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Initiation and Propagation Steps in the Equibinary Polymerization of Butadiene by Bis(h^3-Allylnickel Trifluoroacetate)

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Synopsis

Polymerization of butadiene by bis(h^3-allylnickel trifluoroacetate) in benzene and *o*-dichlorobenzene solvents yields an equibinary 1,4-polybutadiene, containing equal amounts of *cis* and *trans* isomers. Initiation proceeds by addition of the allylic moiety of the initiator to a butadiene molecule. The rate of initiation is high enough to ensure complete consumption of the catalyst for a monomer/catalyst molar ratio of about 10 at 5°C. The propagation exhibits the characteristics of a "living" polymerization: the molecular weight is proportional to the conversion, and at the end of the reaction, the average degree of polymerization is equal to the monomer/catalyst molar ratio. Living polybutadienyl-nickel trifluoroacetate is able to reinitiate not only butadiene polymerization but also allene polymerization. However, for high [monomer]/[catalyst] ratios, conversion-dependent transfer reactions limit the molecular weight to 7000 in benzene and to 70,000 in bulk polymerization in the presence of small amounts of *o*-dichlorobenzene.

INTRODUCTION

Bis(h^3-allylnickel trifluoroacetate) is an excellent catalyst for the 1,4-polymerization of butadiene. It exhibits a very high activity, as well as an ability to induce a large variety of microstructures (from 95% *cis* to 99% *trans*), depending on the ligands used and the experimental conditions chosen.[1,2] In aromatic solvents such as benzene or *o*-dichlorobenzene, an "equibinary" polybutadiene is produced by this catalyst;[1] we have studied the initiation and propagation steps of the polymerization under these latter conditions.

EXPERIMENTAL

All manipulations were performed under a dry argon atmosphere or under vacuum in order to exclude oxygen and moisture.

Bis(h^3-allylnickel trifluoroacetate) was prepared by addition of allyl trifluoroacetate on freshly recrystallized bis(*cis,cis* 1,5-cyclooctadiene)-nickel(0).[3]

Butadiene was purified by passing through $CaSO_4$, KOH, BaO, and columns filled with 3Å Molecular Sieves before condensation on a sodium mirror. It was then distilled directly into polymerization vessels.

Polymerization reactions were carried out in sealed tubes. They were stopped by addition of acetic acid to the reaction mixture, the introduction of air being avoided as much as possible. It was found that oxygen causes a coupling reaction of the h^3-allylic ligands of the active sites: this fact was also reported by Harrod and Wallace[4] for a bis(h^3-crotylnickel iodide) catalyst. The nickel was removed from the polymer solution by washing with an aqueous solution of EDTA.

The polybutadienes produced in benzene were isolated by evaporating the solvent (by reduced pressure distillation) while those of higher molecular weights produced in *o*-dichlorobenzene were precipitated in methanol.

Gas–liquid chromatographic analyses were performed on an Intersmat IGG 15 apparatus with the use of silicone SE30 columns, with a temperature increase program from 100 to 250°C at a rate of 10°C/min. Commercially available linear alkanes (Fluka undecane, pentadecane, nonadecane, and tricosane) were used for identification of the products.

Nuclear magnetic resonance spectra were recorded on a Varian HA100 apparatus. The solvent (benzene) was used as internal lock. Tetramethylsilane (TMS) was added in very small amounts so that its intensity was similar to that of the other resonance peaks.

Low molecular weights ($\bar{M}_n < 10{,}000$) were measured on a Knauer vapor-pressure osmometer. Higher molecular weights were determined by viscosity measurements in toluene at 30°C.

Gel-permeation chromatographic study of the molecular weight distributions was performed in THF at 25°C on a Waters apparatus equipped with four Styragel columns. Universal calibration was established with monodisperse polystyrene samples. $\bar{M}_n$ and $\bar{M}_w$ were calculated according to Balke and Hamielec[5] by use of their viscosity–molecular weight relationship for 1,4-polybutadiene

$$[\eta] = 1.56 \times 10^{-4} \bar{M}^{0.80}$$

Infrared spectra were recorded in CS_2 solutions on a Perkin-Elmer 21 apparatus. The microstructure was calculated from the spectra according to Morero[6] for polybutadiene and to Van den Enk[7] for polyallene.

RESULTS AND DISCUSSION

The Initiation Step

A first insight into the initiation step was given by gas-liquid chromatographic (GLC) analysis of the oligomers. Polymerization was carried out in benzene at a low monomer/catalyst ratio (M/C) (i.e., [BD] = 0.2 mole/l. and [h^3-allylnickel trifluoroacetate] = 0.05 mole/l.), at 40°C to a low conversion; the reaction mixture was then directly hydrogenated on palladium dispersed on charcoal.

TABLE I
Yield of Oligomers Detected by GLC Analysis[a]

Product	Yield relative to the butadiene introduced, moles	Yield, g
$C_{11}H_{18}$	2.2	4.4
$C_{15}H_{24}$	2.1	6.3
$C_{19}H_{30}$	1.3	5.2
$C_{23}H_{36}$	0.88	4.4

[a] [Ni] = 0.05 mole/l.; [BD] = 0.2 mole/l.; reaction stopped after 120 min at 40°C.

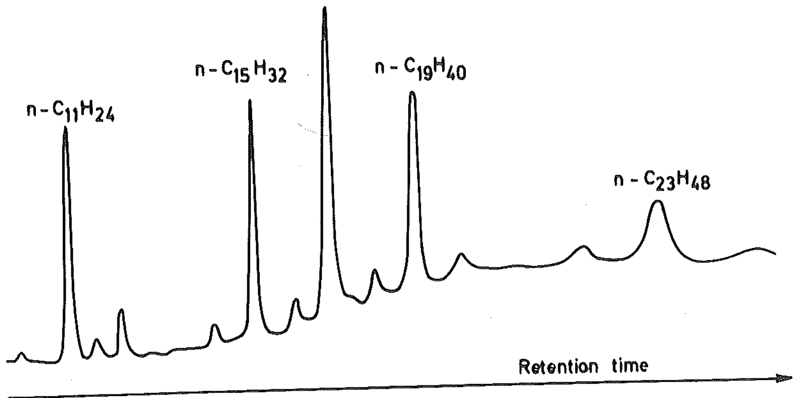


Fig. 1. Gas-liquid chromatography (after hydrogenation) of the oligomers produced in the reaction of bis(h^3-allylnickel trifluoroacetate) with butadiene.

GLC analysis of the solution gave evidence for the formation of undecane, pentadecane, nonadecane, and tricosane, i.e., linear oligomers having (3 + 4*n*) carbon atoms (Fig. 1). No other products were detected in significant amounts, except for a peak appearing between $C_{15}H_{32}$ and $C_{19}H_{40}$; the origin of this product is thought to be a side reaction (leading to a cyclic oligomer; indeed, the retention time of this peak seems to indicate a cyclo-$C_{15}H_{30}$), but its structure was not further investigated, since the presence of small amounts of this side product do not invalidate the above conclusions.

Heptane is expected to be the first product of the reaction but could not be distinguished from the solvent with the type of column used in the experiments. The fact that every oligomer isolated has (3 + 4*n*) carbon atoms indicates clearly that the allylic ligand of the initiator is now bound to the polybutadiene chain.

An experiment performed with the use of cyclododecane as internal reference allowed us to determine the relative yield of oligomer (see Table I). The decrease in yield with increasing molecular weight indicates that, at this stage of the reaction, propagation has occurred only to a small extent, suggesting that rate of initiation and rate of propagation are about of the same order of magnitude.

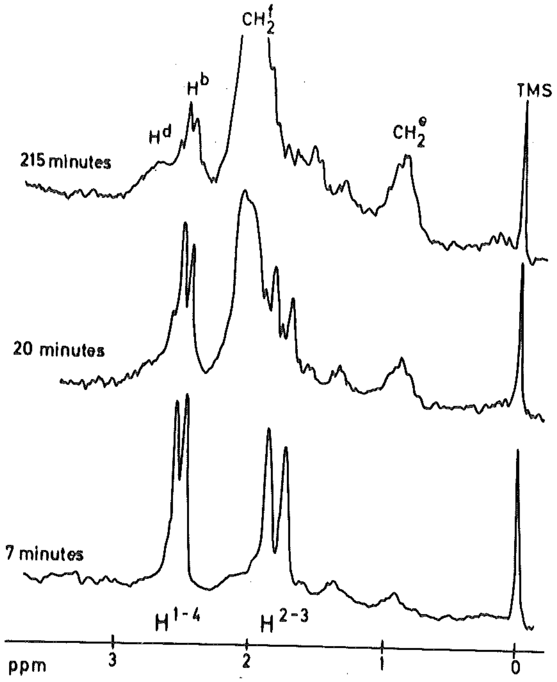
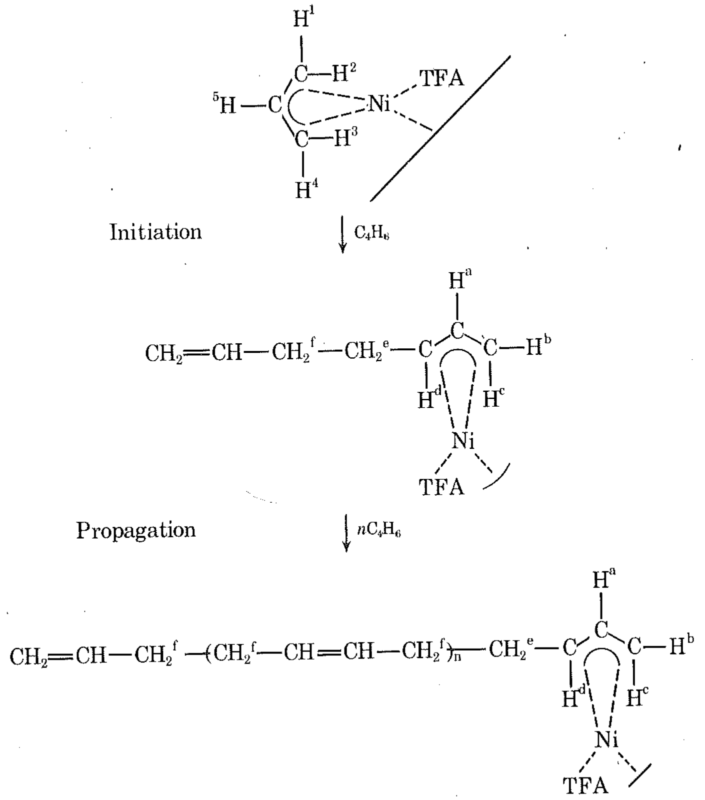


Fig. 2. NMR spectra showing conversion of initiator into endsgroups of growing chains.

Further evidence was obtained from NMR experiments. The NMR spectrum of the initiator bis(h^3-allylnickel trifluoroacetate) shows two doublets centered at $\delta = 2.58$ ppm and $\delta = 1.85$ ppm, corresponding respectively to the 1,4 protons and 2,3 protons (see Scheme I and Fig. 2). Resonance of proton 5 is found at lower field ($\delta = 5.10$).

Adding butadiene to a solution of (h^3-allyl-Ni TFA)$_2$ causes the progressive disappearance of the two doublets, while other resonance peaks were found to grow (Fig. 2). The final spectrum is the same as that of polybutadienyl-nickel trifluoroacetate. The assignments given Figure 2 and Scheme I together with exact chemical shifts have been previously described.[8] The complete disappearance of the doublets due to the initiator suggests that every allyl group bound to a nickel atom of the initiator gives rise to one polybutadiene chain, since new significant resonance peak do not appear in the spectra. However, transfer reactions can be detected for small values of M/C (less than 10). The resulting species exhibit absorptions at $\delta = 0.22$ ppm (doublet) for the methyl group of h^3-crotylnickel trifluoroacetate and at 1.60 ppm (doublet) for the methyl endgroup of the chains initiated by this new catalyst. The last butadiene molecule inserted is bound to the nickel in a h^3-allylic form, at least in most cases (see Scheme I).

It was previously found by Bourdauducq and Dawans,[2] using ^{14}C-labeled carbon monoxide, that every nickel atom of the catalyst is active in the polymerization.



Scheme I

When perdeuterobutadiene was used, the organic moiety of the initiator was found after reaction under the form of $CH_2{=}CH—CH_2—CD_2—CD{=}$ (methylene doublet centered at $\delta = 1.95$ ppm). Similarly, on starting from bis(h^3-crotylnickel trifluoroacetate) as initiator, the methyl resonance at $\delta = 0.26$ ppm was found after reaction with butadiene at $\delta = 1.58$ ppm, corresponding to $—CH{=}CH—CH_3$. The same result was obtained by Lobach and co-workers with a bis(h^3-crotylnickel iodide) catalyst.[9]

Consequently, both GLC analysis and NMR results indicate that the initiation reaction proceeds by addition of the allylic ligand to a coordinated butadiene molecule, as shown on Scheme I, in agreement with a *cis*-rearrangement reaction as proposed by Cossee.[10] Considering this scheme, we can see that the increase of the CH_2^e resonance in the NMR spectra is typical of the initiation step, while the increase of the CH_2^f resonance is due to the growth of the polymeric chain, i.e., the propagation step. The relative intensities to TMS of these two resonances are shown in Figure 3. Also shown in Figure 3 is the integrated intensity of the resonances from $\delta = 2.3$ ppm to $\delta = 3.2$ ppm, corresponding to protons 1 and 4 of the initiator and protons b and d of the growing polymeric chain. As expected, the intensity of this latter group of resonances is found practically

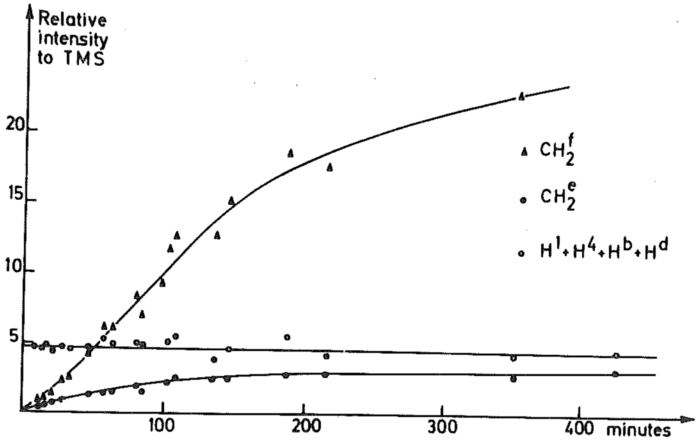


Fig. 3. Evolution with time of the relative intensities in the NMR spectra: (Δ) CH_2^f; (●) CH_2^e; (○) $H^1 + H^4 + H^b + H^d$. [butadiene], 1.1 mole/l.; [Ni], 0.2 mole/l.; temperature, 5°C.

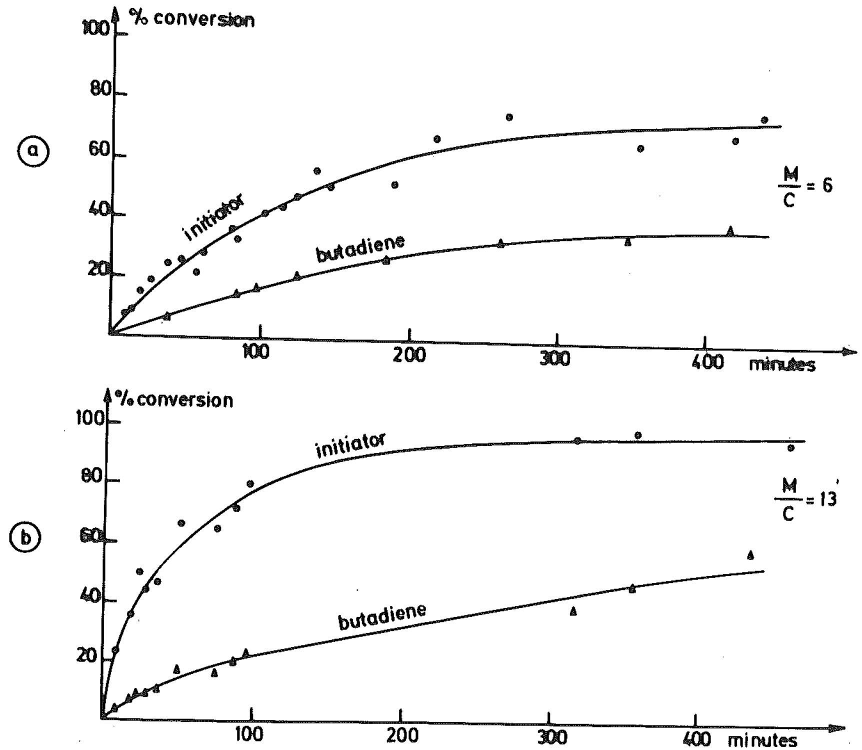


Fig. 4. Conversions of (●) initiator and (▲) butadiene as measured by NMR spectroscopy: (*a*) [BD], 1.1 mole/l., [Ni], 0.2 mole/l., temperature, 5°C; (*b*) [BD], 1.3 mole/l., [Ni], 0.1 mole/l., temperature, 5°C.

TABLE II

Percentage of Converted Butadiene and $\overline{DP}_n$ at Different Stages of Initiation in Benzene at 5°C for Different M/C[a]

	M/C = 6[b]		M/C = 13[c]		M/C = 20[d,e]	
Conversion (initiator), %	Conversion (butadiene), %	$\overline{DP}_n$	Conversion (butadiene), %	$\overline{DP}_n$	Conversion (butadiene), %	$\overline{DP}_n$
25	8	1.9	4	2.1	~2	~1.6
50	22	2.6	11	2.9	~4	~1.6
75	38	3.0	21	3.7	~8	~2.1
100	—	—	~50	~6.5	~17	~4.5

[a] The $\overline{DP}_n$ of the growing polymeric chains is equal to (M/C) CV(butadiene)/CV (initiator).

[b] For M/C = 6, [BD] = 1.1 mole/l., [Ni] = 0.2 mole/l.

[c] For M/C = 13, [BD] = 1.3 mole/l., [Ni] = 0.1 mole/l.

[d] For M/C = 20, [BD] = 1.6 mole/l., [Ni] = 0.08 mole/l.

[e] The accuracy of measurements for M/C = 20 is poor due to the large difference between monomer and catalyst concentrations.

constant during the whole reaction; indeed, for every H^1 and H^4 disappearing through initiation, one H^b and one H^d appear, so that the intensity of the resonances between $\delta = 2.3$ ppm and $\delta = 3.2$ ppm is constant and equal to two protons.

Let us call the intensity of this group of resonances A. The intensity of the other resonances will be B for CH_2 protons of butadiene at $\delta = 5.1$ ppm, E for CH_2^e protons of active site at $\delta = 0.93$ ppm, and F for CH_2^f protons of the polymeric chain at $\delta = 1.95$ ppm.

The percentage of the initiator converted to growing polymeric chains will be given by

$$\% \text{ Conversion (initiator)} \equiv \text{CV (initiator)} = (E/A) \times 100 \qquad (1)$$

The percentage of butadiene converted to polybutadiene will be given by:

$$\% \text{ Conversion (butadiene)} \equiv \text{CV (butadiene)} = [(F + E)/(F + B)] \times 100 \qquad (2)$$

Analyses of the spectra as a function of time were performed according to eqs. (1) and (2). Typical results are shown in Figures 4 and 5. Keeping in mind the monomer/catalyst ratios (M/C) used, it is evident that propagation has started before the end of the initiation step. Thus an excess of monomer is needed to ensure complete consumption of the initiator.

From Figure 4 and Table II, the critical M/C needed under these conditions for complete consumption of the initiator can be estimated to be about 7–10. This is a value expected for a system of competitive and consecutive reactions (i.e., initiation and propagation) occurring at rates having about the same order of magnitude.

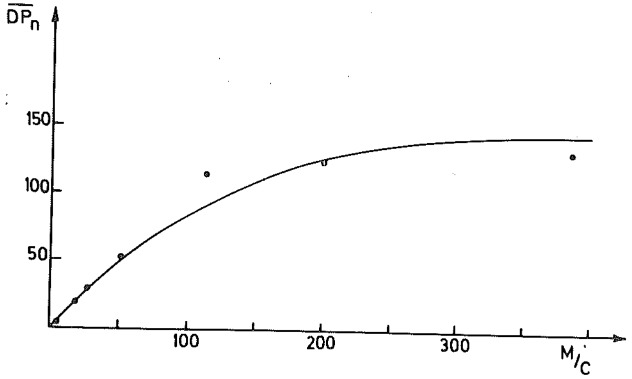


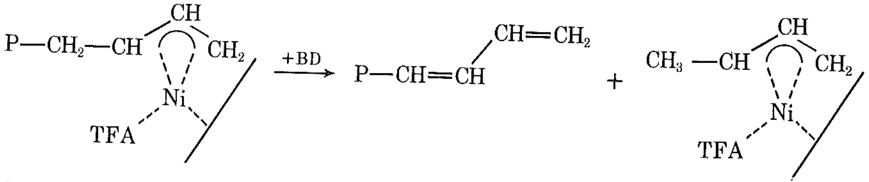
Fig. 5. $\overline{DP}_n$ as a function of M/C, in benzene. [BD], 1.2 mole/l.; temperature, 5°C.

The Propagation Step

Kinetic results on the propagation step, published previously,[1] showed first kinetic order in monomer and catalyst. Our present report deals with the molecular weight of polybutadienes obtained in benzene and *o*-dichlorobenzene.

In Benzene. For low M/C, the initial average degree of polymerization $\overline{DP}_n$ is equal to the M/C used as shown in Figure 5. Thus every nickel atom of the catalyst is the source of one polymeric chain, as was already suggested by our study of the initiation step. However, for higher M/C, no additional increase in molecular weight is observed. This can be ascribed to hydride transfer reactions limiting the molecular weights in benzene to about 4000 at 40°C and 7000 at 5°C; simultaneously, a broadening of the molecular weight distribution is observed.

In some of the NMR spectra recorded during polymerization, small amounts of h^3-crotylnickel trifluoroacetate have been detected at high conversion and suggest that a transfer reaction occurs via a hydride abstraction, the h^3-crotylnickel trifluoroacetate



formed being able to reinitiate (more slowly) the polymerization. Similar transfer reactions were found by Harrod and Wallace[4,11] and by Henrici-Olivé et al.[12] in the *trans*-1,4-polymerization of butadiene by bis(h^3-crotylnickel iodide).

Evidence for the "living" character for low M/C ratios was given by seeding experiments. After consumption of a first lot of monomer, introduction of an additional monomer causes further polymerization with the expected increase in the molecular weight (see Table III).

TABLE III
Seeding Experiments[a]

Run	First lot of butadiene, mole × 10^2	Second lot of butadiene, mole × 10^2	Nickel, mole × 10^4	$\bar{M}_n$ Exptl.	$\bar{M}_n$ Calcd
Ia	3.3	—	6.2	2930	2900
Ib	3.3	4.5	6.2	6270	6820
IIa	6.0	—	21.	1620	1550
IIb	6.0	6.0	21.	3140	3100

[a] Solvent, benzene; temperature, 5°C; runs Ia and Ib, [Ni], 0.01 mole/l., runs IIa, IIb [Ni], 0.04 mole/l.

TABLE IV
Relation of Microstructure of Polybutadienes to Their Molecular Weight

	Microstructure found			% Vinyl calcd
$\overline{DP}_n$	% *cis*	% *trans*	% Vinyl	
3	30	45	25	25
6	30	54	16	14
7	35	50	15	12.5
23	48	47	5	4
40	51	48	1.2	2.5
96	53	45	2	1.0

Experimental $\bar{M}_n$ was measured at total conversion of butadiene, the weight of polybutadiene being equal to the weight of butadiene introduced before the polymerization.

The microstructures of the polybutadienes produced in the "living" range of conditions were also significant of the mechanistic process. The vinyl content decreased with increasing molecular weight in such a way that it can be exactly attributed to the allyl group of the initiator bound at the end of the polymeric chain. This is shown in Table IV, where the calculated vinyl content has been computed according to the above hypothesis.

In *o*-dichlorobenzene. The same trend was found when *o*-dichlorobenzene was used as solvent, except that much higher molecular weights are reached (Fig. 6).

The "living" character was proved by the linear increase of the molecular weight with conversion in a certain range of $\overline{DP}_n$ (Fig. 7); gel permeation chromatography data are also indicative of the progressive appearance of transfer reactions when higher values are reached (see Table V).

A surprising factor controlling the molecular weights is the amount of solvent used, in other words, the relative concentrations of butadiene and *o*-dichlorobenzene (*o*-DCB). The data of Table VI show that an increase in the concentration of *o*-dichlorobenzene causes a relative decrease in the experimental molecular weight versus the calculated one, i.e., the transfer reaction is favored.

These latter experiments are in fact bulk polymerizations in which *o*-dichlorobenzene is used as an "additive" to obtain the equibinary microstructure. If still smaller amounts of *o*-dichlorobenzene are used, an increase in cis-1,4 content is observed, along with an increase of the molecular weight (Table VII), as expected from the competitive nature of the equibinary phenomenon.

TABLE V

Molecular Weight and Dispersity of Polybutadienes Obtained in Presence of *o*-Dichlorobenzene at 5°C

[Ni] × 10³, mole/l.	Catalyst ×10³, mole	Butadiene, mole	Additional butadiene, mole[a]	$\bar{M}_n$ ×10⁻³	$\bar{M}_w$ ×10⁻³	$\bar{M}_w/\bar{M}_n$
7.4	0.3	0.10	—	15.4	20.7	1.35
7.4	0.3	0.10	0.10	25.6	34.3	1.34
3.8	0.17	0.47	—	62.8	162.0	2.57

[a] Seeding experiment; this amount of butadiene was introduced after polymerization of the first lot of monomer.

TABLE VI

Effect of *o*-DCB Concentration on Molecular Weights

[*o*-DCB], mole/l.	Microstructure, % *cis*	Molecular weight ×10⁻³ Exptl (viscometric)	Molecular weight ×10⁻³ Calcd (from M/C)	$M_{\text{exptl}}/M_{\text{calcd}}$
0.95	52	66.0	119.0	0.55
2.1	49	70.4	230.0	0.32
4.2	53	32.42	119.0	0.27

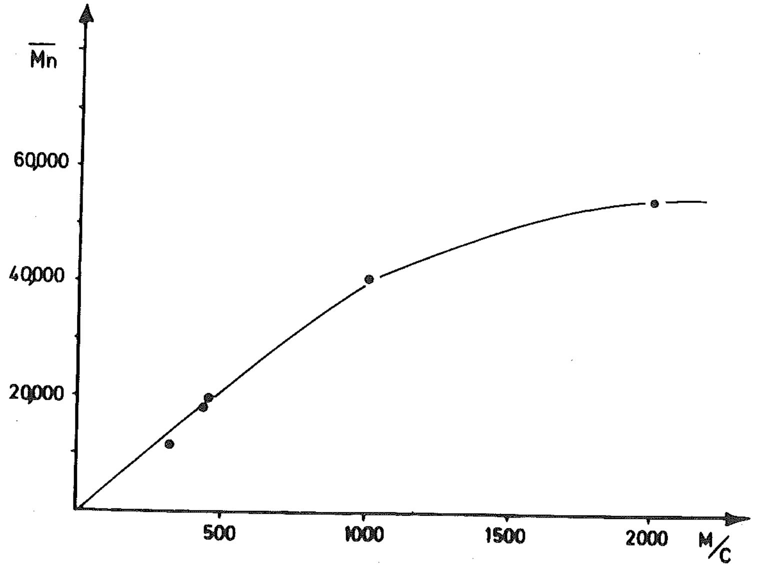


Fig. 6. Number-average molecular weights as a function of M/C. Solvent, *o*-dichlorobenzene; [BD], 2 mole/l.; temperature, 5°C.

TABLE VII

Dependence of Molecular Weight and Microstructure on the Ratio [*o*-DCB]/[Ni][a]

[*o*-DCB]/[Ni]	Molecular weight ×10⁻³ (viscometric)	% *cis*-1,4
1850	32.0	47
820	66.0	56
500	99.1	65
0	180.0	84

[a] M/C = 2000; temperature, 5°C; [Ni] = 5 × 10⁻³ mole/l.

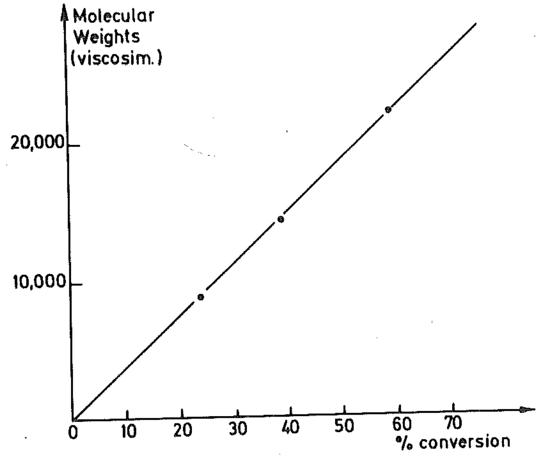


Fig. 7. Molecular weight (viscometric) as a function of conversion in *o*-dichlorobenzene. [BD], 2.5 mole/l.; [Ni], 3.7 × 10⁻³ mole/l.; temperature, 5°C.

A possible cause for the transfer reaction was thought to be the presence of monoolefins (up to 0.5 %) in commercial butadiene. Monoolefins are indeed known to induce transfer reactions in h^3-allylic polymerization by formation of an unstable Ni–C σ bond. However experiments with rigorously purified butadiene (via butadienyl sulfone) have shown no difference in the molecular weights compared to those obtained in experiments with commercial butadiene.

It appears consequently that the transfer process might be related to the concentration and nature of the aromatic solvent, most probably because of its destabilizing interactions within the coordination sphere.

Reactivity of the Active Chain End

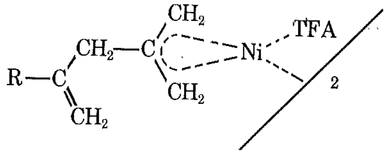
The oligomeric polybutadienyl-nickel trifluoroacetates are living species, not only able to reinitiate butadiene polymerization, but also to be involved in organic reactions typical of the h^3-allylnickel bond. We have performed, e.g., reactions with benzyl bromide, acrylonitrile, and allene.

Benzylic bromides were shown by Corey[13] to react with h^3-allylnickel halides in a Wurtz-like reaction. We found that after addition of benzyl bromide to polybutadienyl-nickel trifluoroacetate, about 85% of the chain ends were capped with a benzylic group, as determined by ultraviolet spectroscopy.

Acrylonitrile is also known to add to the allylic moiety of h^3-allylnickel compounds.[14] When acrylonitrile was added at the end of a polymerization, the polybutadiene isolated from the reaction mixture contained about one nitrile group per chain, as shown by the infrared spectrum.

Whereas only one molecule of acrylonitrile is added to the allylic moiety, allene is homopolymerized by h^3-allylnickel halides.[7,8] First, we checked homopolymerizability of allene by our initiator. Its addition to a solution of bis(h^3-allylnickel trifluoroacetate) resulted in a deep red coloration, and a rapid polymerization, much faster, in fact, than that of butadiene itself under similar conditions. Polyallene displaying a 1,2–1,2 structure, of molecular weight up to 3000 was obtained.

Another experiment was also performed in which allene was added to an oligomeric polybutadienyl-nickel trifluoroacetate. Again, an immediate deep red color appeared, and polymerization of allene occurred. GPC analysis of the product indicated a monomodal distribution, with a peak appearing on the elution scale at higher molecular weights than the peak of a reference sample where allene was not added. The product is therefore thought to be a block copolymer of butadiene and allene. When allene and butadiene are added together to the initiator, as in the usual random copolymerizations, allene is polymerized, but not butadiene. The active chain end of polyallene is probably of the h^3-allylic type, i.e., very stable and reluctant to add butadiene owing to allylic substitution on C-2 of the h^3-allyl ligand.



An attempt to synthesize a stereoblock polybutadiene was also made, starting from "living" equibinary polybutadienylnickel trifluoroacetate, to which triphenyl phosphite (TPP) was added together with a second lot of butadiene. (TPP is known indeed to induce trans-1,4-polymerization of butadiene.[2]) This second lot of monomer was polymerized and the crude product was found to contain 75% of *trans*-1,4 units. However, fractionation of this crude product at low temperature resulted in the separation of a high *trans*-1,4-polybutadiene from an equibinary-type polymer (Table VIII).

Thus, as soon as the catalyst structure is modified to produce *trans*-1,4 polymerization, a transfer reaction occurs separating the equibinary chain from the incipient *trans*-1,4 chain.

TABLE VIII
Fractionation of Polybutadiene in Diethyl Ether at −50°C

Nature of the fraction	% of total weight	Microstructure		
		% *cis*	% *trans*	% Vinyl
Crude product	100	22	75	3
Ether-insoluble	58	11	86	3
Ether-soluble	42	41	57	2

CONCLUSIONS

In equibinary polymerization of butadiene by h^3-allylnickel trifluoroacetate, initiation and propagation steps display the same fundamental characteristic, i.e., the addition of the h^3-allylic ligand to a butadiene molecule. The similarity of the two steps can be taken as the source of the following features: not only is all of the initiator active in polymerization, but the rate of initiation is high enough to ensure easily a complete consumption of the complex. Two other initiators are known to behave similarly: bis(h^3-crotylnickel-iodide) is consumed completely in the initiation step of the *trans*-1,4 polymerization of butadiene;[9,10] with tris-(h^3-allyl)Cr as initiator for the 1,2 polymerization of butadiene, the three allyl groups of every initiator molecule disappear in the beginning of the polymerization.[15]

With bis(h^3-allylnickel trifluoroacetate), however, we have shown with certainty that the allyl group which has disappeared during the initiation step is bound to the polymeric chain. Moreover, under certain conditions, this initiator leads to a "living"-type polymerization rarely observed in coordination polymerization. However, hydride transfer reactions may also take place in this system and limit the molecular weights.

There is a relationship between the occurrence of transfer reactions and the equibinary phenomenon, as the same bis(h^3-allyl-nickel trifluoroacetate) in the absence of an aromatic ligand gives a *cis*-rich polybutadiene of high molecular weight. This confirms that a definite catalytic species is formed in aromatic solvents which is specific towards equibinary polymerization. The existence and the stereospecificity of such a species has been strongly supported by analysis of the variable distribution of *cis* and *trans* double bonds in the polybutadiene chains.[16]

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Reactivity of Methacrylates in Anionic Copolymerization with Methyl Methacrylate by *n*-BuLi

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Synopsis

Monomer reactivity ratios, r_1 and r_2, were determined in the anionic copolymerizations of methyl methacrylate (MMA, M_1) with ethyl (EtMA), isopropyl (*i*-PrMA), *tert*-butyl (t-BuMA), benzyl (BzMA), α-methylbenzyl (MBMA), diphenylmethyl (DPMMA), α,α-dimethylbenzyl (DMBMA), and trityl (TrMA) methacrylates (M_2) by use of *n*-BuLi as an initiator in toluene and THF at −78°C. The order of the reactivity of the monomers towards MMA anion was DPMMA > BzMA > MMA > EtMA > MBMA > *i*-PrMA > *t*-BuMA > TrMA > DMBMA in toluene and TrMA > BzMA > MMA > DPMMA > EtMA > MBMA > *i*-PrMA > DMBMA > *t*-BuMA in THF. Except for the extremely low reactivity of TrMA and DPMMA in toluene due to steric hindrance, the order was explained in terms of the polar effect of the ester groups. A linear relationship was found between $\log(1/r_1)$ and Taft's σ^* values of the ester groups, where the ρ^* value was 1.1. The plots of $\log(1/r_1)$ vs. the ^1H_a (*cis* to the carbonyl) and $^{13}C_\beta$ chemical shifts of the monomers were also on straight lines. The polymer obtained in the copolymerization of MMA with TrMA in toluene by *n*-BuLi at −78°C was a mixture of poly-MMA and a copolymer, suggesting that there exist two kinds of growing centers.

INTRODUCTION

Only monomers having a similar polarity can be copolymerized by anionic initiators; for instance, styrene derivatives can be copolymerized with each other but styrene is unable to add to MMA anion.[1–3]

Although a number of studies have been done on the stereospecific polymerizations of methacrylates by anionic initiator,[4–13] there have been a few reports on anionic copolymerizations between methacrylates. Ito et al.[14] have reported the anionic copolymerization of methyl methacrylate (MMA) with benzyl methacrylate (BzMA) by various anionic catalysts in toluene and THF at 0°C. Bevington et al.[15] studied the system of MMA and cyclohexyl methacrylate, using sodium naphthalene in dioxane. Vlcek and co-workers have investigated the copolymerization of MMA with 2-methoxyethyl and 2-(*N*,*N*-dimethylamino)ethyl methacrylates with lithium *tert*-butoxide in benzene at 20°C.[16] These authors have determined monomer reactivity ratios in the copolymerizations. In a previous communication,[17] we reported preliminary results on the monomer reactivity ratios in the copolymerizations of MMA with the methacrylates (RMA) of