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Copolymerization of ethylene and carbon monoxide using [(dppp)Pd(H_2O)(TsO)](TsO) as a catalyst precursor: rate equation

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Abstract

The influence of CO and C_2H_4 pressures on their copolymerization catalyzed by the precursor [(dppp)Pd(H_2O)(TsO)](TsO) in MeOH has been studied up to 8 Mpa of total pressure at 363 K. Several rate equations, based on two different models, are presented. The so called "one site model" involves a tetracoordinate Pd^{II} cation in which only one coordination site is available to the monomers. The "two sites model" involves a pentacoordinate Pd^{II} cation in which the monomers coordinate the metal simultaneously at two different sites. In both cases, the other three sites are occupied by the growing polymer chain and the chelating diphosphine. The rate equation that fits the experimental data better is used to optimize the ratio of the monomers pressures to obtain a maximum reaction rate for a given total pressure. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The palladium-catalyzed perfectly alternating copolymerization of an olefin with CO, described by reaction (1) with ethylene, is of much interest for the following reasons:

1. the predicted engineering-plastic type properties of the polyketone (for the characterization of the copolymer see [1,2] and references therein),
2. the monomers are easily available at a low cost, and
3. the polyketone can be modified through reactions with the carbonyl group to give a large variety of new materials [3,4].

$$nC_2H_4 + nCO \xrightarrow{\text{catalyst}} -\!\!\left(CH_2CH_2CO\right)_{n}\!- \quad (1)$$

Several catalysts have been reported for reaction (1). The best results were obtained by Shell researchers [1,4–6] with a catalytic system prepared in situ from $Pd(OAc)_2$, a chelating phosphine, such as for example dppp=1,3 bis(diphenylphosphino)propane, and an acid of a weakly coordinating anion, such as *p*-toluenesulfonic acid (PTSA). When a Pd: dppp:PTSA ratio of 1:1:2 was used at 4–5 MPa (total pressure) and 363 K, a catalyst productivity was as high as 6000 g polymer (g Pd)$^{-1}$ h^{-1}.

Extensive studies on these types of catalysts have been reported in [1,4–9] A recent paper [10] reports a detailed mechanistic study of the key steps in the chain growth reactions using bipyridine ligand instead of dppp. However, the reaction conditions (low tempera-

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ture and low pressure) were far from those of industrial interest. Under these conditions there are only a few reports published on kinetic modeling [11–14]. However, the information on the kinetics reported, is not complete and rather qualitative in nature. The main aim of this work was to develop the reaction rate equation in order to optimize the ratio of the partial pressures of the monomers to achieve maximum rate of copolymerization.

2. Experimental

2.1. Materials

The catalyst precursor [(dppp)Pd(H_2O)(TsO)](TsO) was prepared following the procedure described in [15] from palladium acetate Pd$(OAc)_2$, 1,3-bis(diphenylphosphino)propane (Aldrich, 98% and 97%, respectively.) and *p*-toluenesulfonic acid monohydrate (Janssen, 99%). All the experiments were carried out using the catalyst precursor just reported. When starting from the three components Pd$(OAc)_2$, dppp and PTSA, poor reproducibility of the catalyst activity was observed due to the difficulty of dosing small amounts of the components in the exact stoichiometric ratio.

Methanol, 99.99%, (water content 400 ppm), was a Baker product. CO and C_2H_4, both 99.99% (research grade), were supplied by SIAD.

2.2. Copolymerization reactor

All the experiments were carried out in a 280 ml stainless steel AISI 316 autoclave, provided with a four bladed hastelloy stirrer and a thermocouple to measure the temperature of the reaction. A pyrex glass liner was used to avoid contamination with the reactor wall. In order to monitor the CO/C_2H_4 consumption, a gas reservoir, charged with 1:1 CO/C_2H_4 mixture, was used along with a constant pressure regulator. The pressure in the reservoir was recorded by using a pressure transducer connected to a personal computer.

2.3. Experimental procedure

A known quantity of catalyst precursor, typically 2.5 mg (2.8×10^{-3} mmol), was added to the reaction vessel together with 80 ml of methanol as a solvent. The contents of reactor were flushed with C_2H_4 to remove air. After pressurizing with a desired CO/C_2H_4 mixture, the reactor was heated to the required temperature in a short time (ca. 15 min). During all the course of the reaction the pressures of the monomers in the reactor were kept constant by supplying the two gases from a reservoir (see above). Independently from the CO/C_2H_4 mixture charged in the reactor at the beginning of the reaction, the gas reservoir is always charged with a 1:1 CO/C_2H_4 mixture because the copolymerization proceeds with a strictly alternating mechanism with a equimolar consumption of the monomers.

During the reaction, the composition of the gas phase in the reactor was determined by gas chromatographic analysis using a HP 5890 series II GC with a packed silica gel column of 2.9 m length. The reaction was stopped by degassing and cooling the reactor. The product, which is insoluble in methanol, was recovered by filtration, washed with methanol and dried at 343–353 K for 24 h under vacuum. In the filtered solution, no low molecular weight carbonylation products were present in significant amount.

3. Results

3.1. Check of kinetic regime

The copolymerization reaction involves simultaneous absorption of C_2H_4 and CO followed by a catalytic reaction leading to a solid product. Therefore, it was important to ensure that gas–liquid mass transfer steps (dissolution of C_2H_4 and CO) are not rate limiting. The initial experiments showed that rate of copolymerization was independent of agitation speed beyond 500 rpm and linearly dependent on catalyst loading (from 2.5 to 10 mg of the precursor). This indicates that the rate data is in kinetic regime.

In addition, it should be pointed out that, as the reaction proceeds, the polymer precipitates, since it is insoluble in methanol. Since the growing chain remains bound to the metal catalytic center till the termination step, it may be necessary to take into account that the possibility of the catalyst being heterogeneous. On the other hand, if the polymer chain remains soluble while growing and precipitates only after the termination step, the catalyst acts as a homogeneous system. Thus, in the case of heterogeneous catalyst system, we have to consider also the liquid–solid as well as the intraparticle diffusion effects.

The polymer obtained consists of separate small particles as well as aggregate particles of sizes between ca. 5 and 30 μm, with an average size of ca. 20 μm, as established by SEM technique. As the reaction proceeds, it is likely that the relative amount of larger aggregate particles of the polymer increases, with consequent decreasing of external area and increasing average diameter of the particles, thus increasing resistance to diffusion at the liquid–solid interface and into the pores of the solid. Since we observed that the reaction rate remains constant for the entire period of reaction time (4–5 h) before the experiments were turned off, it appears that the liquid–solid as well as the intraparticle diffusional resistance is not important. Also, for the particles in the range of 20 μm, it can be shown that these mass transfer effects are not significant.

3.2. Rate equation

The effect of CO and C_2H_4 pressure on copolymerization rate was studied in a total pressure range 2.0–8.0 Mpa at 363 K and the results are shown in Fig. 1. We also carried out experiments at different lower

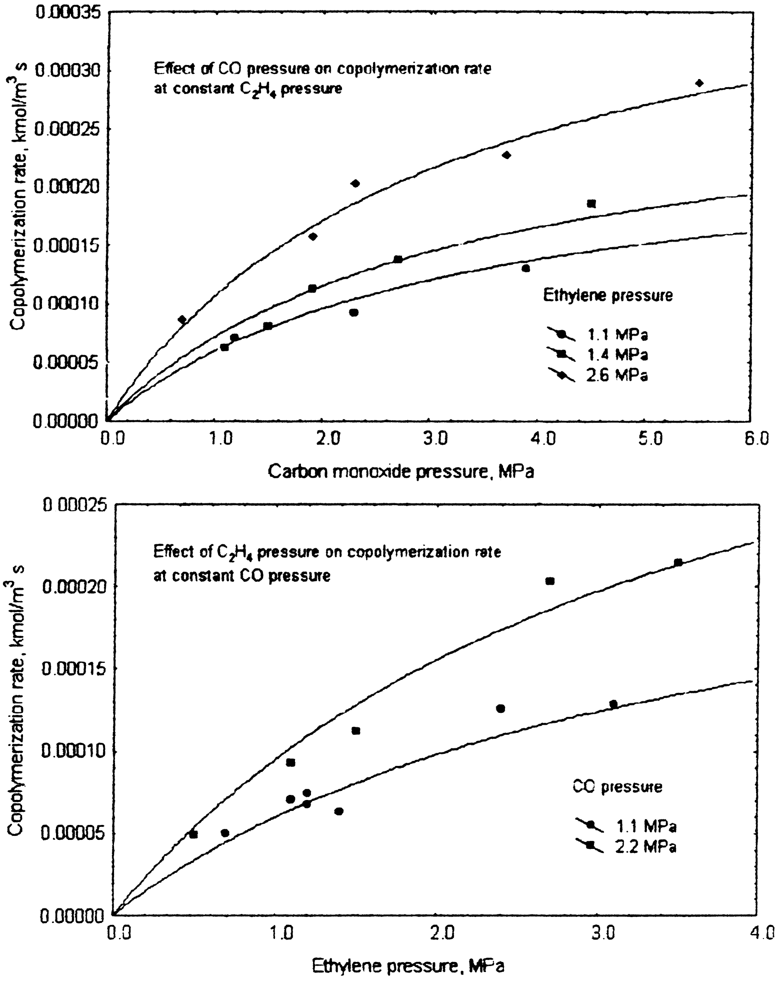

Fig. 1. Influence of CO and C_2H_4 pressures on the rate of copolymerization. The data are fitted with Eq. I of Table 2.

Table 1
Range of conditions studied for the kinetics of copolymerization

Catalyst charge	2.5–10 mg
Carbon monoxide pressure	0.75–5.5 MPa
Ethylene pressure	0.50–3.5 MPa
Temperature	298–363 K
Solvent	Methanol
Water content of the solvent (ppm)	400
Solvent volume	8×10^{-5} m^3

temperatures in order to determine the apparent activation energy of the reaction. The ranges of conditions covered are reported in Table 1.

The reaction was carried out for 4–5 h during which the reaction rate remained constant. This suggests that deactivation of the catalyst does not occur.

The reaction rate was found to increase with increasing pressures of the monomers as shown in Fig. 1.

3.3. *Apparent activation energy of copolymerization*

The apparent activation energy was determined using a power law rate equation having only one constant that includes also the Pd concentration

$$r = k_{\mathrm{obs}}\, p_{\mathrm{co}}^{\alpha}\, p_{\mathrm{et}}^{\beta} \qquad (2)$$

With this equation, the reaction order for CO is 0.55, for C_2H_4 is 0.67 and k_{obs} is 6.04×10^{-5} kmol m^{-3} (MPa)$^{-1.22}$ s^{-1}. In addition to this, we carried out some experiments at 303, 323 and 343 K. The apparent activation energy from the Arrhenius plot was evaluated as 11.2 kcal mol^{-1}.

4. Discussion

Chain propagation of CO/C_2H_4 copolymerization proceeds by a strictly alternating insertion of CO and C_2H_4 in the growing chain. Double consecutive CO insertion does not occur because of thermodynamics [16]. The complete absence of double C_2H_4 insertion is remarkable because C_2H_4 insertion into a Pd–alkyl species is possible. For example, in the absence of CO, the palladium system used by Drent [5] catalyses the dimerization of C_2H_4 to butenes. Moreover, the perfectly alternated copolymer forms even when CO is used at a low pressure.

These facts suggest two possibilities:

1. CO coordinates the metal center more rapidly than C_2H_4, occupying all the vacant sites on Pd, while C_2H_4 has to displace the coordinated CO to coordinate itself and consequently insert in the growing chain,
2. on the contrary, if the Pd atom has two vacant sites, one coordinating CO and the other coordinating C_2H_4, then CO insertion into a Pd–C σ bond is faster than C_2H_4 insertion.

We propose two kinetic models. A "one site model", that involves the palladium atom in the more common four-coordinate state with the monomers coordinating the metal center alternatively in the only available site. Of the other three sites, two are occupied by the chelating diphosphine and the third by the growing polymer chain. As the monomer inserts into the growing polymer chain, the coordination site is available for both the monomers to coordinate with the metal. However, only the alternating monomer insertion is feasible and therefore the two monomers compete for a single coordination site.

In the "two sites model" the palladium atom is in the less common five-coordinate state. Three of these five sites are occupied by the diphosphine and the growing polymer chain, (as in the other model), while the other two are occupied by two molecules of the monomers. For each of the two models, the vacant sites on the Pd atom can be occupied by the solvent. In this case, if no monomer displaces methanol, it inserts in the polymer chain giving the final product and the catalyst back to the catalytic cycle.

In the "one site model" we suppose the existence of two reaction intermediates (Fig. 2), named A and B. Each one can coordinate the monomers but the insertion of CO into the growing polymer can occur only in A and the insertion of C_2H_4 in the growing polymer can occur only in B. Therefore, we obtain a perfectly alternating copolymer.

The rate equations considered and the relevant hypothesis at the basis of them are summarized in Table 2. Tables 3 and 4 report the values of the rate parameters obtained by fitting the experimental data. The values of σ^2, the minimized sum of the squares of the differences between the observed and the predicted

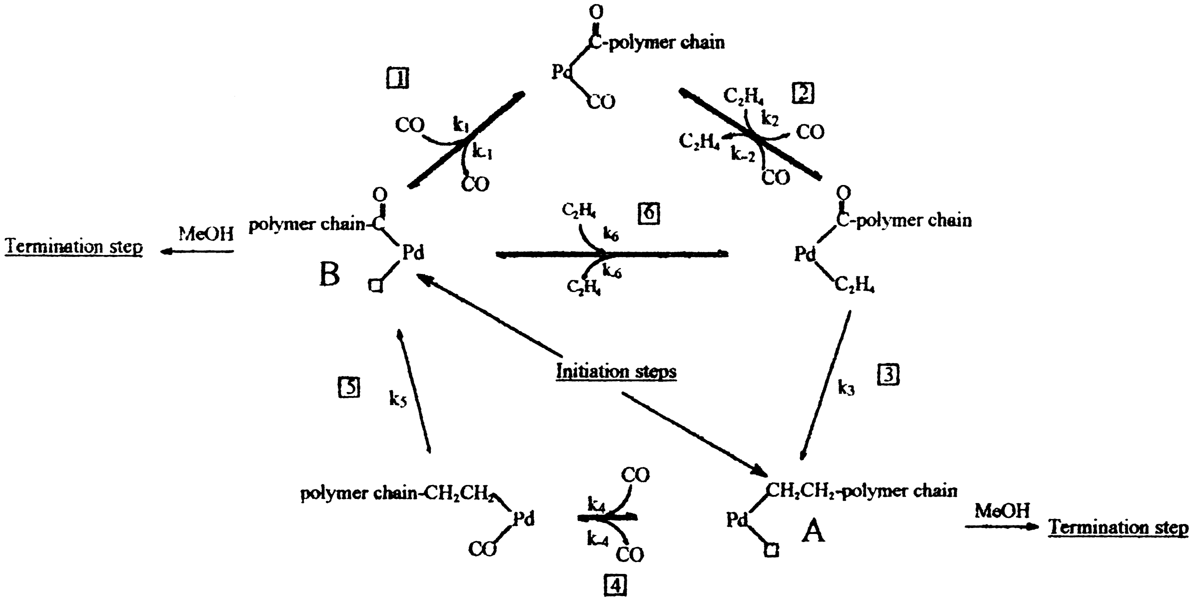

Fig. 2. Mechanism of the propagation step for the reaction of copolymerization for "one site model". The chelating diphosphine binds to the Pd atom is not represented. The symbol □ on the Pd atom represents a vacant site.

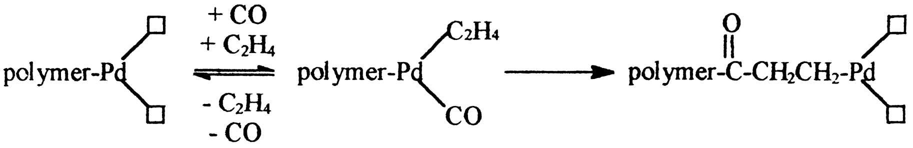

Fig. 3. Mechanism of the propagation step for the reaction of copolymerization for "two sites model". The chelating diphosphine binding to the metal center is not represented. The symbols □ on the Pd atom represent two vacant sites.

rates, for each kinetic equation, are also reported. Fig. 3 reports all the reactions involved in the mechanism of the "two sites model", while Fig. 4 shows the experimental data and the fitted function obtained from Eq. I.

4.1. Maximization of the reaction rate

Eqs. I–IV describes the experimental data equally well, therefore a model discrimination is not possible. In order to optimize the copolymerization rate, model I was chosen. Using this equation we calculated the values (Table 5) of the partial pressures of the monomers which give maximum reaction rate, at a given total pressure. For example, under 7.0 MPa of total pressure, the best $P_{CO}/P_{C_2H_4}$ ratio is 0.99.

5. Conclusions

The effect of CO and C_2H_4 pressure on the rate of copolymerization using a Pd[(dppp)(H_2O)(TsO)](TsO) catalyst precursor has been studied at 363 K. The rate was found to be 0.55th and 0.67th order with respect to CO and C_2H_4. The rate data were also fitted to several rate equations based on single site and two site models and it was observed that the models (Eqs. I–III) based on the two site model represent the data satisfactorily. However, the single site model given in Eq. IV also fitted the data with adequate accuracy (<10% error). The rate parameter have been determined for different models and the apparent activation energy was found to be 11.2 kcal mol^{-1}.

Table 2
Kinetic equations used and hypothesis on the propagation steps for the copolymerization

	Kinetic equations	Hypothesis
I[b]	$r_{\text{pol}} = \dfrac{k_r K_{\text{CO}} K_{\text{et}} p_{\text{CO}} p_{\text{et}}}{(1 + K_{\text{CO}} p_{\text{CO}})(1 + K_{\text{et}} P_{\text{et}})}$	Of the two sites on Pd atoms, one can coordinate only CO and one only C_2H_4. The rate limiting step is the insertion of one monomer from an intermediate in which the two monomers are simultaneously coordinated
II[b]	$r_{\text{pol}} = \dfrac{k_r K_{\text{CO}} K_{\text{et}} p_{\text{CO}} p_{\text{et}}}{(1 + K_{\text{CO}} p_{\text{CO}} + K_{\text{et}} p_{\text{et}})^2}$	The two sites on Pd atoms are equivalent and can coordinate each monomer. The rate limiting step is the insertion of one monomer from an intermediate in which the two monomers are simultaneously coordinated
III[b]	$r_{\text{pol}} = \dfrac{k_r K_{\text{CO}} K'_{\text{et}} p_{\text{CO}} p_{\text{et}}}{(1 + K_{\text{CO}} p_{\text{CO}} + k_{\text{et}} p_{\text{et}})(1 + K'_{\text{CO}} p_{\text{CO}} + K'_{\text{et}} p_{\text{et}})}$	The two sites on Pd atoms are not equivalent and they can coordinate each monomer. The rate limiting step is the insertion of one monomer from an intermediate in which the two monomers are simultaneously coordinated
IV	$r_{\text{pol}} = \dfrac{k_2 k_4 K_1 p_{\text{CO}} p_{\text{et}} [Pd]}{k_4 + k_4 K_1 p_{\text{CO}} + k_2 K_1 p_{\text{et}}}$	The free site on Pd atom is rapidly occupied by CO, and the rate limiting step is the substitution of coordinated CO and C_2H_4 (reaction (2) in Fig. 2). Reactions (3) and (5) are so quick to make steps 2 and 4 irreversible
V	$r_{\text{pol}} = \dfrac{k_3 k_4 K_6 p_{\text{CO}} p_{\text{et}} [Pd]}{k_4 p_{\text{CO}} + k_4 K_6 p_{\text{CO}} p_{\text{et}} + k_3 K_6 p_{\text{et}}}$	On A and B intermediate (Fig. 2) can coordinate only CO and C_2H_4, respectively. The rate limiting step is reaction (3) and the insertion of CO (reaction (5)) is fast
VI	$r_{\text{pol}} = \dfrac{k_5 k_6 K_4 p_{\text{CO}} p_{\text{et}} [Pd]}{k_6 p_{\text{et}} + k_6 K_4 p_{\text{CO}} p_{\text{et}} + k_5 K_4 p_{\text{CO}}}$	As Eq. V with rate limiting step reaction (5)
VII	$r_{\text{pol}} = \dfrac{k_3 k_4 K_6 p_{\text{CO}} p_{\text{et}} [Pd]}{k_4 p_{\text{CO}} + k_4 K_6 p_{\text{CO}} p_{\text{et}} + k_3 K_6 p_{\text{et}} + k_4 K_1 p_{\text{co}}^2}$	As Eq. V but intermediate B (Fig. 2) can also coordinate CO
VIII[b]	$r_{\text{pol}} = k_{\text{obs}} p_{\text{CO}}^{\alpha} p_{\text{et}}^{\beta}$	Power equation used to study the apparent activation energy

Eqs. I–III are derived from "two sites model", Eqs. IV–VII from "one site model". Eq. VIII has been used for the determination of the apparent activation energy[a].

[a] The reaction number refers to Fig. 2.

[b] The Pd concentration is included in k_r and in k_{obs}.

Table 3
Comparison of different rate models proposed for the "two sites model"

Rate model	k_r (kmol m^{-3} s^{-1})	K_{CO} (Mpa^{-1})	K_{et} (Mpa^{-1})	K'_{CO} (Mpa^{-1})	K'_{et} (Mpa^{-1})	$\sigma^2 \times 10^{10}$
I	1.03×10^{-3}	3.21×10^{-1}	2.87×10^{-1}			3.27
II	4.20×10^{-3}	1.44×10^{-1}	1.55×10^{-1}			3.34
III	1.85×10^{-1}	6.21×10^{-3}	2.01×10^{-1}	3.60×10^{-1}	8.51×10^{-2}	3.29

Table 4
Comparison of different rate models proposed for the one site model

Rate model	K_1 (Mpa^{-1})	k_2 (Mpa^{-1}s^{-1})	k_3 (s^{-1})	k_4 (Mpa^{-1}s^{-1})	K_4 (Mpa^{-1})	k_5 (s^{-1})	k_6 (Mpa^{-1}s^{-1})	K_6 (Mpa^{-1})	$\sigma^2 \times 10^{10}$
IV	0.856	5.584		6.042					3.45
V			2102.1	4.038				2.38×10^{-3}	4.58
VI					30.805	39.898	2.527		16.5
VII	3.0×10^{-6}		0.613	0.219				0.534	173

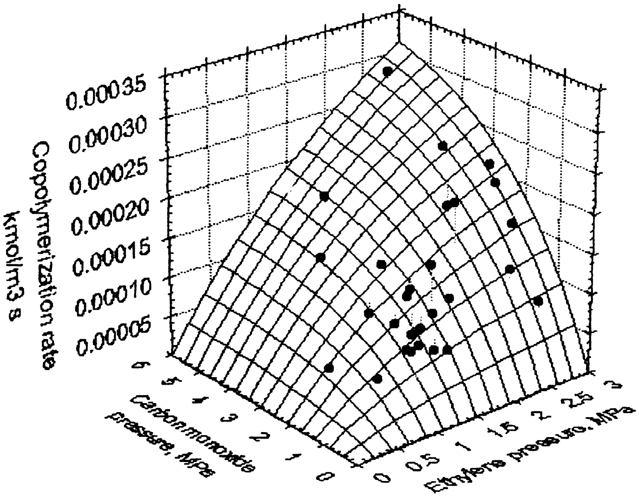

Fig. 4. Copolymerization rate obtained from Eq. I and experimental data.

Table 5
CO pressure and $P_{CO}/P_{C_2H_4}$ ratio for maximum reaction rate

Total pressure (MPa)	MeOH pressure (MPa)	CO pressure (MPa)	$P_{CO}/P_{C_2H_4}$
7.0	0.50	3.27	0.99
6.0	0.45	2.79	1.01
5.0	0.40	2.31	1.01
4.0	0.36	1.82	1.00

6. Nomenclature

K_{CO}	equilibrium constant for CO coordination on Pd atom (MPa^{-1})
K_{et}	equilibrium constant for C_2H_4 coordination on Pd atom (MPa^{-1})
K_n	equilibrium constant for reaction n (MPa^{-1})
k_n, k_{-n}	rate constants for reversible reaction n
k_{obs}	rate constant in Eq. VIII Table 2 (kmol m^{-3} $MPa^{-(\alpha+b)}$ s^{-1})
k_r	reaction rate constant (kmol m^{-3} s^{-1})
p_{CO}	CO pressure (MPa)
p_{et}	C_2H_4 pressure (MPa)
[Pd]	palladium concentration (3.5×10^{-5} kmol m^{-3})
r_{obs}	observed rate of copolymerization (kmol m^{-3} s^{-1})
r_{pol}	rate of copolymerization obtained from fittings (kmol m^{-3} s^{-1})

Greek letters

α	reaction order for CO in Eq. VIII Table 2 (dimensionless)
β	reaction order for C_2H_4 in Eq. VIII Table 2 (dimensionless)

References

[1] E. Drent, J.A.M. van Broekhoven, M.J. Doyle, J. Organomet. Chem. 417 (1991) 235.
[2] B.J. Lommerts, E.A. Klop, J. Aerts, J. Polym. Sci., Part B: Polym. Phys. 31 (1993) 1319.
[3] A. Sen, Adv. Polym. Sci. 73 (1986) 125.
[4] E. Drent, European Patent 121 965 A2 (1984).
[5] E. Drent, Pure Appl. Chem. 62 (1990) 661.
[6] E. Drent, P.H.M. Budzelaar, Chem. Rev. 96 (1996) 663.
[7] A. Sen, T.W. Lai, J. Am. Chem. Soc. 104 (1982) 3520.
[8] A. Sen, J.S. Brumbaugh, J. Organomet. Chem. 279 (1985) C5.
[9] A. Vavasori, L. Toniolo, J. Mol. Catal. 110 (1996) 13.

[10] F.C. Rix, M. Brookhart, P.S. White, J. Am. Chem. Soc. 118 (1996) 4746.

[11] W. Tschanen, Dissertation N.9118, ETH Zurigo, Switzerland (1990).

[12] X. Zhao, J.C.W. Chien, J. Polym. Sci., Part A: Polym. Chem. 30 (1992) 2735.

[13] G.P. Belov, O.N. Golodkov, Z.M. Dzhabieva, Macromol. Symp. 89 (1995) 455.

[14] Y. Koide, A.R. Barron, Macromolecule 29 (1996) 1110.

[15] F. Benetollo, R. Bertani, G. Bombieri, L. Toniolo, Inorg. Chim. Acta 233 (1995) 5.

[16] J.T. Chen, A. Sen, J. Am. Chem. Soc. 106 (1984) 1506.