temperature. This procedure gave results that were consistently reproducible to within ±5% in reaction rate. Alternative procedures, such as admission of monomer to a thermally equilibrated solution of catalyst, or mixing monomer and catalyst at room temperature and then heating to reaction temperature, gave more scattered results due to poorer control over the two modes of catalyst decomposition.

Polymerization rates were measured continuously by butadiene uptake measurements at constant pressure. Initial rates were determined by back extrapolation of the uptake curve to zero time; all other rates were determined by taking tangents to the uptake curve.

The decomposition of the catalyst in the presence and absence of added triethylphosphite was followed using a Varian T60 NMR spectrometer. Saturated solutions of the complex were sealed in NMR tubes under argon and heated to the required temperature. Periodically the samples were cooled rapidly to room temperature and their spectra were recorded.

Microstructures of polymers were determined by the infrared method of Hampton[14] and by the ^{13}C NMR technique reported by Clague et al.[15]

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References and Notes

(1) L. Reich and A. Schindler, "Polymerization by Organometallic Compounds", Interscience, New York, N.Y., 1966, p 166.
(2) G. J. van Amerongen, *Adv. Chem. Ser., No.* **52,** 136 (1966).
(3) R. P. Hughes and J. Powell, *J. Am. Chem. Soc.,* **94,** 7723 (1972).
(4) B. D. Babitskii, B. A. Dolgoplosk, V. A. Kormer, M. I. Lobach, E. I. Tinyakova, and V. A. Yakolev, *Dokl. Akad. Nauk SSSR,* **166,** 583 (1965).
(5) L. Porri, M. C. Gallazzi, and J. Vitalli, *J. Polym. Sci., Part B,* **5,** 629 (1967).
(6) L. Porri, G. Natta, and M. C. Gallazzi, *J. Polym. Sci., Part C,* **16,** 2525 (1967).
(7) M. I. Lobach, V. A. Kormer, I. Y. Tsereteli, G. P. Kondratenkov, B. D. Babitskii, and V. I. Klepikova, J. Polym. Sci., *Part B,* **9,** 71 (1971).
(8) T. Matsumoto and J. Furukawa, *J. Polym. Sci., Part B,* **5,** 935 (1967).
(9) P. Bourdauducq and F. Dawans, *J. Polym. Sci., Part A,* **10,** 2527 (1972); R. Warin, Ph. Teyssié, P. Bourdauducq, and F. Dawans, *J. Polym. Sci., Part B,* **11,** 177 (1973); J. M. Thomassin, E. Walkiers, R. Warin, and Ph. Teyssié, *ibid.,* **13,** 1147 (1975).
(10) C. A. Tolman, *J. Am. Chem. Soc.,* **92,** 6777 (1970).
(11) J. F. Harrod and L. R. Wallace, *Macromolecules,* **5,** 685 (1972).
(12) K. Laidler, "Chemical Kinetics", McGraw-Hill, New York, N.Y., 1965, p 89.
(13) P. W. Jolly and G. Wilke, "The Organic Chemistry of Nickel", Vol. 1, Academic Press, New York, N.Y., 1974, p 169.
(14) R. R. Hampton, *Anal. Chem.,* **21,** 923 (1969).
(15) A. D. Clague, J. A. M. van Broekhouen, and L. P. Blaaw, *Macromolecules,* **7,** 348 (1974).