

SOME ASPECTS OF THE CATALYTIC ACTIVITY OF π -ALLYLNICKEL IODIDE

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SUMMARY

The polymerization of butadiene catalyzed by π -allylnickel iodide proceeds predominantly by a living polymer mechanism which may, however, be influenced to a certain extent by the solvent. The rates of propagation as well as of a chain transfer reaction increase in the series benzene < THF < 1,2-dichloroethane. Both phenomena point to involvement of the solvent in the active species.

The stereospecific dimerization of styrene to *trans*-1,3-diphenyl-1-butene with the same catalyst was found to involve a π -allylic mechanism, comparable with that of butadiene polymerization. Other monomers which are unable to form a π -allylic structure destroy the catalyst.

Styrene exerts a strong chain transfer action on the polymerization of butadiene drastically reducing the molecular weight (styrene end groups); there is also some copolymerization (inner styrene groups).

1. INTRODUCTION

Since Wilke *et al.*¹ isolated in 1961 a di- π -allylnickel intermediate from the cyclization reaction of butadiene to cyclododecatriene, the π -allylnickel compounds have been much studied as catalysts for several reactions. In 1964, Natta *et al.*² polymerized butadiene to linear *trans*-1,4-polymer with π -allylnickel bromide, and other groups³⁻⁶ investigated various aspects of this catalysis, particularly the influence of the cation (Cl, Br, I) and of the solvent on stereospecificity. Wilke *et al.*⁷ showed that the catalytic activity can be increased considerably by adding aluminum halides or organoaluminum halides. In conjunction with these Lewis acids, the π -allylnickel halides also dimerize monoolefins such as ethylene and propene, and the addition of organic phosphines directs the dimerization to particular isomers⁷. Not only α -olefins and conjugated diolefins but also styrene react with π -allylnickel halides. The chloride and the bromide produce oligomers, whereas the iodide and the trifluoroacetate undergo predominantly a stereospecific dimerization to *trans*-1,3-diphenyl-1-butene^{8,9}. We have now carried out several experiments, especially kinetic measurements designed to clarify some mechanistic aspects of these interesting reactions.

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2. POLYMERIZATION OF BUTADIENE

2.1. Polymerization rate

We investigated the polymerization of butadiene by the dilatometric method in different solvents, using π -allylnickel iodide as catalyst (see Fig. 1).

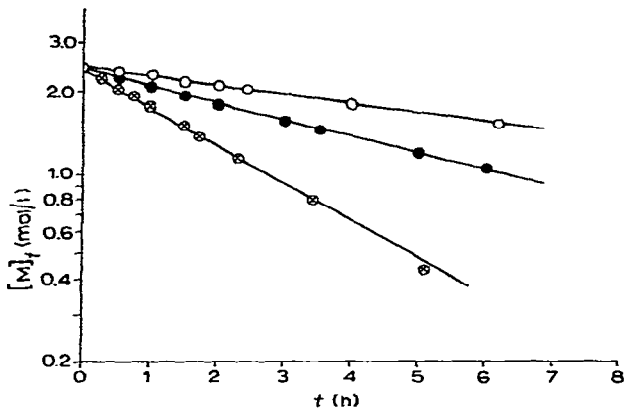


Fig. 1. Polymerization of butadiene with π -allylnickel iodide. $[C_4H_6]_0 = 2.4$ mol/l; temp. 50° . \circ : $[Ni] = 11.3 \times 10^{-3}$ g-atom/l; benzene. \bullet : $[Ni] = 17.0 \times 10^{-3}$ g-atom/l; tetrahydrofuran. \odot : $[Ni] = 10.8 \times 10^{-3}$ g-atom/l; 1,2-dichloroethane.

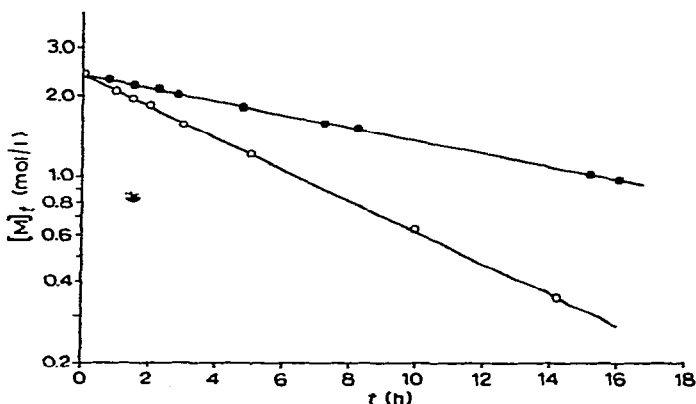


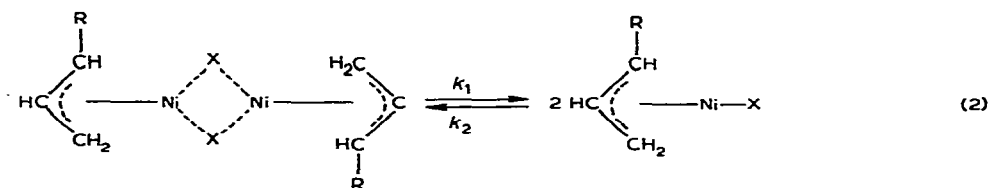
Fig. 2. Polymerization of butadiene with π -allylnickel iodide. Solvent: THF; $[C_4H_6] = 2.4$ mol/l. \circ : $[Ni] = 17.0 \times 10^{-3}$ g-atom/l; \bullet : $[Ni] = 4.3 \times 10^{-3}$ g-atom/l.

The polymerization is first order with respect to the monomer concentration up to relatively high conversion (compare also Fig. 2), indicating that the concentration of active nickel remains constant. The rate in benzene was previously investigated with π -allylnickel iodide and π -crotylnickel iodide by Dolgoplosk *et al.*³ and by Harrod *et al.*¹⁰, respectively. Both groups found the empirical eqn. (1) to apply with values of K ($l^{0.5} \cdot mol^{-0.5} \cdot sec^{-1}$) at 50° of 1.4×10^{-4} in the former and

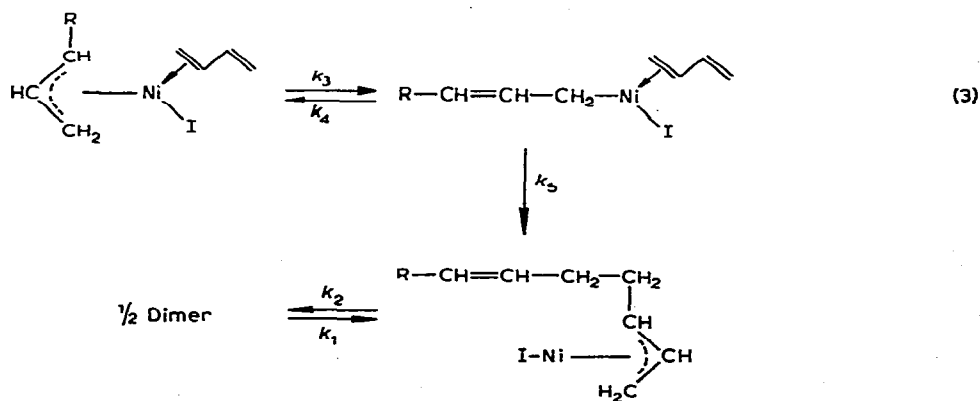
$$v = K \cdot [Ni]^{0.5} \cdot [C_4H_6] \quad (1)$$

1.5×10^{-4} in the latter case*. Assuming this rate law, we found $K = 1.8 \times 10^{-4}$ for benzene, in reasonable agreement with the reported data.

The square root dependance of the rate on the nickel concentration has been attributed to the presence of a dimer–monomer equilibrium (2), involving the catalyst and the growing chains^{5,10} ($R = H$ or growing chain; $X = \text{halogen}$; $k_1 \ll k_2$), in which



only the monomeric form is active. This mechanism presupposes that the growing chain end is stabilized as a π -allyl complex, which participates in the dimer–monomer equilibrium at the same time and (or) in the same manner as the catalyst itself. Such a stabilization of the chain end was postulated in 1964 by Natta *et al.*², and is now generally accepted as an important part of the polymerization process of butadiene with transition metal catalysts. The square root dependance and the constancy of the active Ni concentration up to high conversions corroborate strongly this π -allyl growth mechanism for butadiene polymerization, which may then be formulated as follows. First the monomer coordinates to the monomeric Ni complex [presumably the equilibrium (2) already involves the monomer, since the dissociative reaction is unlikely to be spontaneous¹⁰]. This coordination increases the electron density at the Ni center, and causes the π -allylic ligand to adopt the σ -configuration. Such π - σ equilibria of allyl ligands, under the influence of donor ligands, are well known^{11,12}. A butadiene molecule then inserts into the relatively unstable (*i.e.* reactive) carbon–nickel σ -bond and the chain end is stabilized again as a π -allyl group.



To check whether this mechanism is also valid for the polymerization in

* The value obtained by Harrod *et al.*¹⁰ was originally calculated with the catalyst concentration expressed as $[(C_4H_7Ni)_2]$, and has been recalculated with reference to the total amount of nickel, $[Ni]$.

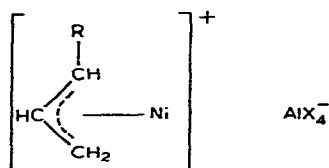
polar solvents, we varied the catalyst concentration by a factor of 4 in THF (see Fig. 2). The rate varied by a factor of 2.4, which approaches satisfactorily the square root relationship, particularly if one takes into account that the lower concentration of catalyst is more sensitive to losses due to impurities (*i.e.* the factor 2.4 is an upper limit). Additional evidence comes from measurements of the magnetic susceptibility: the π -allylnickel iodide catalyst is diamagnetic in the three solvents, in the absence or in the presence of butadiene. Since free Ni^{II} has two unpaired electrons, this behavior must be due to metal-metal interaction via the halogen bridges in the dimeric compound. It also confirms the assumption made above that $k_1 \ll k_2$ (see eqn. 2). It thus appears that the dimeric form of the π -allylnickel halides, previously reported only for nonpolar solvents^{5,10}, also prevails in polar solvents.

TABLE 1

BUTADIENE POLYMERIZATION WITH π -ALLYLNICKEL IODIDEEmpirical rate constant K (eqn. 1) in different solvents. Temp. 50°.

Solvent	$K \times 10^4$
Benzene	1.8
Tetrahydrofuran	2.9
1,2-Dichloroethane	8.5

The empirical constants K of eqn. (1) for the three solvents under investigation are given in Table 1. The variation of K with the solvent may arise from more than one cause. The solvent might compete with the monomer for the coordination site (see eqn. 3); in this case the coordination ability of the solvent would decrease in the series benzene > THF > 1,2-DCE, which does not appear unreasonable. An effect due to polar influences can not be disregarded either. It should be remembered that the increase of activity provoked by the addition of AlX_3 etc. was attributed to ionic forms^{7,13}:



Thus, the activity might depend on the positive charge on the Ni, and this might vary with the dielectric constant of the solvent (benzene 2.3, THF 7.4, 1,2-DCE 10). The high polymerization activity found by Natta *et al.*⁶ in pentane appears to favor the first explanation.

2.2. Degree of polymerization and molecular weight distribution

The mechanism so far envisaged should give living polymers. In fact the polymers obtained with π -allylnickel iodide show the characteristics of this type of polymer, at least at lower conversions, and in certain cases also up to high conversions (see Figs. 3 and 4, Table 2, and also ref. 10): the molecular weight (number average)

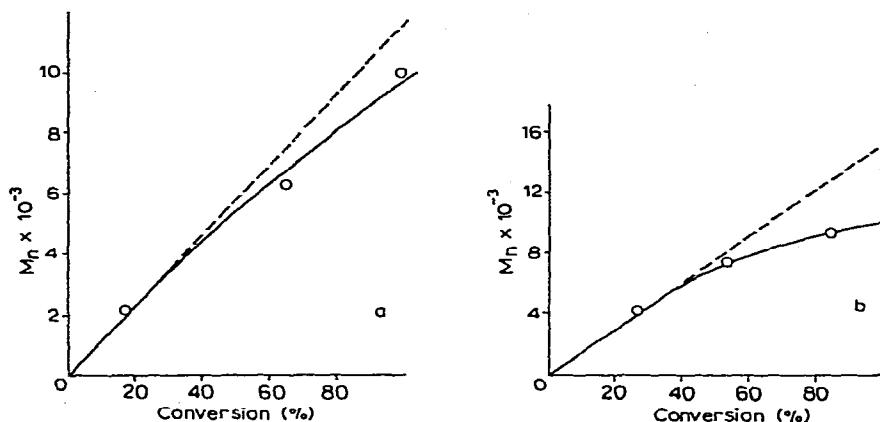


Fig. 3. Molecular weight (vapor pressure osmometry) as a function of conversion. $[C_4H_6]_0 = 2.4$ mol/l; temp. 50° . (a) Benzene; $[Ni] = 11.3 \times 10^{-3}$ g-atom/l. (b) 1,2-DCE; $[Ni] = 8.5 \times 10^{-3}$ g-atom/l. -----: calculated with eqn. (4).

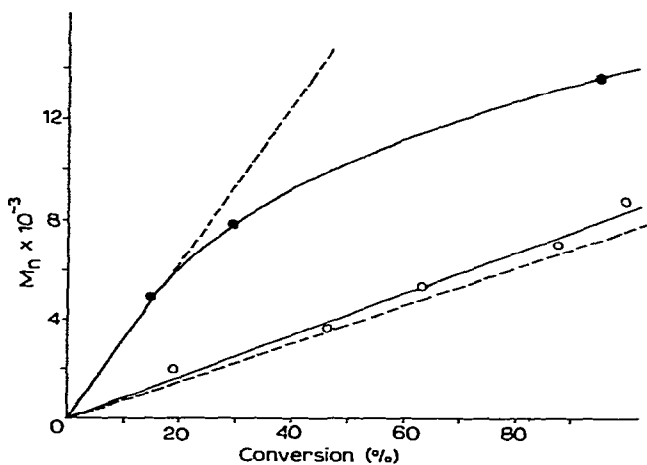


Fig. 4. Molecular weight (vapor pressure osmometry) as a function of conversion and nickel concentration. $[C_4H_6] = 2.4$ mol/l; temp. 50° ; solvent THF. O: $[Ni] = 17.0 \times 10^{-3}$ g-atom/l. ●: $[Ni] = 4.3 \times 10^{-3}$ g-atom/l. -----: calculated from eqn. 4.

TABLE 2

MOLECULAR WEIGHT DATA^a OF POLYBUTADIENE, OBTAINED WITH π -ALLYLNICKEL IODIDE IN 1,2-DCE

$[C_4H_6]_0 = 2.4$ mol/l; $[Ni] = 8.5 \times 10^{-3}$ g-atom/l; temp. 50° .

Conversion (%)	M_n	M_w	M_w/M_n
26.4	3800	5200	1.4
53.3	5800	10700	1.85

^a Obtained from GPC measurements.

increases linearly with the degree of conversion, and is given by eqn. (4). [The dotted lines in Figs. 3 and 4 are calculated from eqn. (4).]

$$M_n = 54 \times \frac{[C_4H_6]_0 - [C_4H_6]_t}{[Ni]_0} \quad (4)$$

The dependence of the molecular weight on the catalyst concentration deserves particular attention, since it confirms the reaction mechanism depicted in eqns. (2) and (3). Whereas this mechanism requires the polymerization rate to be proportional to the square root of the nickel concentration, the molecular weight should obviously be inversely proportional to the first power of this concentration. This is indeed the case, at least at lower conversions, as shown in Fig. 4. (The deviation at higher conversion will be discussed below.)

The molecular weight distribution is relatively narrow, as indicated by the ratio M_w/M_n in Table 2, although for a simple living polymer mechanism it is still rather broad. (The data in Table 2 have been obtained by gel permeation chromatography; the absolute values of M_n vary somewhat from those in Fig. 3; they may be subject to some uncertainty in the calibration of the method but are valid for a comparative study.)

To explain the fact that the molecular weight distribution is broader than expected for living polymers, and to account for the increase of the ratio M_w/M_n with the conversion, an additional reaction has to be assumed. The deviation of the molecular weight from the straight lines in Figs. 3 and 4 has to be taken into account. This deviation, in a range in which the overall rate still follows first-order kinetics with respect to the monomer, indicates a chain transfer mechanism, with a small but significant rate as compared with that of the polymerization. The observation that the deviation appears particularly at higher conversions can be explained by postulating the existence of a transfer reaction which is independent of the monomer. The molecular weight at the moment of quenching of the growing chains, could then be calculated as the sum of all monomer molecules converted to polymer ($[C_4H_6]_0 - [C_4H_6]_t$), divided by the sum of all chains growing at that time (which is equal to $[Ni]_0$), and by the number of transfer steps ($[Tr]$) which have occurred up to this moment. The value of $[Tr]$ is obtained, assuming that the chain transfer is independent of the monomer concentration as suggested, from:

$$\begin{aligned} \frac{d[Tr]}{dt} &= k_{tr} \cdot [Ni]_0 \\ \int_0^t d[Tr] &= k_{tr} \cdot [Ni]_0 \cdot \int_0^t dt \\ [Tr]_t &= k_{tr} \cdot [Ni]_0 \cdot t \end{aligned}$$

From this can be derived the following expression for the molecular weight:

$$M_n = 54 \times \frac{[C_4H_6]_0 - [C_4H_6]_t}{k_{tr} \cdot [Ni]_0 \cdot t + [Ni]_0} \quad (5)$$

If $k_{tr} \cdot t \ll 1$, eqn. (4) gives an approximation to the molecular weight, and the observed data lie on the straight lines. The deviation from these lines permits an estimate of k_{tr} with the aid of eqn. (5). The results are: $k_{tr} \approx 1 \times 10^{-6}$ for benzene, $k_{tr} \approx 4 \times 10^{-6}$

for THF, and $k_{tr} \approx 2 \times 10^{-5}$ for 1,2-DCE. This dependence of k_{tr} on the solvent suggests that the solvent may form part of the chain transfer process.

Probably more important, broadening of the molecular weight distributions must also be due to the fact that these distributions are binodal. Interestingly, the molecular weight of both maxima increase with the degree of conversion (see Fig. 5). The reason for this dual distribution, which has been observed previously¹⁰, is not clear. The existence of two isomeric forms of the catalyst has been suggested (*e.g.* growing chain *cis* or *trans* to the halide), although it is difficult to understand why these two forms would not rapidly exchange. Perhaps the double bonds along the polymeric chains compete to a certain extent with the monomer for the coordination

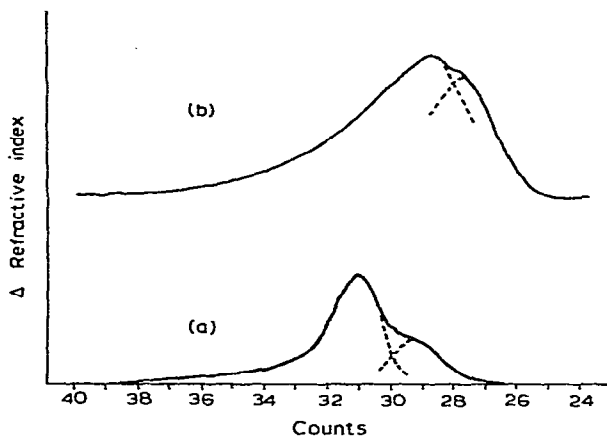


Fig. 5. Gel permeation chromatograms of two polybutadiene samples with different conversion. $[C_4H_6]_0 = 2.4$ mol/l; $[Ni]_0 = 8.5 \times 10^{-3}$ g-atom/l; temp. 50° ; solvent 1,2-DCE. (a) 26.4%, (b) 53.5% conversion.

site at the Ni. Incorporation of such a double bond into a growing chain, followed by β -hydrogen abstraction, would lead to a branched growing chain and Ni-H, and thus obviously to a broadening of the distribution.

3. DIMERIZATION OF STYRENE

The dimerization of styrene to *trans*-1,3-diphenylbutene (DPB) with π -allylnickel complexes has been reported recently^{8,9}. We now describe kinetic measurements carried out in order to obtain some insight into the mechanism of this interesting catalytic reaction.

We found that π -allylnickel iodide, at 0° , produces DPB with essentially 100% selectivity. At a higher temperature (60°), some thermal polystyrene was also found. The π -allylnickel iodide was prepared according to Wilke *et al.*¹⁴. Catalyst and styrene, and solvent (benzene) as required were introduced into glass ampoules, degassed, and the ampoules were sealed off. After the specified reaction time, the solution was filtered in the air to destroy and remove the catalyst, and analyzed by NMR. The degree of conversion was calculated according to:

$$\text{Conversion} = \frac{\frac{2}{3} I(\text{CH}_3)}{\frac{2}{3} I(\text{CH}_3) + \frac{1}{2} I(\text{CH}_2)} \times 100\%$$

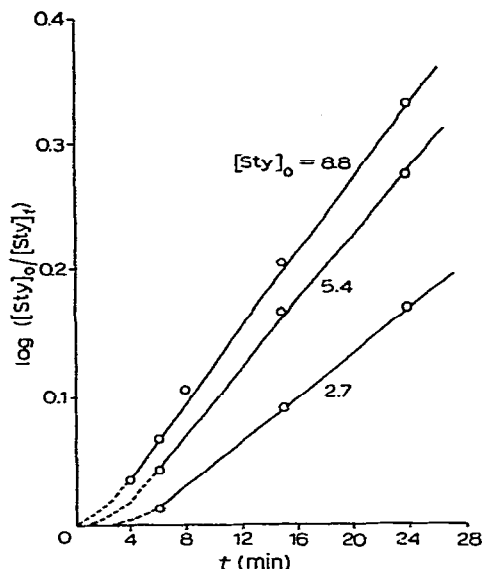


Fig. 6. Dimerization of styrene with π -allylnickel iodide. $[\text{Ni}]_0 = 1.2 \times 10^{-3}$ g-atom/l; temp. 0° ; solvent benzene.

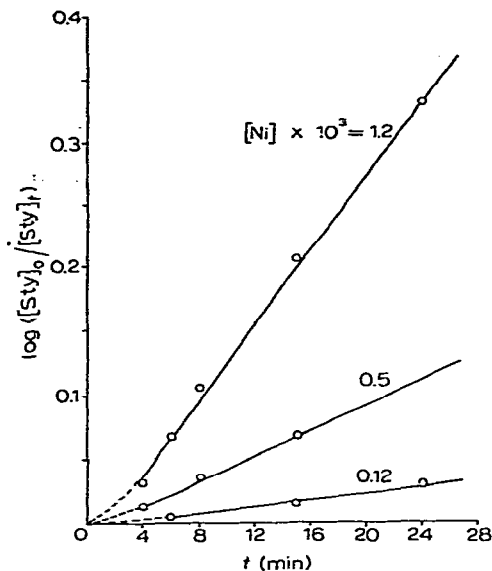


Fig. 7. Dimerization of styrene with π -allylnickel iodide $[\text{Sty}] = 8.8$ mol/l; temp. 0° .

TABLE 3

EMPIRICAL RATE CONSTANT K OF EQN. (6), UNDER VARYING CONDITIONS

Temp. 0° ; solvent benzene.

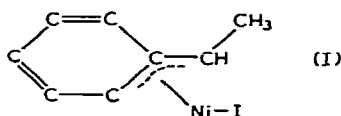
$[\text{Sty}]$ (mol/l)	$[\text{Ni}] \times 10^3$ (g-atom/l)	$K \times 10^3$
2.7	1.2	4.8
5.4	1.2	7.0
8.8	1.2	8.0
8.8	0.5	6.5
8.8	0.12	7.0

where $I(\text{CH}_2)$ is the intensity of the NMR peak in the CH_2 region (4.9–6.2 ppm, representative for the monomeric styrene), and $I(\text{CH}_3)$ that in the CH_3 region (1.35–1.55 ppm, representative for the dimer, DPB).

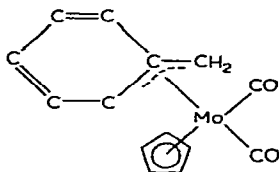
Fig. 6 and Table 3 show that the dimerization is first-order with respect to the styrene concentration; the apparent first-order rate constant depends to some extent on the reaction medium, however. Induction periods are observed, they decrease as the concentration of styrene increases. The dependence on the nickel concentration is linear (Fig. 7 and Table 3). Thus, the experimental rate law is:

$$-\frac{d[\text{Sty}]}{dt} = K \cdot [\text{Sty}] \cdot [\text{Ni}]_0 \quad (6)$$

that the first styrene molecule, after the incorporation of the hydrogen [see eqn. (7)] loses its aromaticity, and thus makes a π -allyl group available for the stabilization of the Ni:



There is a precedent for such a formulation in the following molybdenum complex¹⁵:



for which this kind of allylic structure has been demonstrated by X-ray analysis¹⁶.

In contrast to the butadiene case, for the dimerization of styrene we found proportionality between the rate and the nickel concentration [Table 3, eqn. (6)]. This means that either the dimeric form of the π -allylnickel iodide must be the catalyst, or that the greater bulk of the styrene ligand precludes dimer formation. The latter seems to be more probable. It must then be assumed that the addition of the second styrene molecule [step 2 in eqn. (7)] is the slowest step, whereas all others are fast. The nickel is then present for most of the time in form of the stabilized, bulky complex (I).

The slight dependence of the overall rate constant on the medium (Table 3) can be explained by a competition between the solvent and the monomer for the coordination to this complex (benzene apparently coordinating somewhat better than styrene). The induction period (Figs. 6 and 7) may be interpreted as the time needed for all the catalyst to reach the monomeric form.

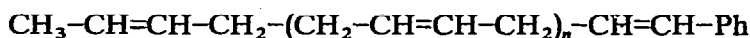
Finally the destruction of the catalyst may be envisaged as starting from the hydrido-complex:



This Ni^0 sponge is ferromagnetic, and although at 0° it is formed only in minor quantities in the earlier stages of the reaction, it strongly disturbs magnetic susceptibility as well as ESR measurements. Nevertheless it was possible to detect a Ni^{II} signal at $g=2.2$ at the very beginning of the reaction, confirming the view that the nickel is present predominantly as the complex (I). No such signal could be observed with butadiene.

4. COPOLYMERIZATION OF BUTADIENE AND STYRENE

The pronounced chain transfer capacity of styrene, considered above, induced us to carry out a series of experiments aiming at short polybutadiene chains with styrene end groups:



The two monomers were brought into reaction together with π -allylnickel iodide in sealed glass ampoules at 60°. The product was roughly fractionated into a polymeric and an oligomeric part by precipitation with methanol (polymer) and evaporation of the filtrate (oligomer). The number average molecular weight (M_n) of each fraction was measured by vapor pressure osmometry, and the number average molecular weight of the total product (\bar{M}_n) was calculated according to:

$$\bar{M}_n = \frac{1}{\sum w_i/M_{n,i}}$$

(w_i = weight fraction). Table 5 shows that in fact a drastic reduction of the molecular weight occurs with increasing styrene concentration. A careful analysis of the products by NMR showed, however, that styrene not only acts as chain transfer agent, but also copolymerizes with butadiene. In other words: when a styrene molecule has entered into a growing polybutadiene chain, the chain growth is not always interrupted by β -hydrogen abstraction [compare eqn. (7), step 3], a normal chain propagation sometimes taking place.

TABLE 5

COPOLYMERIZATION OF BUTADIENE AND STYRENE

$[\text{Ni}]_0 = 2.4 \times 10^{-3}$ g-atom/l; temp. 60°; time 24 h.

No.	Butadiene (g)	Styrene (g)	$[\text{C}_8\text{H}_8]_0 /$ $[\text{C}_4\text{H}_6]_0$	Polymer		Oligomer		\bar{M}_n
				(g)	M_n	(g)	M_n	
1	26.4	24.6	0.48	9.2	1400	2.8	370	845
2	19.8	36.3	0.97	9.0	777	6.0	326	500
3	13.3	72.5	2.9			25.8	267	267

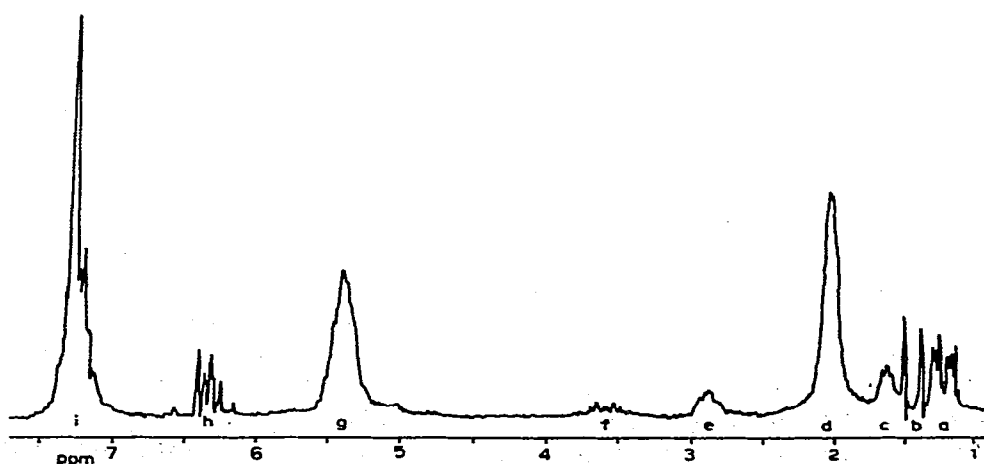


Fig. 8. NMR spectrum of copolymer butadiene/styrene (oligomeric part). This figure is combined from two original NMR spectra, since in no case were all the peaks present with sufficient intensity.

TABLE 6

ASSIGNMENT OF THE NMR PEAKS FOR BUTADIENE/STYRENE COPOLYMERS (see Fig. 8)

Peak	ppm	Chemical group ^a	Taken from
a	1.22	CH ₃ [*] -CHPh-CH ₂ -	Cumene
b	1.42	CH ₃ [*] -CHPh-CH=	DPB
c	1.63	CH ₃ [*] -CH=CH-	2-Pentene
d	2.05	-CH ₂ [*] -CH ₂ [*] -	1,4- <i>trans</i> - Polybutadiene
e	2.85	-CH=CH-CH ₂ -CH=CHPh	
f	3.6	CH ₃ -CH [*] Ph-CH=	DPB
g	5.4	-CH [*] =CH [*] -	1,4- <i>trans</i> - Polybutadiene
h	6.3	-CH [*] =CH [*] Ph	DPB
i	7.2-7.3	Ph [*] -	Styrene { monomer dimer polymer

^a Pertinent hydrogen atoms marked with an asterisk.

The NMR spectrum of a copolymer is given in Fig. 8. Table 6 shows the assignment of the NMR peaks which was possible with the aid of the spectra of styrene dimer (DPB, compare preceding section), polybutadiene and cumene.

A fairly comprehensive analysis of the composition of the product can be made from the NMR data. The intensity (integral) of each peak gives the number of the corresponding groups (relative values). The assignment can be checked, since several relationships must hold, *e.g.*:

$$A + B + C = H$$

$$H - E = B = F$$

$$A + C = E$$

where A, B, C, \dots are the numbers of groups corresponding to peaks a, b, c, ... B then gives directly the number of DPB molecules, C the number of polymer (oligomer) molecules initiated by butadiene, and A the number of polymer (oligomer) molecules initiated by styrene. H is the sum of all terminal end groups, which is equal to the total number of molecules. (The very small amount of chain transfer occurring in butadiene alone is neglected.) G , the total number of butadiene molecules which have reacted, has to be distributed between $(A + C)$ polymer molecules. $I - (A + B + H)$ is the number of inner styrene groups (no end groups) which have to be distributed between the $(A + C)$ polymer molecules. As an example, the whole process of computation is shown, for the oligomeric part of the first copolymer in Table 5, in Table 7. A final check of such computation can be made by comparing the molecular weight resulting from the calculated composition with the measured molecular weight.

Table 8 gives the composition of all the investigated fractions. The oligomeric product No. 3 (Table 5) was fractionated by vacuum distillation which leads to a more reliable analysis of the NMR spectra. Product No. 2, however, was analyzed before separation into fractions. The relative numbers obtained from the NMR

TABLE 7

CALCULATION OF THE COMPOSITION OF AN OLIGOMERIC PRODUCT FROM NMR DATA

 I = value of the integral.

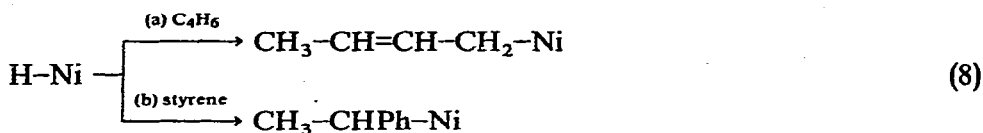
Peak	ppm	Chemical group	I	Number of groups	Computation
a	1.22	$\text{CH}_3^*-\text{CHPh}-\text{CH}_2-$	3	1.0	$A+B+C=6.3$
b	1.42	$\text{CH}_3^*-\text{CHPh}-\text{CH}=\text{}$	3	1.0	$H=6.0$
c	1.63	$\text{CH}_3^*-\text{CH}=\text{CH}-$	13	4.3	$H-E=1$
d	2.05	$-\text{CH}_2^*-\text{CH}_2^*-\text{}$	66	16.5	$B=1$ $F=1$
e	2.85	$-\text{CH}=\text{CH}-\text{CH}_2^*-\text{CH}=\text{CHPh}$	10	5.0	$A+C=5.3$
f	3.6	$-\text{CH}^*\text{Ph}-$	1	1.0	$E=5.0$
g	5.4	$-\text{CH}^*=\text{CH}^*-\text{}$	43	21.5	$I-(A+B+H)=1.3$
h	6.3	$-\text{CH}^*=\text{CH}^*\text{Ph}$	12	6.0	$G=21.5$
i	7.2-7.3	$\text{Ph}^*-\text{}$	46.5	9.3	$1.3/5.3=0.25$ $21.5/5.3=4.06$
Composition:			M_n :		
1 DPB			$\frac{1 \times 208 + 1 \times 453 + 4.3 \times 349}{6.3} = 343$		
1 (Sty Bu _{4.06} Sty _{1.25})					
4.3 (Bu _{4.06} Sty _{1.25})			M_n (measured) = 370		

TABLE 8

COMPOSITION OF THE COPOLYMERS AS DETERMINED FROM NMR

Product No.	Fraction	w_i	$[\text{DPB}] \times 10^2$ (mol/l)	$[\text{Bu}_m\text{Sty}_m] \times 10^2$ (mol/l)	$[\text{StyBu}_m\text{Sty}_m] \times 10^2$ (mol/l)	n	m
1	Oligomer	0.233	1.94	8.33	1.94	4.06	1.25
	Polymer	0.767		6.7	2.87	23.0	1.5
2	Total	1.0	10.9	25.2	13.1	1.14	0.97
3	1	0.082	2.44	9.05		1.2	1.07
	2	0.098	8.80	3.02		1.44	1.39
	3	0.270	29.1	3.9		2.15	1.61
	4	0.373	1.35	9.0	18.0	2.58	1.28
	5	0.177		3.2	6.8	3.8	1.68

analysis (see the example in Table 7) are converted into absolute concentrations taking into account the weight of each fraction. The NMR data show unambiguously that the nickel-hydrido complex formed during the chain transfer step [see eqn. (7)] can give rise to a new molecule by taking up either a butadiene or a styrene molecule:



The relative rates of these two steps can be obtained from the data of Table 8, by summing up, for each product, all molecules that have been initiated with butadiene, and also those initiated with styrene. The results are included in Table 9, and are represented graphically in Fig. 9. It will be seen from this figure that the ratio of initiation via butadiene to initiation via styrene is proportional to the ratio of the concentrations, and that at equal molar concentration of styrene and butadiene both initiation steps occur with the same frequency. The sum of both initiation steps divided by the nickel concentration is equal to the number of transfer steps per nickel center. As expected, this number increases steeply with the styrene content of the reaction mixture (column 8 in Table 9).

TABLE 9

COPOLYMERIZATION OF BUTADIENE AND STYRENE

Results of the evaluation of NMR data; $[\text{Ni}]_0 = 2.4 \times 10^{-3}$ g-atom/l.

No.	$[\text{C}_4\text{H}_6]_0$ (mol/l)	$[\text{C}_8\text{H}_8]_0$ (mol/l)	Conversion		Initiation by		Transfer steps per Ni	Growth steps per Ni
			$[\text{C}_4\text{H}_6]$ (mol/l)	$[\text{C}_8\text{H}_8]$ (mol/l)	C_4H_6 (mol/l)	C_8H_8 (mol/l)		
1	7.3	3.5	2.60	0.36	0.15	0.07	92	1235
2	5.2	5.0	2.46	0.78	0.25	0.24	205	1350
3	2.45	7.1	1.31	1.79	0.28	0.66	392	1290

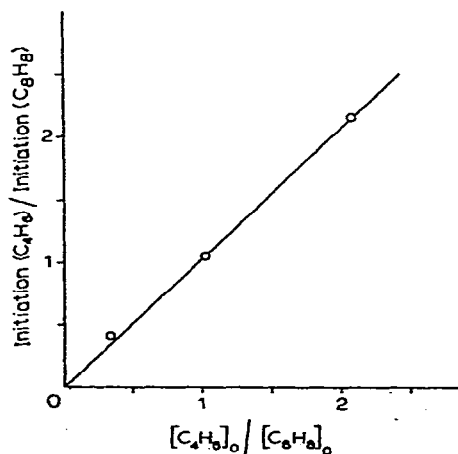


Fig. 9. Relative rates of chain initiation with butadiene [step a in eqn. (8)] and with styrene (step b).

Interestingly, the number of growth steps per nickel center is almost independent of the composition of the reaction solution (last column in Table 9). This appears to indicate that the rate constants of propagation of the two monomers are not very different. This, as well as the similarity of the rate constants of initiation, shown in Fig. 9, may be taken as an additional support for a common allylic growth mechanism for both monomers.

Finally, the data of Table 9 also permit an estimate of the copolymerization parameters according to standard methods¹⁷. The result is $r_1 = 5 \pm 1$, $r_2 = 0.6 \pm 0.2$ ($M_1 = \text{butadiene}$).

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