Origin of Binodal Molecular Weight Distributions in the π-Crotylnickel Iodide Catalyzed Polymerization of Butadiene

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ABSTRACT: The effects of conversion, catalyst concentration, and temperature on the molecular weights and molecular weight distributions of poly(butadienes) produced by π-crotylnickel iodide catalysts have been investigated. The variation of $\bar{M}_n$ and molecular weight distributions with the reaction variables is attributed to a slow stepwise propagation by butadiene insertion into a terminal π-crotyl ligand and termination of chain growth by a slow intramolecular hydride transfer. The observed binodal molecular weight distributions are attributed to the presence of "living" polymer chains that have never undergone transfer and polymer chains that have terminated by transfer. A discrepancy between theoretical and empirical relationships for degree of polymerization as a function of conversion and of catalyst concentration is attributed to coupling of radicals generated by oxidative destruction of actively growing polymer chains.

In a previous report we described the results of a kinetic study of the polymerization of butadiene by π-crotylnickel iodide.[1] Molecular weight determinations, using vapor pressure osmometry (VPO) and gel permeation chromatography (GPC), revealed that the polymerization proceeds by a stepwise process with a slow transfer to catalyst, limiting the ultimately achievable molecular weight. In the course of this earlier study the existence of binodal molecular weight distributions in the product poly(butadienes) was recognized using GPC, but no convincing explanation of this feature was presented. It was subsequently brought to our attention that this type of molecular weight distribution is expected for, and in fact provides additional confirmation of, the kind of transfer mechanism originally proposed.[2,3] In view of the foregoing, we have made further investigations of the molecular weight properties of the poly(butadienes) produced by π-crotylnickel iodide. The results confirm Gatske's suggestion and raise some interesting questions about the nature of the termination process in this polymerization system.

Experimental Section

Synthesis of Catalyst and Polymer. All of the polymers used in this work were prepared in the same gas buret system previously described.[2] This system allowed preparation of polymers under conditions of constant monomer and catalyst concentrations and at constant temperature. The rate of polymerization and the conversion were also accurately determined for each polymer sample produced.

The catalyst was prepared according to the synthesis described by Wilke.[4] The yields of both bis(cyclooctadiene)nickel(0)[5] and bis(crotyl)-μ-diiodo-dinickel(II) are greatly enhanced by the presence of a small amount of butadiene during the synthesis.[6] Provided all reagents used in the synthesis are freshly prepared and purified, we have found this method to give a product which behaves very reproducibly in mechanistic work. Stock solutions of catalyst in benzene could be stored under nitrogen at 0° for several weeks without detectable change in catalytic activity.

After completion of polymerization, polymer samples were recovered by pouring the reaction mixture into acidified methanol in air. The polymer was filtered, washed several times with methanol, and reprecipitated at least three times before drying at room temperature. All polymer samples were stored under vacuum in the absence of light. Polymer yields always agreed with butadiene conversion within $\pm 2\%$.

Determination of Molecular Weight. Number-average molecular weights were determined in benzene using a Hewlett Packard Model 301A vapor pressure osmometer. The instrument was calibrated with narrow-distribution polystyrene samples supplied by Pressure Chemical Co. Several calibrations were performed over the entire range of experimental molecular weights (2,000–15,000).

Gel permeation chromatograms were run on a Waters Model 200 GPC operated at 30° and a flow rate of 1 ml/min of tetrahydrofuran. Optimum resolution and minimum skewing of distributions were achieved with a set of four columns of 100-, 400-, 1000-, and 10,000-Å porosity (cross-linked poly(styrene)).

Results

Stability of Catalyst. Although under most circumstances there was no detectable change in rate during reactions, significant decomposition of catalyst did become a problem in some runs carried out to exceptionally high conversion. The effect of catalyst decomposition on rate for two separate runs is shown in Figure 1. The consequences of this decomposition for interpretation of molecular weight data are discussed further below.

Calibration of the GPC. Because of the unavailability of monodisperse standards of *trans*-1,4-poly(butadiene), an exact primary calibration of the GPC is not possible. The calibration procedure used in the present work involved the following steps. (i) The column set was calibrated using primary standards of poly(styrene) and poly(propylene glycol) (Waters Associates) under conditions identical with those to be used for poly(butadiene) analysis. (ii) The number-average molecular weights of five poly(butadiene) samples were determined using VPO. (iii) The chromatograms of the latter samples were obtained from GPC and number-average molecular weights calculated using a theoretical value of molecular weight per unit equivalent extended chain length (Q) of 12.4 [calculated from known bond angles and bond lengths in poly(butadiene)]. From these data a corrected value of Q was obtained from the relationship

$$Q_{\text{cor}} = Q_{\text{theory}} \frac{\bar{M}_n(\text{VPO})}{\bar{M}_n(\text{GPC})} \qquad (1)$$

The results of this exercise are summarized in Table I.

The average value of Q_{cor} was 20.0 ± 2.3 at the 95% con-

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(1) J. F. Harrod and L. R. Wallace, *Macromolecules*, 2, 449 (1969).

(2) A. L. Gatske, private communication.

(3) See also: A. L. Gatske and E. Vanzo, *Chem. Commun.*, 1180 (1967); A. L. Gatske, *J. Polym. Sci., Part A-1*, 7, 2281 (1969).

(4) 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., Int. Ed. Engl.*, 5, 151 (1966).

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

(6) Although this fact is well known in Wilke's laboratory (D. Walter, private communication), it does not seem to have been recorded in the literature.

TABLE I
CALIBRATION DATA FOR GPC OF POLY(BUTADIENE)

Sample no.	$\bar{M}_n$(VPO)	$\bar{M}_n$(GPC)^a	$\bar{M}_n$(GPC)^b	Q_{cor}
54	3703	2148	3464	21.4
55	2809	1846	2977	18.9
56	2547	1504	2426	21.0
57	2066	1345	2169	19.0
58	1858	1164	1877	19.8

[a] Calculated for $Q = 12.4$. [b] Calculated for $Q = 20$.

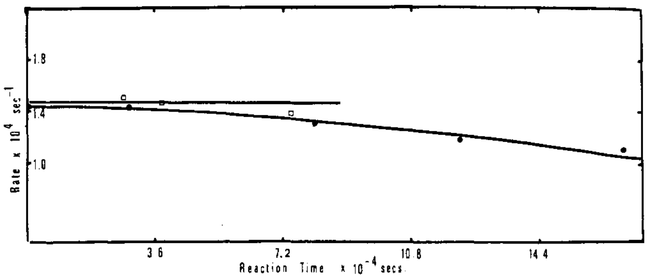

Figure 1. Variation of polymerization with time. [C_4H_6] = 1.5 *M*, [catalyst] = 0.0051 *M*, *T* = 50°. □, ●: duplicate experiments.

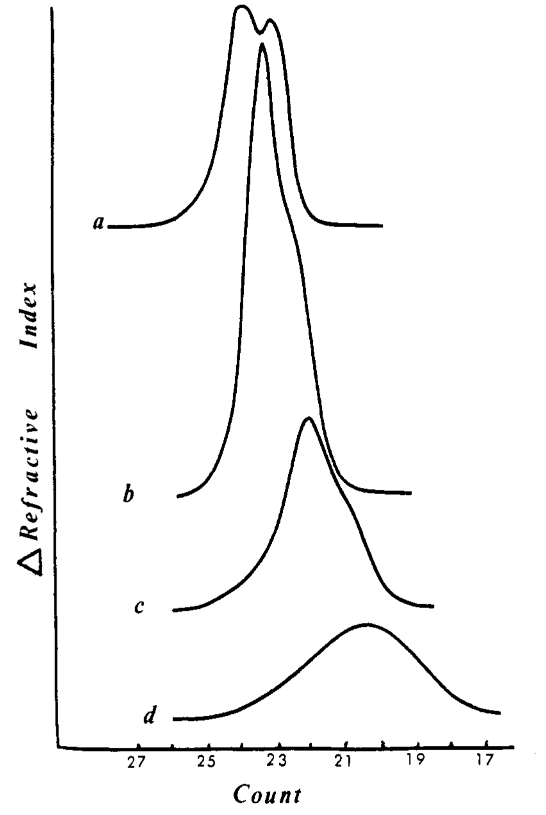

Figure 2. Gel permeation chromatograms for polymers produced at different conversions. [C_4H_6] = 1.5 *M*, [catalyst] = 0.004 *M*, *T* = 50°. Conversions: (a) 0.25 *M*; (b) 0.30 *M*; (c) 0.75 *M*; (d) 1.92 *M*.

fidence level. The small standard deviation of Q_{cor} confirms that the calibration curve for poly(styrene) parallels that for poly(butadiene) over the narrow range of molecular weight studied. That this is also true for higher molecular weight is suggested by the results of Runyon, *et al.*,[7] who concluded that not only are the calibration curves for poly(styrene) and poly(butadiene) parallel but, for polymer fractions eluting at the same volume, the molecular weight of poly(butadiene) is almost exactly one-half that of poly(styrene) [*i.e.*, the *Q* value for poly(styrene) is twice that of poly(butadiene)]. Alliet and Pacco[8] have experimentally determined the *Q* value for poly(styrene) in tetrahydrofuran to be 41.0 which, when combined with the aforementioned conclusion of Runyon, *et al.*, gives a value of 20.5 for poly(butadiene). It was therefore concluded that the calibration curves of poly(styrene) and poly(butadiene) are parallel throughout the range of our experiments and that the displacement of the latter from the former is validly obtained from the data in Table I.

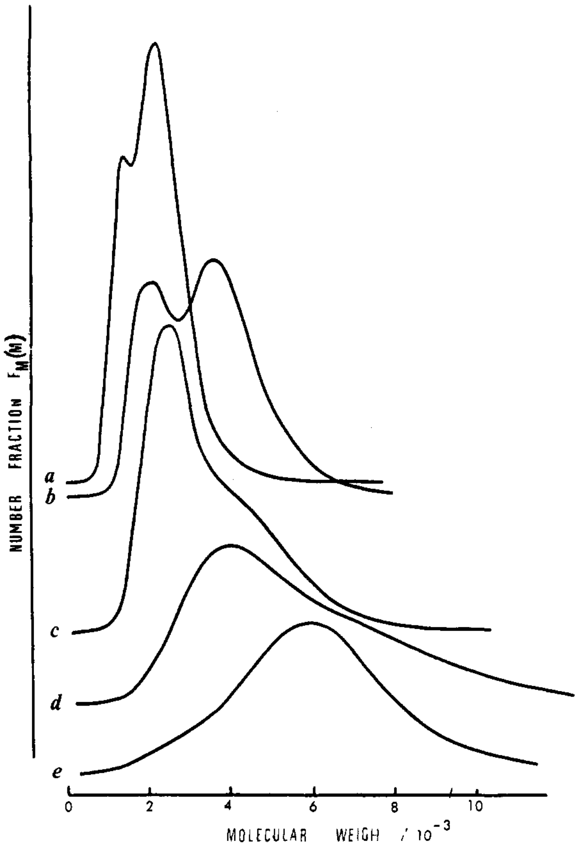

Figure 3. Molecular weight distributions for polymers produced at different catalyst concentrations. [C_4H_6] = 1.5 *M*, conversion = 0.36 *M*, *T* = 50°. Catalyst concentrations: (a) 0.0134 *M*; (b) 0.0086 *M*; (c) 0.0065 *M*; (d) 0.0036 *M*; (e) 0.0020 *M*.

The GPC was checked for zone broadening using the method of Hendrickson,[9] as modified by Tung and Runyon.[10] Instrumental spreading was found to be negligible and the chromatograms were not corrected for it.

Effects of Conversion and Catalyst Concentration on Molecular Weight. Some chromatograms for poly(butadienes) produced at progressively increasing conversion, but with all other reaction parameters held constant, are shown in Figure 2. Visual examination of these curves reveals the following facts: (i) the average molecular weight increases with conversion; (ii) the higher molecular weight component of the binodal distribution diminishes with increasing conversion; (iii) the breadth of the distribution increases with conversion.

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(7) J. R. Runyon, D. E. Barnes, J. F. Rudd, and L. H. Tung, *J. Appl. Polym. Sci.*, **13**, 2359 (1969).

(8) D. F. Alliet and J. M. Pacco, *J. Polym. Sci., Part C*, **21**, 199 (1968).

(9) J. G. Hendrickson, *J. Polym. Sci., Part A-2*, **6**, 1903 (1968).

(10) L. H. Tung and J. R. Runyon, *J. Appl. Polym. Sci.*, **13**, 2397 (1969).

TABLE II
EFFECTS OF EXPERIMENTAL VARIABLES ON MOLECULAR WEIGHTS[a]

Catalyst	Active [catalyst], M	$[C_4H_6]$, M	Conversion, M	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
$(C_4H_7NiI)_2$	0.004	1.53	0.30	2997	3592	1.2
	0.004	1.53	0.32	3423	3979	1.16
	0.004	1.53	0.75	5465	7581	1.39
	0.004	1.53	1.92	7946	16,252	2.05
	0.004	1.53	3.61	10,568	34,781	3.29
	0.0020	1.50	0.36	5363	6939	1.29
	0.0036	1.50	0.36	4289	5052	1.19
	0.0044	1.50	0.36	3574	4211	1.18
	0.0050	1.50	0.36[c]	3429	4123	1.20
	0.0050	1.50	0.36[c]	3268	3924	1.20
	0.0049	1.50	0.36[c]	3489	4282	1.23
	0.0065	1.50	0.36	3004	3498	1.16
	0.0086	1.50	0.36	2690	3181	1.18
	0.0104	1.50	0.36	2394	2774	1.16
	0.0134	1.50	0.36	1880	2149	1.14
$(C_4H_7NiI)_2 + O_2$[b] 4:1	0.0025	1.50	0.20	3260	8284	2.54
	0.0025	1.50	0.30[c]	3929	11,289	2.87
	0.0025	1.50	0.30[c]	4100	9112	2.22
	0.0025	1.50	0.42	5047	9909	1.96
	0.0025	1.50	0.65	6381	12,318	1.93
	0.0025	1.50	0.88	7129	13,246	1.86
	0.0025	1.50	1.31	7684	15,927	2.07
$(C_4H_7NiI)_2 + (PhCO\cdot O)_2$ 1:1	0.0025	1.50	0.48	4683	5973	1.28
	0.0036	1.50	0.48	3577	4293	1.20
	0.0051	1.50	0.48	2885	3363	1.17
	0.0051	1.50	0.48	2720	3148	1.16
	0.0072	1.50	0.48	2647	3078	1.16
	0.0103	1.50	0.48	2106	2282	1.15
	0.0154	1.50	0.48	1536	1765	1.15
	0.0206	1.50	0.48	1404	1590	1.13

[a] All data obtained at 50°. [b] The high polydispersity obtained with this catalyst is probably due to oxidative cross-linking. [c] Duplicate runs.

TABLE III
EFFECT OF TEMPERATURE ON MOLECULAR WEIGHT AND POLYMER MICROSTRUCTURE[a]

T, °C	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Microstructure, % Cis-1,4	Trans-1,4	1,2
40	5326	7488	1.41	1.4	95.4	3.2
50	5465	7581	1.39	2.6	94.1	3.3
60	5326	7531	1.41	1.8	95.2	3.0
70	5186	7278	1.40	2.5	93.9	3.5

[a] Polymerization conditions: $[C_4H_6] = 1.5\ M$; [catalyst] = 0.005 M; conversion = 0.55 M; solvent benzene.

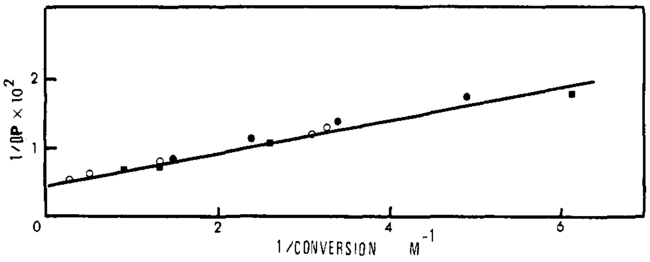

Figure 4. Dependence of $(\overline{DP})^{-1}$ on $(\text{conversion})^{-1}$ at a constant catalyst concentration (0.0025 M). ○, $(C_4H_7NiI)_2$, 0.0025 M; ●, $(C_4H_7NiI)_2 + O_2$ (4:1). Charged catalyst = 0.005 M. ■, $(C_4H_7NiI)_2 + (PhCO\cdot O)_2$ (1:1).

The effects apparent in the experiments with changing conversion are much more dramatically evident in the series of runs at different catalyst concentrations (Figure 3). In this case, the chromatograms have been converted to true molecular weight distribution functions with a resulting enhancement of the resolution of the two peaks that constitute the binodal distribution. Increasing catalyst concentration, while keeping all other reaction parameters constant, is equivalent to decreasing conversion, since there is a partition of a fixed supply of monomer between an increasing number of polymer molecules. In Figure 3 the disappearance of the high molecular weight peak that dominates for high catalyst concentration (low $\bar{M}_n$) is particularly evident.

Studies of catalysts partially killed by O_2, I_2, or benzoyl peroxide have also been carried out at different conversions and different catalyst concentrations, and the results are qualitatively the same as those obtained for pure catalyst.[11] Results obtained in the presence of oxygen are of questionable validity since these polymers were generally incompletely soluble in tetrahydrofuran, presumably because of oxidative cross-linking. Numerical data on molecular weights of polymers obtained under various conditions are summarized in Table II.

Effect of Temperature on Molecular Weight. A series of runs, where temperature was the only variable, were performed to establish the effects of temperature on molecular weight, polydispersity, and microstructure. The results are summarized in Table III.

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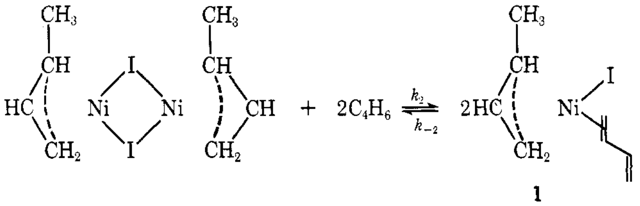
(11) L. R. Wallace and J. F. Harrod, *Macromolecules*, 4, 656 (1971).

Discussion

The Degree of Polymerization. We previously proposed the mechanism of eq 2–4 for the π-crotylnickel iodide catalyzed polymerization of butadiene.



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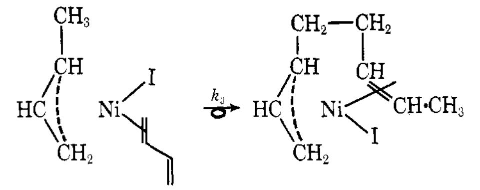
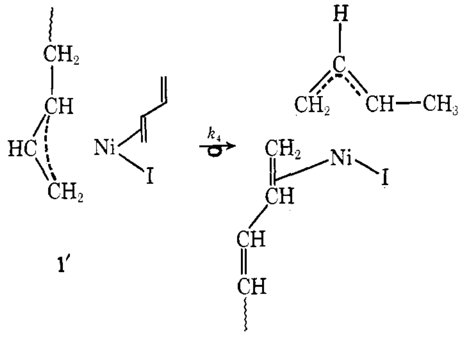
(2)



(3)



(4)

1′

Equation 3 may be identified as the propagation step of the reaction and eq 4 represents an intramolecular hydride transfer from a homologated crotyl chain to coordinated butadiene. An important feature of the two processes is that they both happen to have a common intermediate, **1**, or **1′**, and they will have rate laws differing only in the magnitude of the unimolecular rate constants k_3 and k_4.

On the basis of the mechanism outlined above, we can deduce a theoretical relationship for the degree of polymerization in terms of the kinetic parameters. The number-average degree of polymerization ($\overline{\mathrm{DP}}_\mathrm{n}$) is defined thus:

$$\frac{1}{\overline{\mathrm{DP}}_\mathrm{n}} = \frac{\text{moles of polymer}}{\text{moles of mer units in polymer}} \tag{5}$$

If every nickel atom is involved in propagation, and since each transfer step produces a new polymer molecule

$$\frac{1}{\overline{\mathrm{DP}}_\mathrm{n}} = \frac{2[\mathrm{C}_2] + \text{moles of transfer}}{\text{moles of butadiene conversion}} \tag{6}$$

$$\mathrm{C}_2 = \text{catalyst dimer}$$

The conversion is a measure of the amount of **1** and **1′** formed and used up and according to the mechanism it is partitioned such that

$$\text{moles of transfer} = \text{moles of conversion} \times \frac{k_4}{k_3 + k_4} \tag{7}$$

thus from (6)

$$\frac{1}{\overline{\mathrm{DP}}_\mathrm{n}} = \frac{2[\mathrm{C}_2]}{\text{conversion}} + \frac{k_4}{k_3 + k_4} \tag{8}$$

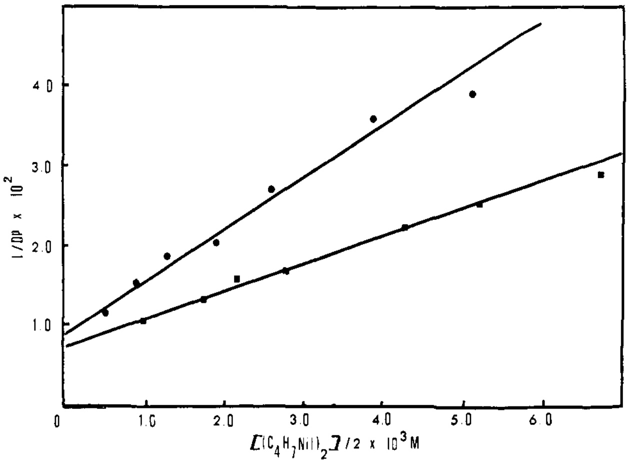


Figure 5. Dependence of $(\overline{\mathrm{DP}})^{-1}$ on [catalyst]/2. $[\mathrm{C_4H_6}] = 1.5\ M$, conversion = 0.35 M, T = 50°. ■, $(\mathrm{C_4H_7NiI})_2$; ●, $(\mathrm{C_4H_7NiI})_2$ + $(\mathrm{PhCO{\cdot}O})_2$ (1:1). Charged catalyst = 4 × abscissa value in the latter case.

TABLE IV
EMPIRICAL MOLECULAR WEIGHT PARAMETERS

Catalyst	Method	α[a]	B[b]
$[\mathrm{C_4H_7NiI}]_2$	Conversion	0.50	0.0044
	Catalyst	0.31	0.0072
$[\mathrm{C_4H_7NiI}]_2$– $(\mathrm{C_7H_5O_2})_2$	Conversion	0.46	0.0040
	Catalyst	0.62	0.0082

[a] Average α = 0.47 ± 0.15 average deviation. [b] Average B = 0.0060 ± 0.002 average deviation.

An equivalent expression was previously derived by Litt and Szwarc using a generalized statistical approach.[12]

Although preliminary results[2] confirmed the linear relationship between $1/\overline{\mathrm{DP}}_\mathrm{n}$ and 1/conversion predicted by eq 8, the much larger body of data now available reveals further features that were unexpected. Figures 4 and 5 show plots of $1/\overline{\mathrm{DP}}_\mathrm{n}$ *vs.* 1/conversion and [C$_2$], respectively, for a variety of reactions. The curves in Figures 4 and 5 may be represented by the empirical relationship 9.

$$\frac{1}{\overline{\mathrm{DP}}_\mathrm{n}} = \frac{2\alpha[\mathrm{C}_2]}{\text{conversion}} + B \tag{9}$$

Some experimental values for α and B are tabulated in Table IV. The low values of B for the conversion experiments are probably due to the effect of catalyst decomposition which is greatest in the region of the intercept. The catalyst variation experiments were all carried out to relatively low conversion levels.

The most significant difference between the theoretical expression 8 and the empirical relationship 9 is the value of the coefficient α. There is absolutely no doubt that α is substantially less than unity and is close to 0.5. The significance of this fact is that the molecular weight of polymer that has not undergone transfer at all is roughly twice that predicted by theory. Only two likely explanations of this feature have occurred to us. The first, that only half of the nickel atoms are involved in propagation, may be dismissed in the light of the convincing demonstration by Lobach, *et al.*, that all of the crotyl groups react with butadiene-d_6.[13] The second, that

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(12) M. Litt and M. Szwarc, *J. Polym. Sci.*, **42**, 159 (1960).

(13) 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).

termination of the polymerization occurs by coupling of polymer chains, seems more likely.

In our work the polymerization reactions are terminated by oxidation of the catalyst–polymer mixture in methanol saturated with air. It is not unreasonable to expect that the oxidation of an organometallic compound would generate free radicals and that, if they were allylically stabilized, these radicals would terminate by recombination. Indeed, Babitskii, *et al.*, have claimed that oxidation of crotylnickel chloride in methanol yields crotyl dimers.[14] We have attempted similar experiments with the iodide complex, but experimental difficulties have thus far prevented unequivocal identification of the oxidation products.

If we assume that all live polymer chains terminate by coupling, eq 8 becomes:

$$\frac{1}{\overline{\mathrm{DP}}_{\mathrm{n}}} = \frac{[\mathrm{C_2}]}{\text{conversion}} + \frac{k_4}{k_3 + k_4} \tag{10}$$

which can be rearranged to

$$\text{number of polymer chains per Ni} = 0.5 + \frac{k_4 \times \text{conversion}}{2(k_3 + k_4)[\mathrm{C_2}]} \tag{11}$$

In the same way that eq 10 illustrates that transfer leads to an asymptotic approach to a limiting degree of polymerization ($k_3 + k_4/k_4$) at infinite conversion, eq 11 shows that the fraction of polymer chains attached to nickel declines from 100% at zero conversion to 0% at infinite conversion.

Since the intercept of a plot of the number of polymer chains per nickel *vs.* conversion is not sensitive to catalyst decomposition, it should provide more convincing proof of the live polymer chain coupling hypothesis. Such a plot is shown in Figure 6, and it does indeed confirm the validity of eq 11, yielding an intercept of almost exactly 0.5.

The Origin of the Binodal Distribution. One of the properties of a polymerization reaction proceeding by a slow stepwise propagation with occasional transfer is that it will produce a polynodal molecular weight distribution.[3] The mechanism proposed in eq 2, 3, and 4 will give rise to three separate kinds of polymer molecule:

(i) *Growing polymer chains* that have never transferred and which all started growing at the beginning of the reaction. Such chains are "living" polymers and will be characterized by a very narrow molecular weight distribution. These chains will represent a continuously diminishing fraction of the total, and their molecular weight will be proportional to conversion.

(ii) *Dead polymer chains* resulting from random transfer. Such chains will constitute a progressively increasing fraction of the total polymer with increasing conversion and should asymptotically approach a most probable distribution.

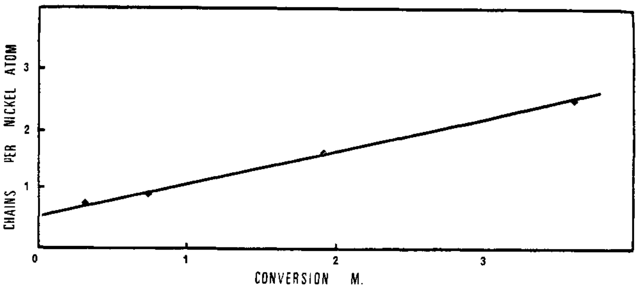

Figure 6. Dependence of the number of polymer chains per nickel atom on conversion. Data obtained partly from Figure 2, partly from data omitted from Figure 2 for purposes of clarity.

(iii) *Reinitiated Polymer Chains.* These actively growing chains, resulting from reinitiation by transfer to monomer, will appear in the system at the same rate as the type i chains disappear. By this time most of the polymer is type ii, this fraction will not be so evident as the other two. It will also have a lower $\bar{M}_{\mathrm{n}}$ than types i and ii in the early stages of reaction, but will asymptotically approach the same most probable distribution as type ii at infinite conversion. It is important to note that the coupling of live chains described above will cause the distribution of type i to move away from type ii but will cause type iii to move toward type ii.

The distributions in Figure 3 manifest very clearly all of the attributes we would anticipate for the proposed mechanism. In fact, it seems that the crotylnickel iodide system is an ideal system for demonstrating the principles outlined by Gatske. This kind of behavior is the normal behavior of free-radical vinyl addition polymerization in the period before equilibrium molecular weight distribution is achieved, but the duration of the latter period is in the range 10^{-3}–10^{1} sec and polymer chain growth is not experimentally observable. In Figure 3 we see this chain of events, as it were, proceeding in slow motion.

Effects of Temperature on Polymer Properties. Within the context of the proposed mechanism, the results in Table III indicate that the activation enthalpies for k_3 and k_4 are almost identical. Hence the difference in k_3 and k_4 may be attributed almost entirely to entropic effects. However, little significance can be attributed to this modest difference in entropy of activation (*ca.* 2.5 eu).

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(14) B. D. Babitskii, V. A. Kormer, M. I. Lobach, I. Y. Poddubnyi, and V. N. Sokolov, *Dokl. Akad. Nauk SSSR*, **180**, 420 (1968).