

Homo- and Copolymerization with a Highly Active Ziegler–Natta Catalyst

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Synopsis

The copolymerization of ethylene and 1-butene with a highly active Ziegler–Natta catalyst has been investigated at different temperatures. The r parameters and the propagation rate constants have been determined. From the temperature dependence of the rate constants, entropy and enthalpy values have been calculated. These data show the enthalpy values to be small in comparison to entropy, which means that these processes are predominantly controlled by entropic factors.

INTRODUCTION

In homogeneous as well as heterogeneous Ziegler–Natta processes, polyethylene formation increases with ethylene pressure or ethylene concentration in the reaction medium.^{1–5} For classical Ziegler–Natta systems it has been found that the rate of polymerization is proportional to the ethylene concentration in the hydrocarbon solvent.^{6,7} Highly active catalytic systems show the same behavior, provided the monomer concentration, or ethylene pressure, exceeds a critical value, which can be different for each catalytic system.⁸ Consequently, it can be concluded from these results that the rate of polymerization is proportional to monomer concentration if the polymerization process is kinetically controlled.

This correlation between rate of polymerization and monomer concentration and other experimental observations can be best understood by assuming that this catalytic process occurs as described by the Rideal mechanism.⁹ It has been shown^{2,10} that the Rideal mechanism also includes the Cossee model,¹¹ which has been proposed to explain the Ziegler–Natta polymerization process. According to this mechanism the most important step is the complexation of the active transition metal center by the monomer molecule.¹²

To get more insight in this complexation process, polymerizations with different monomers have been performed. It is well known that the two r parameters for the binary copolymerization of ethylene and α -olefins with different Ziegler–Natta systems are different by orders of magnitude.^{13–15} For the copolymerization of ethylene and 1-butene with Ziegler–Natta systems the r parameters differ by factors in the range of 1000. On the contrary, they are only different by factors in the range of 2 in the case of radical copolymerization.¹⁶ This shows again that there are specific interactions between active site and monomer in Ziegler–Natta processes.

In this paper the homopolymerization of ethylene and the copolymerization

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of ethylene and 1-butene with a highly active Ziegler–Natta system as functions of temperature have been studied. The experiments have been evaluated on the basis of a copolymerization model for Ziegler–Natta processes,¹⁷ which is consistent with the Mayo–Lewis theory¹⁸ for binary copolymerization. Using this model, r parameters and rate constants can be calculated from experimental results. From the temperature dependence of these rate constants enthalpy and entropy data can be calculated.

EXPERIMENTAL

The experiments have been performed in diesel oil as described elsewhere.^{12,17} To get reproducible results, the polymerization process was started with ethylene alone over a period of 10 min in comparison to 4 h for the total experiment. After 10 min the comonomer (1-butene) was rapidly added over a maximum period of 5 min to reach a certain comonomer level in comparison to ethylene in the gaseous phase of the reactor. The gaseous phase composition was controlled by GC. All components (C_2H_4 , 1-butene, H_2) were then fed to the reactor continuously to maintain a constant gaseous phase composition. From total pressure (between 2 and 6 bar) and gaseous phase composition the concentrations of the different compounds in the reaction medium were calculated using Henry's equation with the following coefficients: $\log \lambda_{C_2H_4} (\text{mol}\cdot\text{dm}^{-3}\cdot\text{bar}^{-1}) = -2.209 + 410/T$ (K), $\log \lambda_{C_4H_8} = -3.38 + 1130/T$, and $\log \lambda_{H_2} = -0.819 - 543/T$.

When high amounts of 1-butene are added, the solubility of ethylene in the diesel oil 1-butene mixture changes. This has been considered by calculating the Henry coefficient of ethylene in 1-butene from our and published data¹⁹: $\log \lambda_{C_2H_4} = -2.200 + 480/T$. In the range between 50°C and 120°C, the solubility of ethylene in 1-butene compared to diesel oil is higher by a factor of around 1.5. The Henry coefficient of ethylene in the diesel oil 1-butene mixture was calculated using the following equation: $\lambda = \lambda_s X_s + \lambda_{C_4H_8} \cdot X_{C_4H_8}$. The copolymer composition was investigated by ¹³C-NMR measurement according to the procedure described elsewhere.²⁰ At 120°C the copolymer is soluble in diesel oil. At temperatures lower than 100°C there is a soluble and an insoluble copolymer fraction. The composition of both fractions must be determined by analyzing these fractions separately, as previously described.¹⁷ Both the ratio of ethylene and 1-butene concentrations, and copolymer composition can be evaluated in the range of $\pm 5\%$.

However, there is a further uncertainty in calculating the Mayo–Lewis parameters because these copolymers have a very broad molecular weight distribution in combination with a broad range of copolymer composition.¹⁷ Therefore, all data have to be regarded as average values, and it is not known over what range these data scatter.

DETERMINATION OF THE r PARAMETERS

The copolymerization data are collected in Table I. The data for 85°C have been published elsewhere.¹⁷ From these data the copolymerization parameters have been calculated on the basis of the following considerations. It is known that these parameters differ by orders of magnitude, and it has often been re-

TABLE I
Copolymerization of Ethylene (1) and 1-Butene (2) at Different Temperatures

Reaction conditions	$[M_2]/[M_1]$	$(n_2/n_1)_P$
120°C, without H ₂	0	0
	0.22	0.0050
	0.44	0.0101
	0.66	0.0142
	1.10	0.0204
	1.96	0.0462
	2.12	0.0370
	3.81	0.0930
	7.48	0.166
	13.7	0.266
	19.0	0.445
	37.5	1.24
	49	1.56
65°C, without H ₂	99	8.43
	0	0
	0.17	0.0016
	0.18	0.0018
	0.37	0.0024
	0.50	0.0042
	0.81	0.0066
	1.15	0.0097
	1.71	0.0154
	2.08	0.0230
	2.36	0.0262
	2.57	0.0254
	4.32	0.0725
65°C, 18 vol % H ₂	5.29	0.0756
	0.23	0.0030
	0.69	0.0081
	1.53	0.0160
	2.64	0.0382
	2.97	0.0430
65°C, 44 vol % H ₂	4.26	0.0774
	0.46	0.0050
	1.32	0.0124
	4.71	0.0760
50°C without H ₂	6.46	0.124
	0	0
	0.15	0.0014
	0.67	0.0026
	1.70	0.0128
	3.20	0.0371
50°C, 28 vol % H ₂	5.58	0.0964
	0.18	0.0004
	0.36	0.0028
	0.92	0.0059
	1.79	0.0148
	4.81	0.0633
50°C, 62 vol % H ₂	6.81	0.102
	0.44	0.0030
	2.79	0.0386
	6.75	0.0883
	7.85	0.112

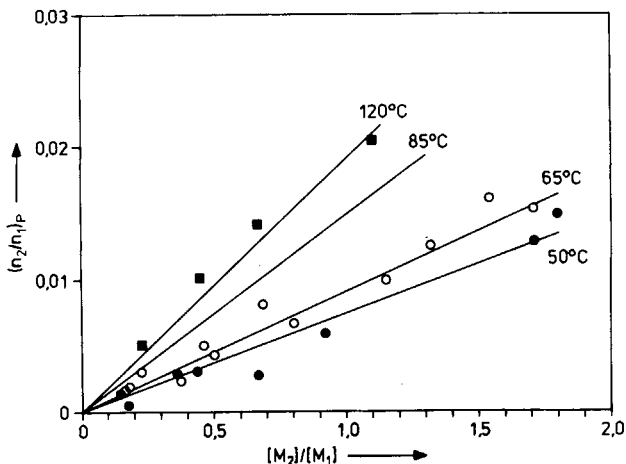


Fig. 1. Plot of copolymerization data according to eq. (1); ethylene (1) and 1-butene (2); parameter: temperature. The data for the 85°C experiments can be found elsewhere.¹⁷

ported that r_1 multiplied by r_2 is close to 1.^{3,13-15} For small comonomer contents in the copolymer, the Mayo-Lewis equation can thus be written as

$$\left(\frac{n_2}{n_1}\right)_P = \frac{1}{r_1} \frac{[M_2]}{[M_1]} \quad (1)$$

For different temperatures the data are plotted according to eq. (1) in the range of proportionality between $(n_2/n_1)_P$ and $[M_2]/[M_1]$ (Fig. 1). From the slope of these lines the parameters r_1 can be calculated. These values are collected in Table IV.

Using these r_1 values, the r_2 parameters can be evaluated by approximating the experimental data by calculated lines according to the Mayo-Lewis equation.¹⁸ In all cases the experimental values arrange themselves along the same line whether or not hydrogen is present.

In Table IV the parameters r_2 are again given as functions of temperature. It is seen that the r parameters differ by 3 orders of magnitude, that the temperature dependence is not very strong, and that the $r_1 \cdot r_2$ values are approximately 1 or slightly higher.

The temperature dependence can be described within experimental error by the following equations: $\log r_1 = -0.2 + 750/T$ and $\log r_2 = -3.2 + 750/T$. These lines are shown in Figure 2.

DETERMINATION OF THE RATE CONSTANTS

These values have been determined by investigating rates of copolymerization as functions of comonomer, monomer ratio according to¹⁷

$$\frac{F}{R_p} = \frac{1}{k_{12}} + \frac{1}{k_{21}} \frac{[M_2]}{[M_1]} \quad (2)$$

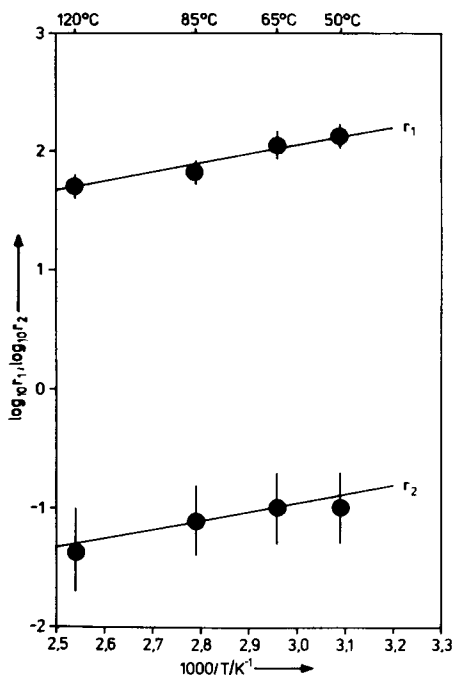


Fig. 2. Arrhenius plots of the r parameter; ethylene (1) and 1-butene (2).

with

$$F = M_{0,1} \left[r_1 + 3 \cdot \frac{[M_2]}{[M_1]} + 2r_2 \left(\frac{[M_2]}{[M_1]} \right)^2 \right] [M_1] \cdot \frac{n^*}{n_k} \quad (3)$$

To calculate the function F , the catalyst efficiency n^*/n_k must be known. These values have been determined for the homopolymerization process only, according to a procedure described elsewhere.¹² The experimental results are collected in Table II. The rate constants ($k_{11} \cdot n^*/n_k$) and k_{11} are shown as Arrhenius plots in Figure 3.

It can clearly be seen that the Arrhenius plot of the rate constant ($k_{11} \cdot n^*/n_k$) is curved, which means that under comparable conditions the rate of polymerization increases to a maximum at 85°C, and then falls with rising temperature. This effect corresponds to a change in catalyst efficiency. The rate constants for the homopolymerization of ethylene k_{11} show the familiar Arrhenius plot.

TABLE II
Determination of Rate Constants $k_{11} \cdot n^*/n_k$ and k_{11} , and Catalyst Efficiency n^*/n_k for Ethylene Homopolymerization

T (°C)	$k_{11} \cdot n^*/n_k$ (dm ³ /mol·s)	n^*/n_k	k_{11} (dm ³ /mol·s)
120	33	0.165 ± 0.05	200 ± 50
85	75	0.75 ± 0.2	100 ± 25
65	53	0.76 ± 0.2	70 ± 20
50	20	0.33 ± 0.1	60 ± 20

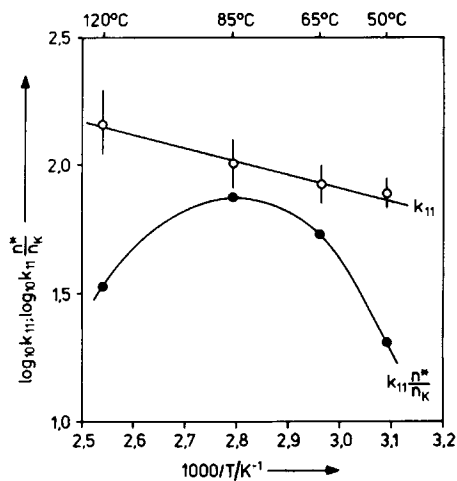


Fig. 3. Homopolymerization of ethylene; Arrhenius plots of rate constants $k_{11} \cdot n^*/n_k$ and k_{11} ; no hydrogen is present.

TABLE III
Determination of Rate R_p as Function of Ethylene and 1-Butene Concentration for Different Temperatures

Experimental conditions	$[M_2]/[M_1]$	$[M_1]$ (mol/dm ³)	R_p (g/mol·s)	(F/R_p) (g/mol·s)
120°C, without H ₂ , $r_1 = 51, r_2 = 0.02,$ $n^*/n_k = 0.165,$ $M_{0,1} = 28.054$ g/mol	0	0.257	243	0.25
	0.22	0.233	237	0.26
	0.44	0.205	226	0.25
	0.66	0.195	158	0.31
	1.10	0.188	140	0.35
	1.96	0.182	160	0.30
	2.12	0.165	146	0.30
	3.81	0.150	99	0.44
	7.48	0.140	98	0.50
	13.7	0.136	73	0.86
65°C, without H ₂ , $r_1 = 110, r_2 = 0.1,$ $n^*/n_k = 0.76$	19.0	0.136	69	1.12
	0	0.273	408	1.57
	0.17	0.229	337	1.60
	0.18	0.244	348	1.65
	0.37	0.238	342	1.65
	0.50	0.230	332	1.65
	0.81	0.213	301	1.70
	1.15	0.213	304	1.70
	1.71	0.218	299	1.80
	2.08	0.224	311	1.80
	2.36	0.230	313	1.85
	2.57	0.218	299	1.85
50°C, without H ₂ , $r_1 = 130, r_2 = 0.1,$ $n^*/n_k = 0.33$	4.32	0.137	181	2.05
	5.29	0.146	200	2.05
	0	0.518	287	2.17
	0.15	0.488	263	2.24
	0.67	0.434	236	2.25
	1.70	0.300	157	2.40
	3.20	0.135	72.5	2.44
5.58	0.161	82.6	2.76	

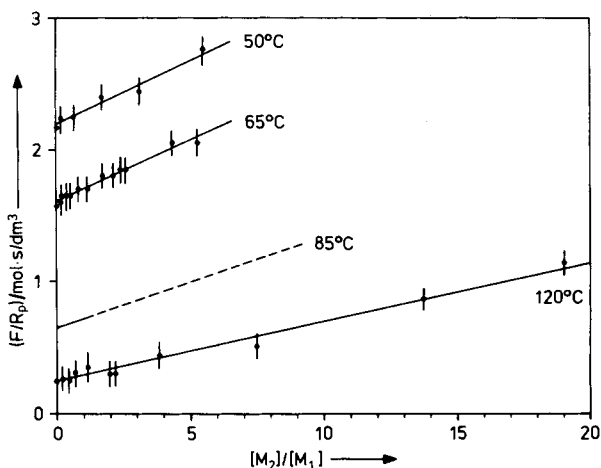


Fig. 4. Plot of copolymerization data according to eqs. (2) and (3); copolymerization without hydrogen; parameter: temperature. The data for the 85°C experiments can be found elsewhere.¹⁷

The rate constants k_{12} and k_{21} were determined by plotting the experimental data according to eq. (2), and by assuming that catalyst efficiency is constant for all homo- and copolymerization experiments under the described experimental conditions. The experimental data of these investigations are summarized in Table III. Data for 85°C can be found elsewhere.¹⁷ Figure 4 shows plots of these data. From the slope and intercept of these straight lines the rate constants can be calculated. In Table IV these data are collected in dependence of temperature together with the Mayo-Lewis parameters. The temperature dependence of these four rate constants which are the minimum requirement to describe binary copolymerization on the basis of the Mayo-Lewis theory is shown in Figure 5. It can be seen that the rate constants k_{12} and k_{22} are indistinguishable within experimental error. The data plotted in Figure 5 show that again the rate constants are different by orders of magnitude, but their temperature dependence is similar.

DISCUSSION

To interpret the Arrhenius plots of the different rate constants, it is necessary to look in more detail at the rate equation which has been evaluated on the basis of the Rideal mechanism.⁹ As it has been found that the rate of polymerization

TABLE IV
 r Parameters and Rate Constants of the Copolymerization Process of Ethylene (1) and 1-Butene (2) for Different Temperatures

T (°C)	r_1	r_2	k_{11} (dm ³ /mol-s)	k_{12} (dm ³ /mol-s)	k_{21} (dm ³ /mol-s)	k_{22} (dm ³ /mol-s)
120	51 ± 5	0.04 ± 0.02	200 ± 50	3.9 ± 2.5	22 ± 6	0.82 ± 0.6
85	67 ± 8	0.08 ± 0.04	100 ± 25	1.5 ± 1	14 ± 5	1.1 ± 0.5
65	110 ± 20	0.1 ± 0.05	70 ± 20	0.64 ± 0.3	11 ± 4	1.1 ± 0.5
50	130 ± 25	0.1 ± 0.05	60 ± 20	0.46 ± 0.2	10 ± 4	1 ± 0.5

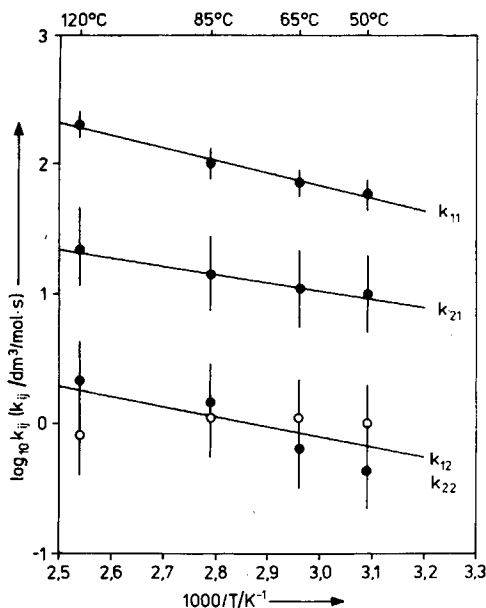


Fig. 5. Arrhenius plots of the four rate constants of binary copolymerization: ethylene (1) and 1-butene (2): (●) k_{11} ; k_{21} ; k_{12} ; (○) k_{22} .

is proportional to monomer concentration if this process is kinetically controlled, the rate equation can be written as

$$R_p = k_a \frac{k_p}{k_p + k_d} [M] \cdot \frac{n^*}{n_k} \quad (4)$$

with the rate constants k_a and k_d for formation and dissociation of the active center monomer complex and the rate constant k_p for the insertion of the complexed monomer into the transition metal carbon bond. Inhibition of this process by hydrogen and cocatalyst is not considered, because it is not relevant for this interpretation.

Two different cases have to be treated. If $k_p \gg k_d$, eq. (4) reduces to

$$R_p = k_a \cdot [M] \cdot (n^*/n_k) \quad (5)$$

In this case the polymerization rate depends only on the rate of complex formation, because each complexed monomer molecule is inserted at once. This is a bimolecular process, the temperature dependence of which can be described by the Eyring equation.²¹ So the temperature dependence of the propagation rate constant for this case is given by eq. (6)

$$k_{ij} \approx \frac{kT}{h} \exp \left(\frac{\Delta S_{ij}^\ddagger}{R} - \frac{\Delta H_{ij}^\ddagger}{RT} \right) \quad (6)$$

with ΔS_{ij}^\ddagger and ΔH_{ij}^\ddagger the activation entropy and enthalpy values.

On the other hand, if $k_d \gg k_p$, the rate R_p is given by

$$R_p = k_p \cdot \frac{k_a}{k_d} \cdot [M] \cdot \frac{n^*}{n_k} = k_p \cdot K \cdot [M] \cdot \frac{n^*}{n_k} \quad (7)$$

In this case the polymerization rate depends on the rate constant k_p and the equilibrium constant of complex formation K . If the temperature dependence of the first-order rate constant k_p is described by the Herzfeld equation,²² and the temperature dependence of the equilibrium constant K by the Van't Hoff equation, the propagation rate constant as function of temperature can be written as

$$k_{ij} \approx \frac{kT}{h} \exp\left(-\frac{E_{a,ij}}{RT}\right) \exp\left(\frac{\Delta S_{ij}}{R} - \frac{\Delta H_{ij}}{RT}\right) \quad (8)$$

The temperature dependence of the propagation rate constants k_{ij} are given by similar equations, (6) and (8), irrespective of whether complex formation between the monomer molecule and the active site is rate-determining or there exists an equilibrium between complexed and uncomplexed monomer with the rate of polymerization depending on this equilibrium and the rate of insertion of the complexed monomer into the transition metal carbon bond. In both equations the entropy values are linked with the complexation of the active site by the monomer, although in eq. (6) the entropy value is an activation parameter, while in eq. (8) it is a thermodynamic parameter. On the other hand, in eq. (6) the enthalpy value is again an activation parameter for the complexation of the active site by the monomer, but in eq. (8) there are two enthalpy values, namely, ΔH_{ij} for complexation of the active site by the monomer, and $E_{a,ij}$ for insertion of the complexed monomer into the transition metal carbon bond. The entropy and enthalpy values can be calculated from temperature dependence of the rate constants k_{ij} . These values are collected in Table V together with corresponding thermodynamic data for polymer formation. All values in Table V are calculated for 85°C and polymerization of the monomers in 1 *M* ideal solutions in hydrocarbon solvents to either totally amorphous or crystalline solid polymers. The polymer formation data can be calculated on the basis of thermodynamic data published elsewhere.²³⁻²⁷

CONCLUSIONS

The data of Table V show that polymerization of ethylene or 1-butene are highly exothermic processes, accompanied by a high decrease in entropy. On

TABLE V
Entropy and Enthalpy Values for the Polymerization of Ethylene (1) and 1-Butene (2) with a Ziegler-Natta System^a

Process		Entropy (J/K·mol)	Enthalpy (kJ/mol)
$nM_{1,s}$	$\rightarrow (1/n) (M_{1,n})_c$	-128	-100
$nM_{1,s}$	$\rightarrow (1/n) (M_{1,n})_a$	-110	-92
$\mathcal{M}M_1\text{-Cat} + M_{1,s}$	$\rightarrow \mathcal{M}M_1\text{-Cat}$	$-160 \pm 10\#$	$15 \pm 2\#$
$\mathcal{M}M_1\text{-Cat} + M_{2,s}$	$\rightarrow \mathcal{M}M_2\text{-Cat}$	$-210 \pm 20\#$	$12 \pm 4\#$
$nM_{2,s}$	$\rightarrow 1/n (M_{2,n})_{c,\text{isot}}$	-94	-79
$\mathcal{M}M_2\text{-Cat} + M_{2,s}$	$\rightarrow \mathcal{M}M_2\text{-Cat}$	$-210 \pm 20\#$	$12 \pm 4\#$
$\mathcal{M}M_2\text{-Cat} + M_{1,s}$	$\rightarrow \mathcal{M}M_1\text{-Cat}$	$-200 \pm 20\#$	$9 \pm 3\#$

^a *s* = 1-molar, ideal solution in a hydrocarbon solvent; *a* = amorphous solid polymer; *c* = crystalline solid polymer; isot = isotactic; Cat = active center; # = values calculated from kinetic data.

the other hand, the data calculated from kinetic parameters show that these processes have small enthalpy values and even higher decreases in entropy than expressed by the thermodynamic data. This means that the polymerization process is predominantly controlled by entropy, and that the different kinetic behavior of ethylene and 1-butene is in particular due to different entropy values. The enthalpy parameters are similar for both monomers. Thus it can be concluded from these data that complexation of the active site by the monomer—which has to be regarded as the most important step of the Ziegler–Natta polymerization process—goes along with a significant decrease in entropy depending on monomer structure. This means that the entropy change during complexation of the active site by the monomer is the rate-determining factor for this catalytic process. The entropy parameters differ in the range of 50 J/K·mol, which corresponds to a factor of the order of 100 for the rate constants.

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APPENDIX: NOMENCLATURE

E_a	activation energy (kJ/mol)
h	Planck constant
K	equilibrium constant (dm ³ /mol)
k	Boltzmann constant
k_a	rate constant of complex formation between olefin and transition metal compound (dm ³ /mol·s)
k_d	rate constant of complex dissociation (s ⁻¹)
k_p	rate constant of complexed monomer insertion into the transition metal carbon bond (s ⁻¹)
k_{ij}	propagation rate constant (dm ³ /mol·s)
n^*/n_k	catalyst efficiency, $0 < n^*/n_k \leq 1$
[M ₁]	ethylene concentration in diesel oil (mol/dm ³)
[M ₂]	1-butene concentration
[M]	monomer concentration (mol/dm ³)
$\left(\frac{n_2}{n_1}\right)_P$	mole ratio of 1-butene and ethylene in the copolymer
$M_{0,1}$	molecular mass of ethylene (g/mol)
r	Mayo–Lewis r parameter
R_p	rate of polymerization
R	gas constant
T	temperature
X	mole fraction
ΔH	enthalpy (kJ/mol)
ΔS	entropy (J/K·mol)
λ	Henry coefficient (mol/dm ³ ·bar)

Indexes

1	ethylene
2	1-butene
S	solvent (diesel oil)

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