

**Emulsion Copolymerization of α -Olefins with Carbon Monoxide
Using Water-Soluble Palladium(II) Complexes**

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**Emulsionscopolymerisation von α -Olefinen und Kohlenmonoxid
mit wasserlöslichen Palladium(II)-Komplexen**

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Im Namen Allahs, des Sich Erbarmenden, des Barmherzigen



In the Name of Allah, the Most Beneficent, the Most Merciful

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*To my parents, sisters, brothers,
my wife, my daughters Tala and Leen,
and to my developing country*

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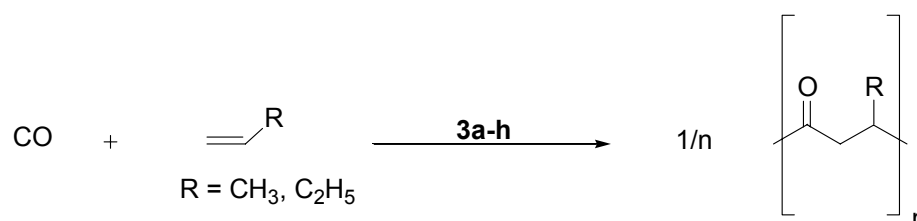
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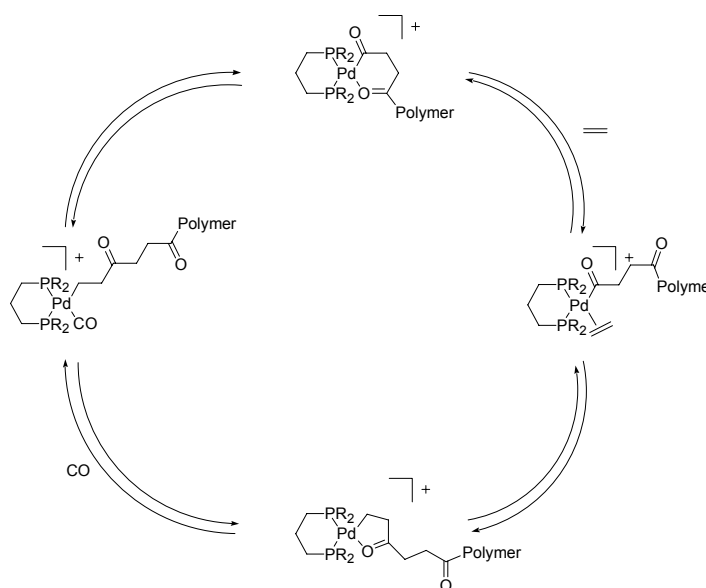
Introduction

The palladium catalyzed strictly alternating copolymerization of alkenes with carbon monoxide still attracts considerable attention (Scheme 1).



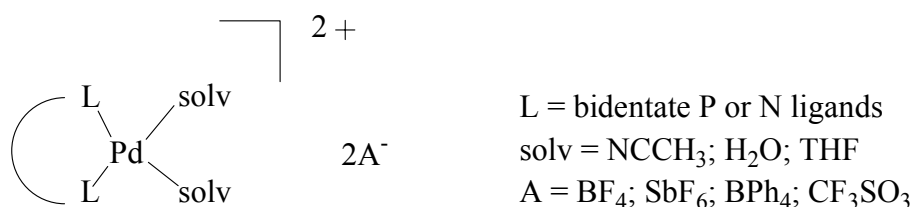
Scheme 1. Copolymerization of 1-Alkenes with Carbon Monoxide

Although the discovery of the transition metal-catalyzed copolymerization of ethene with carbon monoxide dates back to the early fifties,^{1a} it took nearly forty years until the first active palladium catalyst was found by Drent et al.^{1b} Meanwhile this reaction was extended to other olefins². The interest in this strictly alternating copolymerization stems from the easy and cheap access of the starting materials, a well investigated and reasonable reaction mechanism (Scheme 2),³ the potential utility of polyketones, and their properties as photodegradable materials.⁴



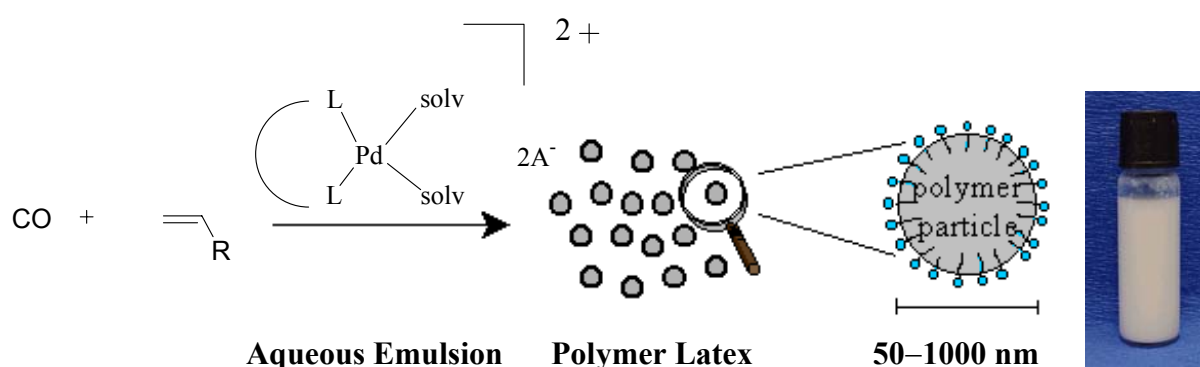
Scheme 2. Catalytic Cycle

Commonly the copolymerization is catalyzed by cationic palladium(II) complexes, provided with bidentate phosphorus and nitrogen ligands^{2,20} and weakly coordinating anions (Scheme 3).²¹



Scheme 3. Catalyst Precursor

Another important topic of polyketones is their application as emulsion polymers (latices) for coatings and paints.⁵ To date, emulsion polymerization is carried out industrially by free radical processes exclusively. Remarkably, transition metal-catalyzed coordination polymerization reactions particular in water have received less attention (Scheme 4).⁶



Scheme 4. Catalytic Copolymerization of α -olefins with Carbon Monoxide in Water

With catalysts the microstructure of the resulting polymers can be controlled.¹² In addition water offers several unique advantages such as (i) low costs, nontoxic and nonflammable reaction medium, and it is provided with several favorable physical properties; (ii) surfactants can effectively stabilize dispersions of hydrophobic polymer particles in water towards aggregation; (iii) in emulsion all monomers are able to react.⁷ Apart from Reppe et al.^{1a} water was introduced as a solvent in the copolymerization of olefins with carbon monoxide by Sen,⁸ Sheldon,^{9,10} and Bianchini¹¹ in 1994, 1998, 1999, and 2000, respectively. The development of water-soluble catalysts started with the modification of the well known ligand 1,3-bis(diphenylphosphino)propane (dppp) by introduction of sulfonate functions into its lipophilic backbone. Another approach is the fitting of the phosphorus atoms in dppp with hydroxyalkyl groups leading to highly active palladium(II) catalysts in water.^{12a} Moreover these catalysts are able to afford regioregular copolymers with a perfect head-to-tail arrangement of the α -olefinic building blocks. Compared to phenyl substituents in dppp, catalysts with entirely alkyl-substituted diphosphine ligands are particularly well-suited to α -olefin copolymerization. In this context it should also be mentioned that Mecking et al.¹³ were able to make accessible aqueous polyketone latices prepared with water-insoluble palladium(II) catalysts.

However it turned out that hydroxyalkyl modified diphosphinopropane ligands show the tendency to reduce palladium(II) in these complexes to palladium(0) which is considered as a drawback in the polyketone synthesis. Here we report for the first time on the synthesis, properties, and complete characterization of stable and colorless aqueous polyketone latices with high solid contents and molecular weights using palladium(II) catalysts provided with water-soluble hydroxyalkyl, phosphonate, and amine substituted diphosphine ligands of different length and steric demand. With the last-mentioned two ligand types a reduction of palladium could be circumvented and the obtained dispersions were stable and colorless. As cheap comonomers exclusively propene and 1-butene have been employed, and in order to

improve colloidal stability of polyketone latices the polymer particles are stabilized by surface acid groups (undecenoic acid) as a stabilizing agent.

General Section

1. Catalytic Activity of Diacetatodiphosphinepalladium(II) Complexes in the Emulsion Copolymerization of Olefins with Carbon Monoxide

1.1 General Considerations

Three groups of palladium complexes with hydroxyalkyl, phosphonate and amine substituents attached to the phosphorus donors were employed in the emulsion copolymerization of propene/CO, butene/CO, and propene/butene/CO. In order to eliminate the coordinating carboxylate anions, an excess of HBF_4 was added to the catalyst to form the more weakly coordinated complexes **4a-h** (Scheme 5). There is a good evidence that the actual catalytically active species is a cationic palladium complex like $[(\text{diphosphine})\text{Pd}(\text{PK})(\text{L})]^+$ (PK = growing polymer chain, L = monomer, solvent) which is formed under polymerization conditions.^{2c,3,22} The presence of hydroxy groups in complex **3a** is responsible for the dark color of the dispersion, because alcoholic functions are known to reduce palladium(II) complexes to palladium(0). Therefore a reduction of palladium(II) was circumvented by using phosphonate and amine substituted diphosphine ligands of different length and steric demand. Thus obtained dispersions were stable and colorless.

1.2 Synthesis of the Diphos Ligands **2a-h** and Diacetatodiphosphinepalladium(II) Complexes **3a-h**

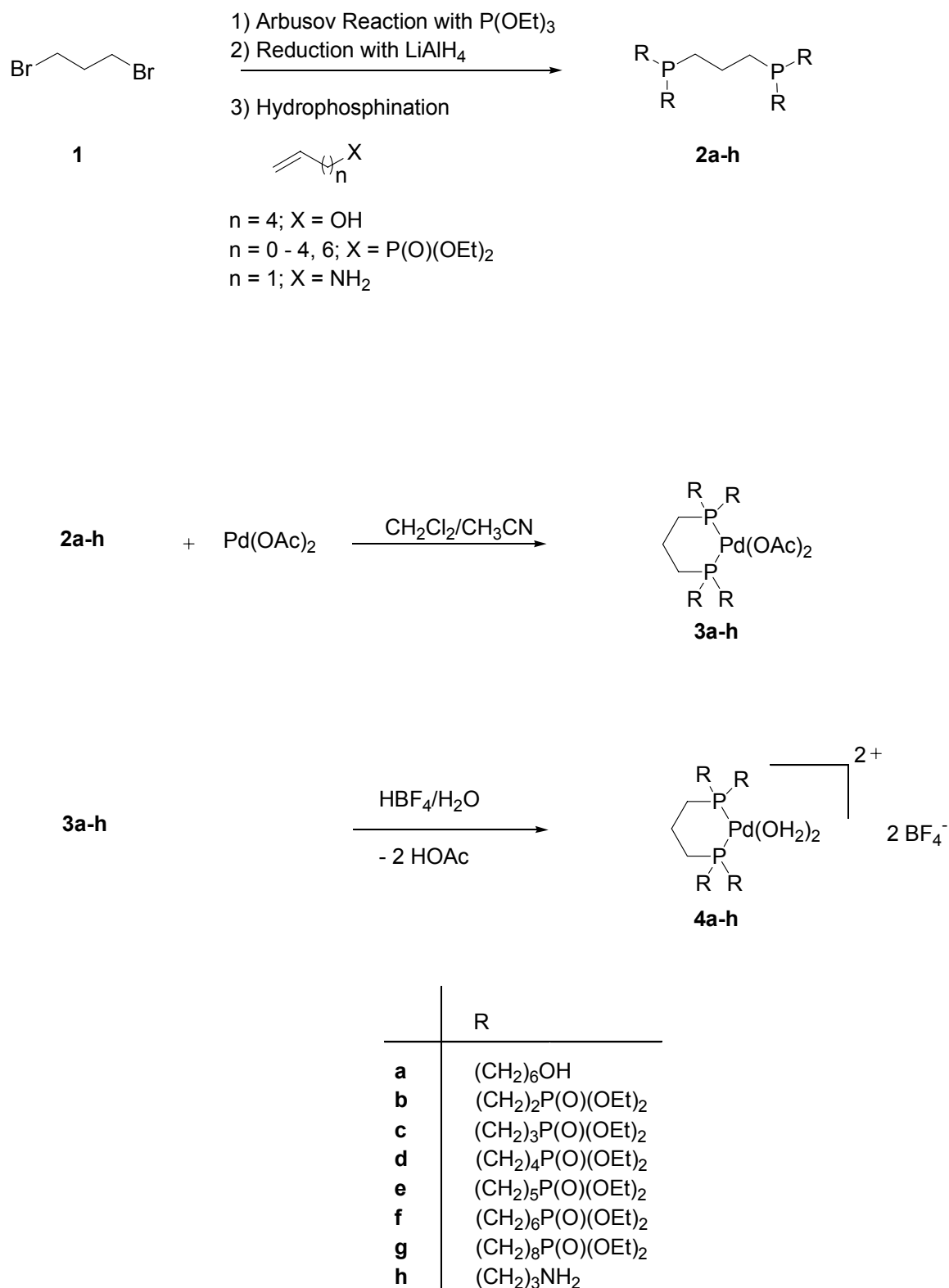
The diphosphines **2a-h** were obtained by heating $\text{P}(\text{OEt})_3$ with 1,3-dibromopropane according to a Michaelis-Arbuzov reaction (Scheme 5), followed by reduction of the resulting

diphosphate with LiAlH_4 in diethyl ether to give $\text{H}_2\text{P}(\text{CH}_2)_3\text{PH}_2$.²⁷ Then an excess of the corresponding olefin $\text{CH}_2=\text{CH}-(\text{CH}_2)_n-\text{X}$ ($\text{X} = \text{OH}$, $n = 4$; $\text{P}(\text{O})(\text{OEt})_2$, $n = 0-4, 6$; NH_2 , $n = 1$) was photochemically hydrophosphinated with the diprimary phosphine $\text{H}_2\text{P}(\text{CH}_2)_3\text{PH}_2$ overnight. This convenient synthesis is nearly quantitative and simplifies the purification of the products.^{16,28} Purification is achieved by removing excess alkene under reduced pressure. The alkenyl phosphonates $\text{CH}_2=\text{CH}-(\text{CH}_2)_n-\text{P}(\text{O})(\text{OEt})_2$ were obtained either from commercial suppliers ($n = 0, 1$) or prepared by literature methods ($n = 2-4, 6$).^{1,2} Also ligand **2a**,⁴ and complex **3a**⁴ were synthesized according to known specifications. All diphosphines **2a-h** represent colorless, air-sensitive and oily products which are expectedly soluble in water and chlorinated hydrocarbons like dichloromethane and chloroform. All ligands were characterized by means of MS, IR, and NMR. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of the phosphonate ligands **2c-g** display two signals in a 2 : 1 ratio representing an A_2X spin system. They are assigned to the phosphonate ($\delta = 32$) and phosphine ($\delta \approx -22$) substituents. In the spectra of ligand **2b** occur two signals with a 2 : 1 ratio representing an A_2X pattern (Figure 1a) with a coupling constant of about 50 Hz. The A-part of this spin system is located at higher field ($\delta = 32$) and displays a doublet which is ascribed to the phosphonate function, whereas the X-part at lower field ($\delta = -22$) shows a triplet attributed to the phosphine groups. It is characteristic that the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of the hydroxyalkyl (**2a**) and amine (**2h**) diphosphine ligands reveal a singlet at $\delta \approx -31$.

Upon reaction of palladium(II) acetate with the ligands **2a-h** in a 1 : 1 mixture of dichloromethane and acetonitrile at room temperature bright orange solutions of **3a-h** are obtained (Scheme 5). For further purification, complexes **3a-h** were dissolved in dichloromethane and precipitated with *n*-hexane to give orange oily materials. The compounds **3a-h** are storable at -21°C , and the time difference between their synthesis and

employment in catalytic runs was never longer than two weeks. The water solubility of **3a-h** is the most important feature of this type of complexes.

The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of the phosphonate complexes **3c-g** are characterized by two signals in a 2 : 1 ratio which are assigned to the phosphonate ($\delta \approx 32$) and phosphine ($\delta \approx 22$) groups. In the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of complex **3b** also two signals in a 2 : 1 ratio occur, however, they represent an $A_2XX'A'_2$ pattern (Figure 1b). The A-part of this spin system is located at higher field ($\delta = 32$) and ascribed to the phosphonate function, whereas the X-part at lower field ($\delta = 22$) is traced back to the phosphines. In the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra the hydroxyalkyl (**3a**) and amine diacetatodiphosphinepalladium(II) complexes (**3h**) give rise to a singlet at $\delta = 19$ and 1.5 ppm, respectively.



Scheme 5. Preparation of the Diphosphine Ligands **2a-h**, and their Related Palladium(II) Complexes **3a-h** and Generation of the Dicationic Palladium(II) Complexes **4a-h**

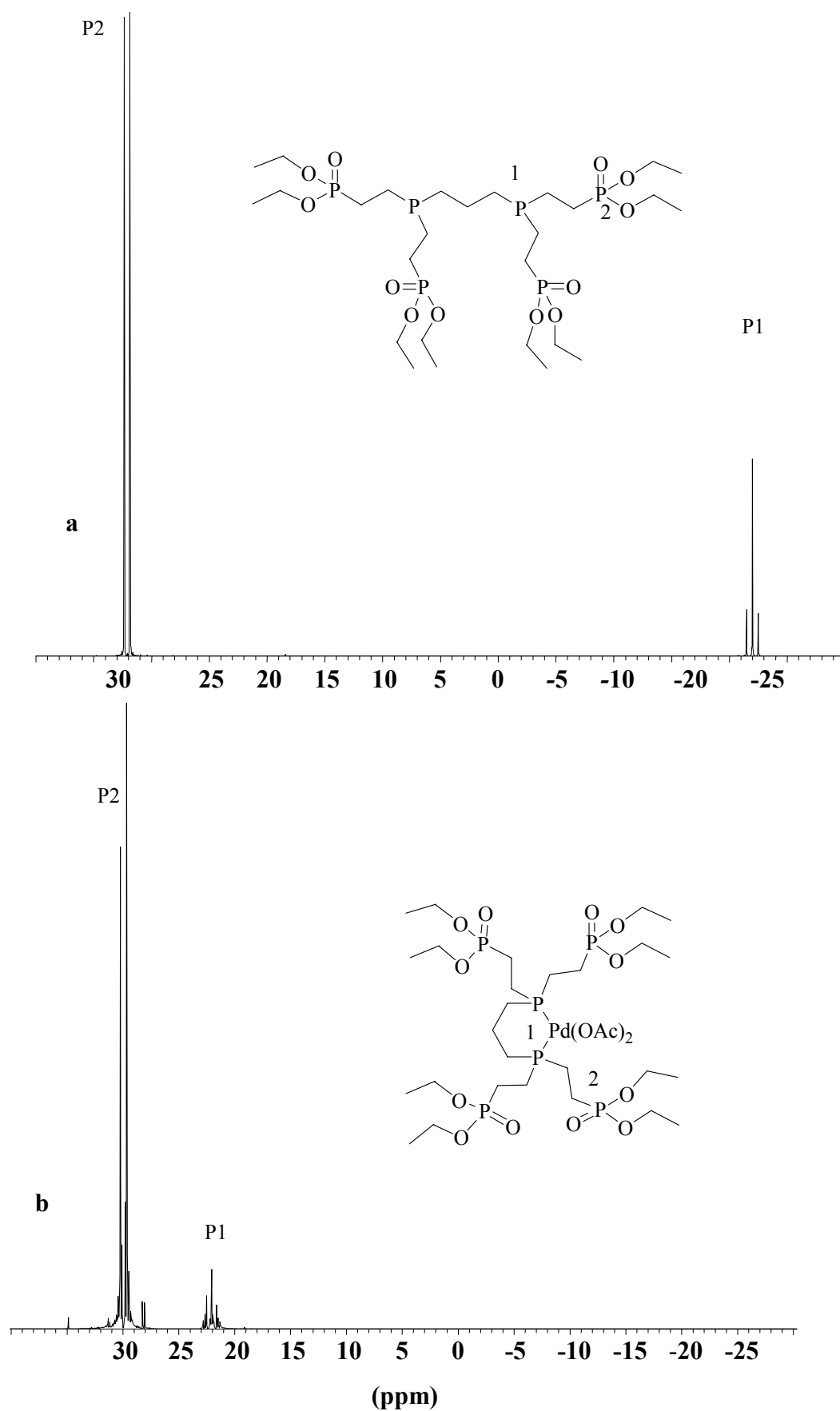


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ -NMR Spectra of the Ligand **2b** Showing an A_2X Pattern (a). $^{31}\text{P}\{^1\text{H}\}$ -NMR Spectra of Complex **3b** Showing an $\text{A}_2\text{XX}'\text{A}'_2$ Pattern (b)

1.3 Crystal Structure of **3a**

The diacetatodiphosphinepalladium(II) complex **3a** crystallizes in the triclinic space group $P\bar{1}$ with two formula units per unit cell. The bond angles P1-Pd-P2 ($95.29(6)^\circ$) and O5-Pd-O7 ($92.47(14)^\circ$) differ slightly from an ideal square planar geometry (see Table 5 and Experimental Part). Pd, P1, P2, O5, and O7 deviate by less than 0.12 Å from planar arrangement. Remarkably, the six-membered ring, formed by the diphos ligand and the metal atom, is flattened at the metal, Pd(1) and C(2) deviate by $-0.095(3)$ Å and $0.700(7)$ Å (Figure 2) from the least-squares plane defined by P(1), P(2), C(1), and C(3).

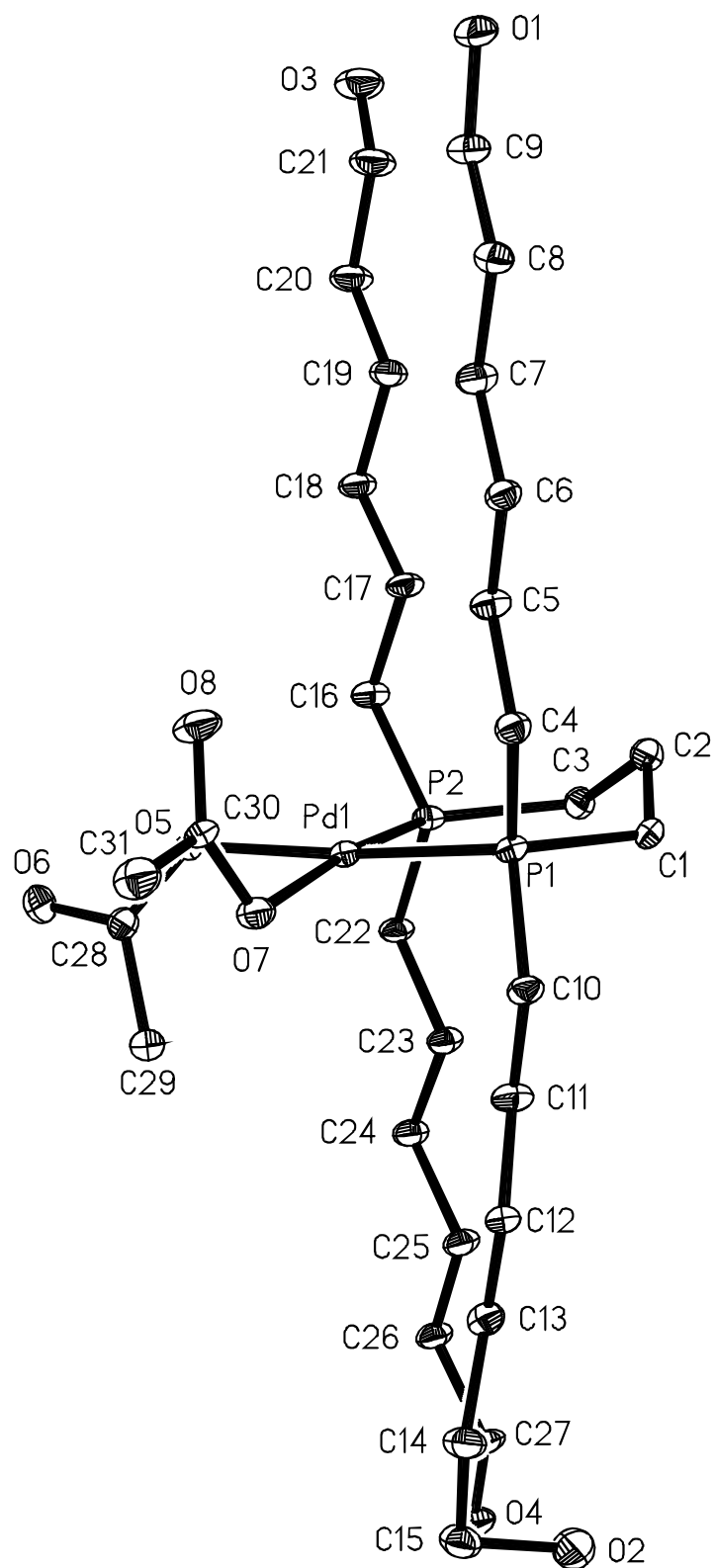


Figure 2. Ortep Plot of **3a** with Thermal Ellipsoids at 20% Probability

1.4 Batch Copolymers

To compare catalysts in the area of copolymerization the activity is usually the important factor. However, the chemical composition of the catalytic system is not the only point which determines the output of the polymer, also the reaction conditions should be taken into consideration. In the case of the alternating copolymerization the geometric dimensions of the used autoclave system, the relation between the gas and liquid phase, the temperature during the run and, in addition, the pressure of the gaseous reactant(s) are also important. Even the stirring mechanism is a crucial point, because of the increase of the interfacial area by rapid stirring. Therefore, the rate of transfer of the gaseous reactant(s) over the gas/liquid boundary is influenced by the stirring mechanism. A comparison of different catalytic systems makes only sense if they are employed under the same reaction conditions in the same reaction vessel. A comparative study, which is based on the variation of one parameter which determines the efficiency of a copolymerization experiment is only possible in an automated and computer controlled system. Therefore copolymerizations were carried out in stainless steel autoclaves (volume 150 ml, 100 ml) equipped with a mechanical stirrer and a heating system (thermostat). The parameters temperature, pressure, and stirring mechanism were measured, controlled, and recorded by a personal computer (Figure 3). Charging and venting steps were also controlled and executed by the computer. Thus a high degree of reproducibility was guaranteed. During these comparative studies the system remains completely unmodified.

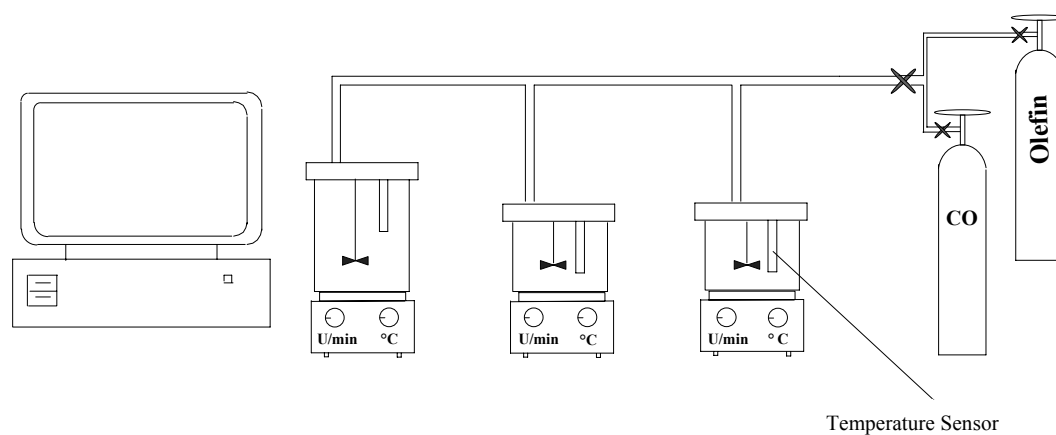


Figure 3. Autoclaves (Volume 150 ml, 100 ml) Controlled and Recorded by a Personal Computer

A study of the time-dependent course of the pressure during the copolymerization (Figure 4) showed, that the highest consumption of the olefin and carbon monoxide took place within the first five hours of the reaction. Figure 4 gives an indication that the catalyst is still active even after 12 hours and no decomposition was observed. From Figure 4 it can also be deduced that the propene/undecenoic acid/CO and butene/undecenoic acid/CO consumption is higher than that of propene/butene/undecenoic acid/CO This is agreement with the solids content and the catalytic activity (Tables 1–3, entry 5 and Figures 6–8).

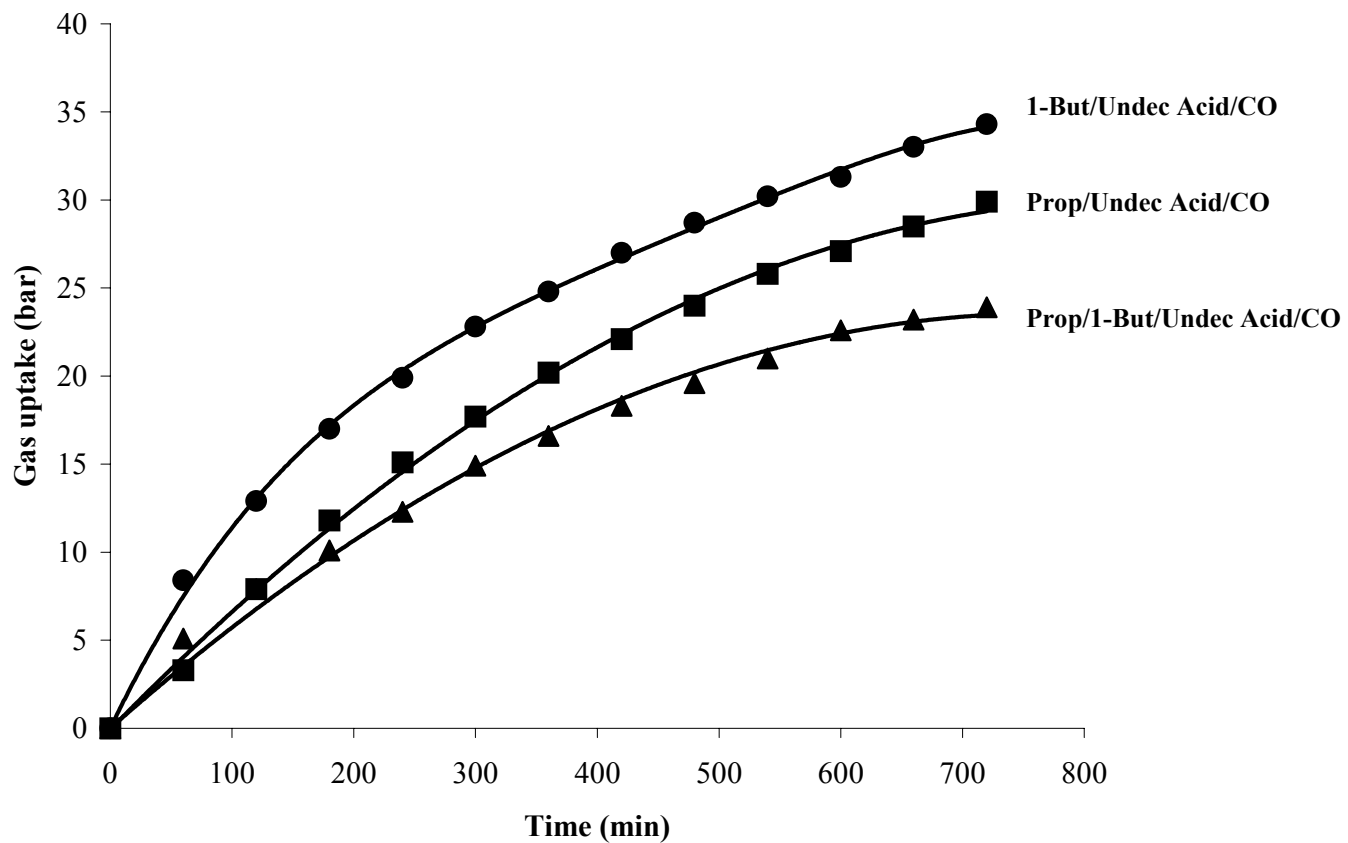


Figure 4. Gas Uptake Against Time During the Copolymerizations Catalyzed by Complex **3c** in Water

1.5 Effect of Methyl- β -Cyclodextrin

The co- and terpolymerization of hydrophobic monomers in the emulsion polymerization in the presence of methyl- β -cyclodextrin (W7 M 1.8) as a phase transfer agent enables the production of higher solids contents of the polyketones and a higher productivity of the catalysts. Water-insoluble molecules become water-soluble by treatment with aqueous solutions of cyclodextrins without any chemical modification of the guest molecule, because there are no covalent bonds formed in the host-guest interaction of cyclodextrin and the water-insoluble molecule. Several experiments with and without cyclodextrin were carried out to investigate the influence of cyclodextrin on the productivity of the catalyst. With cyclodextrin it was increased by 40–60% (Figure 5) and this gives an indication that the employment of cyclodextrin is important. The corresponding technique was simultaneously developed in the laboratories of Rohm & Haas,²³ where the monomer lauryl methacrylate was used, and in BASF Aktiengesellschaft,²⁴ where the monomer stearyl acrylate was preferred. In both companies only a small amount of cyclodextrin was added to the reaction vessel and larger quantities of the very hydrophobic monomers could be polymerized.²⁵

1.6 Effect of Undecenoic Acid

Carboxyl-containing monomers are often introduced into a latex formulation to act as a site for post-polymerization crosslinking reactions (e.g. interfacial crosslinking), for rheology modification of the polymer dispersion, or to enhance the colloidal stability of the latex particles. Carboxyl groups tend to improve the mechanical, shear and freeze-thaw stability of the latex, to improve the tolerance to electrolytes, to improve film hardness, and to improve the adhesion of a latex film to a substrate.^{5a}

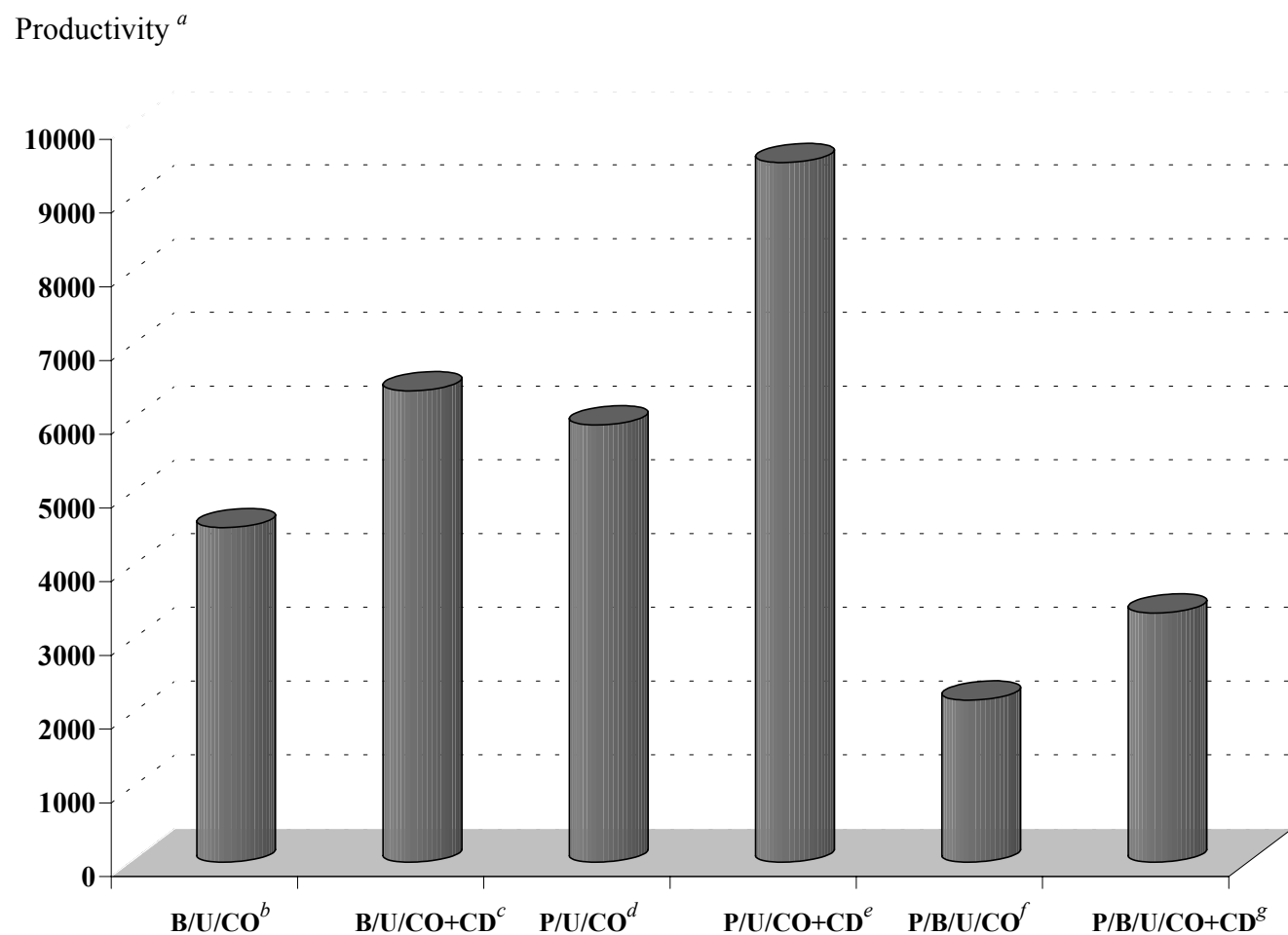
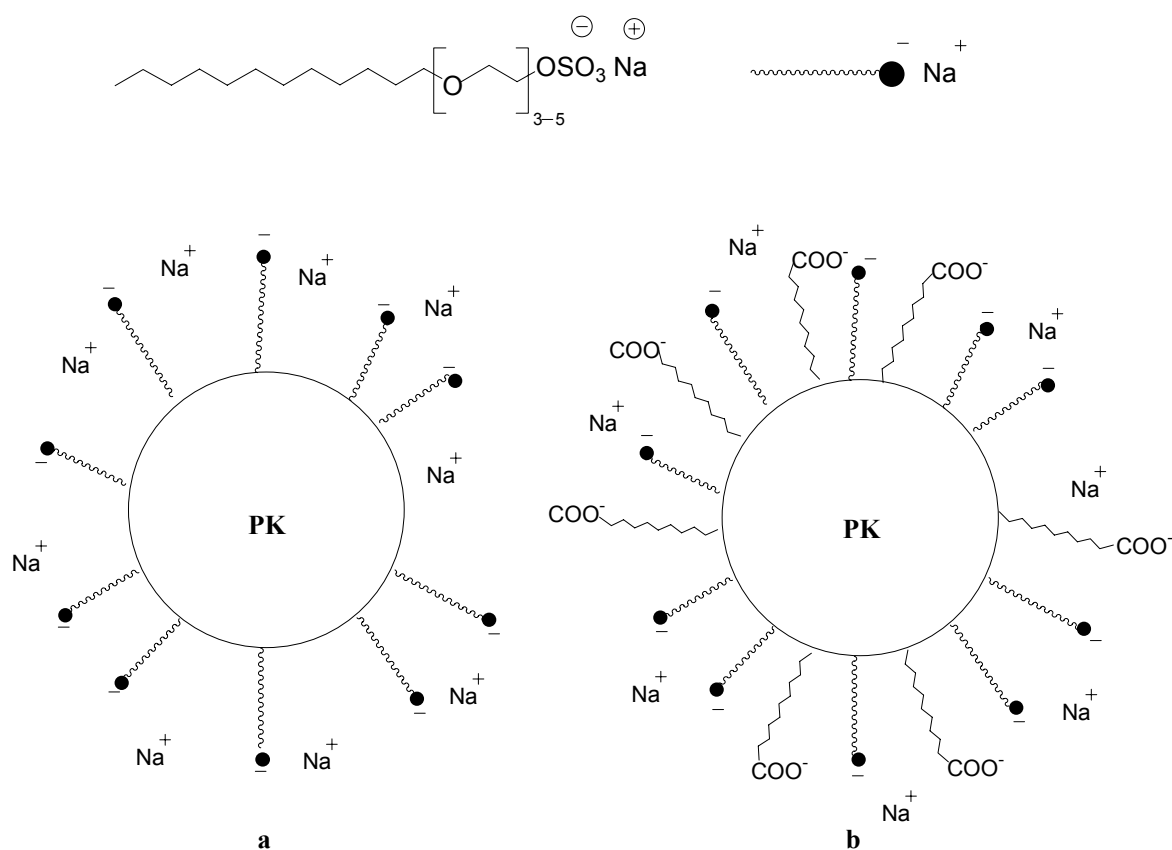


Figure 5. Comparison of the Catalyst Activities with and without Adding Cyclodextrin Using Complex **3c** in Water

^aProductivity in $(\text{mol}(\text{substr}) \times \text{mol}(\text{Pd})^{-1})$. ^bB/U/CO = Butene/Undecenoic Acid/CO. ^cB/U/CO + CD = Butene/Undecenoic Acid/CO + Cyclodextrin, ^dP/U/CO = Propene/Undecenoic Acid/CO. ^eP/U/CO + CD = Propene/Undecenoic Acid/CO + Cyclodextrin. ^fP/B/U/CO = Propene/Butene/Undecenoic Acid/CO. ^gP/B/U/CO + CD = Propene/Butene/Undecenoic Acid/CO + Cyclodextrin

The stability of the resulting propene/CO, butene/CO, and propene/butene/CO dispersions was found to be insufficient, and in the aforementioned experiments the polyketone was largely precipitated after one to two weeks. However, stable dispersions are obtained by the introduction of undecenoic acid as a third or fourth monomer and no phase separation, or the formation of a coagulum within ten weeks were observed. In these latices, hydrophilic carboxylic acid moieties covalently bound to the particle surface contribute to stabilization (Scheme 6).^{5a}



Scheme 6. Polyketone Latex only Stabilized by Texapone (a). Polyketone Latex Stabilized by Texapone and Surface Acid Groups (Undecenoic Acid) (b)

2. Latex Polymer Characterization

2.1 Particle Size and Particle Size Distribution

The particle size of the dispersed phase of the polyketones is important for industrial processes especially in the case of latices and coatings. Particle sizes are in the range of 80–200, 60–148, and 138–224 nm for butene/undecenoic acid/CO, propene/undecenoic acid/CO, and propene/butene/undecenoic acid/CO, respectively (Tables 1–3). In general the stability of the dispersions decreases with increasing particle size or size distribution. Upon drying the dispersions at room temperature, gloss polyketone films were formed. The gloss of a film is a function of the particle size and the particle size distribution, where normally the finer the particle and the more uniform the distribution, the higher the gloss.

2.2 Differential Scanning Calorimetry (DSC)

The two major types of transition temperatures which characterize polymeric materials are the crystalline melting temperature (T_m) and the glass transition temperature (T_g). Both of them are highly influenced by the copolymer composition and the chemical composition distribution and thus are also affected by the type of the emulsion polymerization process. Batch copolymers usually are very different from controlled batch or semi-batch copolymers with the same overall chemical composition.^{5a} Here co- and terpolymerizations were carried out using the batch process. Without undecenoic acid the polyketone latices are unstable. Using catalyst **3c** in this process a gradual decrease of the T_g and T_m values in the sequence propene/CO (Table 1, entry 5: $T_g = 17^\circ\text{C}$, $T_m = 168^\circ\text{C}$) > butene/CO (Table 2, entry 5: $T_g = 12^\circ\text{C}$, $T_m = 160^\circ\text{C}$) was observed. Increasing the chain length of the monomer by one CH_2

residue resulted in a decrease of the T_g value by 5°C. The Incorporation of butene into the propene/carbon monoxide copolymer resulted also in a decrease of the T_g value by 6°C (Table 3, entry 5: $T_g = 11^\circ\text{C}$). For practical applications it is desirable to find routes to set the T_g to values significantly below room temperature. If approximately 5–10% (wt/wt) of undecenoic acid is added to the olefin during the polymerization process the T_g value decreased significantly from room temperature to -2°C . Upon adding undecenoic acid to the starting monomers, stable latices of α -olefin/undecenoic acid/CO copolymers were formed. The CO_2H groups function as polymerizable stabilizers. Using catalyst **3c** the incorporation of undecenoic acid into the butene/CO copolymer resulted in a decrease of the T_g value by 15°C ($T_g = 12^\circ\text{C}$ for butene/CO (Table 2, entry 5) to $T_g = -2.0^\circ\text{C}$ for butene/undecenoic acid/CO (Table 4, entry 2)). Also the introduction of undecenoic acid into the propene/CO copolymer led to a decrease of the T_g value by 6°C ($T_g = 17^\circ\text{C}$ for propene/CO (Table 1, entry 5) to $T_g = 11^\circ\text{C}$ for propene/undecenoic acid/CO (Table 4, entry 1)). By employment of undecenoic acid the propene/butene/CO terpolymer exhibits a glass transition temperature lower than those of propene/CO and butene/CO. The decrease is only 1°C ($T_g = 11^\circ\text{C}$ propene/butene/CO (Table 3, entry 5) to $T_g = 10^\circ\text{C}$ for the polyketone made of propene/butene/undecenoic acid/CO (Table 4 entry 3)) which indicates a relatively low undecenoic acid content. Indeed, the amount of undecenoic acid incorporated into the polymeric chains of propene/butene/CO is about 3% as calculated by inverse gated $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra. In general the T_g value is dependent on the molar percentage of undecenoic acid incorporated into the polyketone. In contrast to the elastic materials obtained with **(dppp)Pd**,²⁶ complexes **3a-h** produce non-elastic thermoplastics. DSC investigations show that there are also crystalline domains in the high molecular weight copolymer. In general the T_g and T_m values increase as the molecular weight of polyketone increases (Tables 1–3), which is responsible for the non-elastic properties.²⁶

Table 1. Propene/CO Copolymerization^a

Run	Catalyst	Productivity/(mol(substr)×mol-(Pd) ⁻¹)	Average Activity/(mol(substr)×mol-(Pd) ⁻¹ h ⁻¹)	$M_w(M_w/M_n)$	M_n	Solids Content/(%)	Particle Size/(nm)	Particle Size Distribution	Thermal Analysis $T_g (T_m)/(°C)$
1	3g	4746	396	60100 (1.68)	35700	7.4	62	0.361	13.18 (146)
2	3f	8844	736	60100 (2.12)	28300	12.1	80.1	0.224	12.95 (133)
3	3e	7880	657	56400 (2.96)	19100	13	147.4	0.055	12.81
4	3d	7151	596	42700 (1.67)	25500	12.4	117.2	0.144	12.65
5	3c	9488	791	39200 (1.89)	20700	16	127.7	0.167	11.34 (107)
6	3b	3428	286	20800 (3.92)	5300	6	104.7	0.39	-2.22
7	3a	5842	487	50400 (2.18)	23100	12.6	93.8	0.162	11.16
8	3h	1304	109	22100 (1.7)	13000	3.88	140	0.09	-2.22

^a Reaction Conditions: 10 μmol of Complexes **3g–3h**; 100 Equiv of HBF₄ (12 ml 1%); 15g of Propene; 30 ml of Water with pH = 5.5; 0.15 g of Emulsifier Texapon; Total Pressure, 60 bar; Reaction Temperature, 60°C; Reaction Time, 12h; 0.15 g of Methyl-β-Cyclodextrin (W7 M 1.8); 1 g of Undecenoic Acid

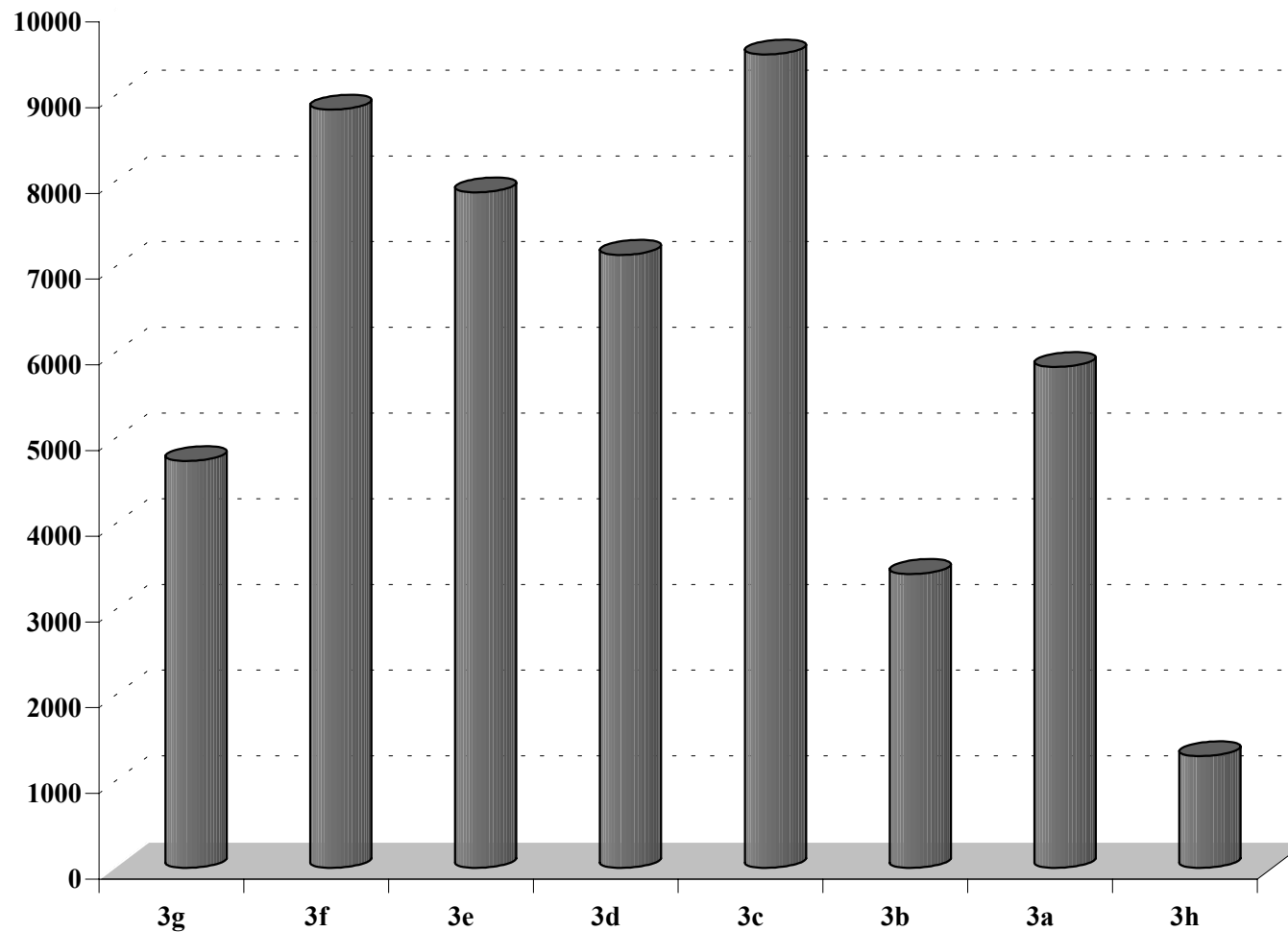
^aProductivity

Figure 6. Propene/CO Copolymerization Using Undecenoic Acid. ^aProductivity in (mol (substr) × mol (Pd)⁻¹)

Table 2. 1-Butene/CO Copolymerization^a

Run	Catalyst	Productivity/(mol(substr)× mol-(Pd) ⁻¹)	Average Activity/(mol(substr) × mol-(Pd) ⁻¹ h ⁻¹)	<i>M_w</i> (<i>M_w</i> / <i>M_n</i>)	<i>M_n</i>	Solids Content/(%)	Particle Size/(nm)	Particle Size Distribution	Thermal Analysis <i>T_g</i> (<i>T_m</i>)/(°C)
1	3g	6561	547	42300 (2.15)	19600	12.7	79.9	0.201	6.98 (99)
2	3f	9004	750	37800 (1.93)	19600	17	167.5	0.246	5.41 (133)
3	3e	7375	615	32600 (1.99)	16400	14.6	141.9	0.18	0.046
4	3d	6587	549	31300 (1.98)	15800	14.2	124.8	0.161	-1.57
5	3c	6393	533	31100 (1.88)	16600	15.5	105.6	0.172	-1.58 (92)
6	3b	2055	171	11900 (2.77)	4300	5.1	134.3	0.562	-0.2
7	3a	7508	625	35300 (1.62)	21900	21.5	200.5	0.248	3.69
8	3h	3879	323	22800 (1.76)	12900	13.2	133.8	0.202	1.98

^a Reaction Conditions: 10 μmol of Complexes **3g–3h**; 100 Equiv of HBF₄ (12 ml 1%); 20 g of Butene; 30 ml of Water with pH = 5.5; 0.15 g of Emulsifier Texapon; Total Pressure, 60 bar; Reaction Temperature, 60°C; Reaction Time, 12 h; 0.15 g of Methyl-β-Cyclodextrin (W7 M 1.8); 1 g of Undecenoic Acid

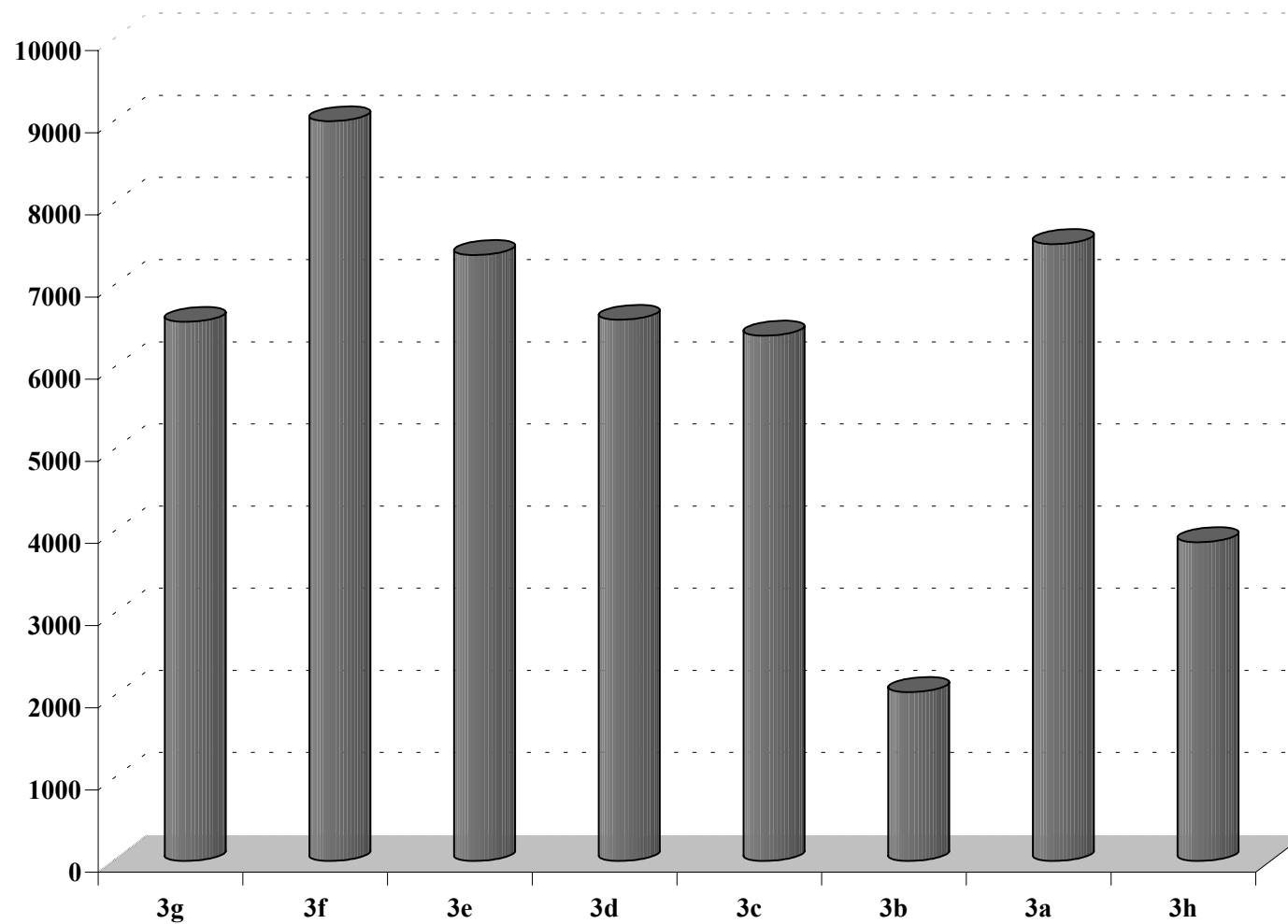
^aProductivity

Figure 7. Butene/CO Copolymerization Using Undecenoic Acid. ^aProductivity in (mol (substr) × mol (Pd)⁻¹)

Table 3. Propene/1-Butene/CO Copolymerization^a

Run	Catalyst	Productivity/(mol(substr)× mol-(Pd) ⁻¹)	Average Activity/(mol(substr)× mol-(Pd) ⁻¹ h ⁻¹)	$M_w(M_w/M_n)$	M_n	Solids Content/(%)	Particle Size/(nm)	Particle Size Distribution	Thermal Analysis T_g (T_m)/(°C)
1	3g	1235	103	62800 (1.93)	32600	4.5	138.2	0.141	15.75 (94)
2	3f	3890	324	52400 (2.19)	23900	13.6	182.1	0.192	14.36 (90)
3	3e	3554	296	41400 (1.85)	22400	12.9	138.9	0.337	12.2
4	3d	3408	284	38700 (2.08)	19000	13	182.7	0.208	11.52
5	3c	3379	282	35900 (2.0)	18000	12.3	178.1	0.148	10.2
6	3a	2816	235	35800 (1.75)	20400	13.7	223.5	0.125	14.2
7	3h	307	26	26800 (1.83)	14600	2.01	659.8	0.035	9.8

^a Reaction Conditions: 10 μmol of Complexes **3g–3h**; 100 Equiv of HBF₄ (12 ml 1%); 15 g of Propene; 20 g of Butene, Propene:Butene (1:1); 30 ml of Water with pH = 5.5; 0.15 g of Emulsifier Texapon; Total Pressure 60 bar; Reaction Temperature, 60°C; Reaction Time, 12 h; 0.15 g of Methyl-β-Cyclodextrin (W7 M 1.8); 1 g of Undecenoic Acid

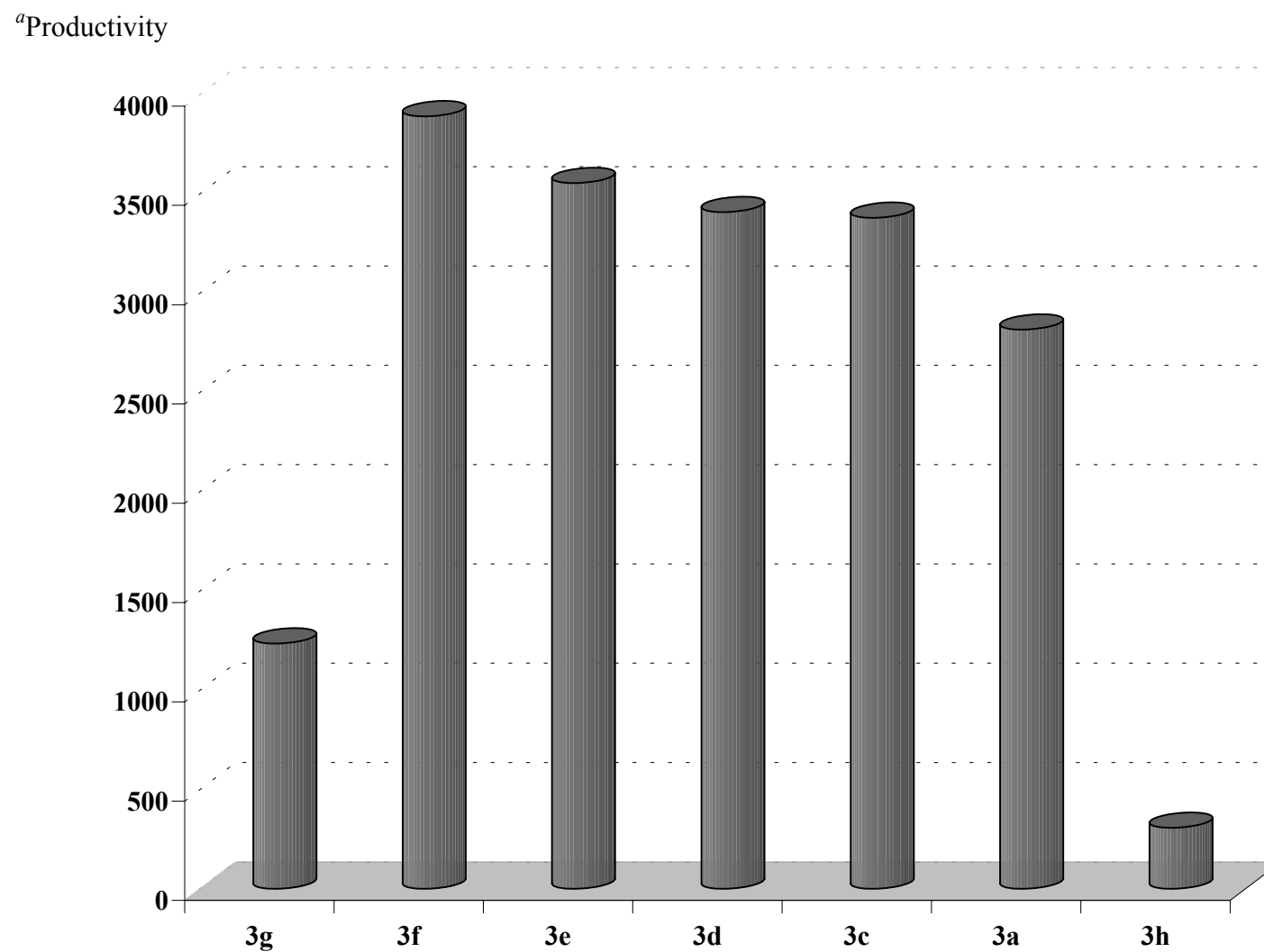


Figure 8. Propene/Butene/CO Terpolymerization Using Undecenoic Acid. ^aProductivity in (mol (substr) × mol (Pd)⁻¹)

2.3 Molecular Characterization

2.3.1 Molecular Weight (M_w)

It is noticed that the molecular weight of the α -olefin/CO copolymers increase significantly as the chain length of the monomers decreases (Tables 1 and 2).¹² There is also a direct relationship between the chain length of the alkyl substituents of the catalyst with the catalytic efficiency and the molecular weight of the resulting polyketone copolymer. These three variables are directly proportional to each other. This indicates clearly that the steric properties of the catalyst control the molecular weights and the microstructure (e.g. the regioregularity) of the copolymers. The most efficient catalyst in the copolymerization of propene/undecenoic acid/CO is catalyst **3c**, and the most efficient catalyst in the copolymerization of butene/undecenoic acid/CO and propene/butene/undecenoic acid/CO is catalyst **3f** (Tables 1–3). These Tables also show and describe for the first time a process by which aqueous polyketone latices with high solids content up to 23% and high molecular weights up to 6.3×10^4 g mol⁻¹ are produced at rates similar to the commercially process performed in methanol.

2.4 Chemical Composition

2.4.1 Analysis of the Propene/CO, Butene/CO, and Propene/Butene/CO Microstructures without Undecenoic Acid

Unlike the alternating copolymers of carbon monoxide with ethylene, which are very high-melting and insoluble, the α -olefin/CO copolymers are either semicrystalline having lower T_m values depending on their microstructure and molecular weight^{2g,29} or amorphous.

^{2g,30} The α -olefin/CO copolymers are quite soluble in common polar organic solvents such as chloroform, acetonitrile, etc. High-molecular-weight α -olefin/CO copolymers can be precipitated by cold methanol. A strong IR absorption band (CDCl_3 or film) at 1706 cm^{-1} is ascribed to the carbonyl group.

$^{13}\text{C}\{^1\text{H}\}$ -NMR spectroscopy is the best technique to determine the regioregularity and stereochemical configuration of the co- and terpolymers of propene/CO, butene/CO, and propene/butene/CO with and without undecenoic acid. The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra (in CDCl_3) (Figures 9a–11a, Table 4) of the propene/CO, butene/CO, and propene/butene/CO copolymers, respectively, show only a single peak for the carbonyl group and this gives an indication that we have perfectly head-to-tail regioregular polyketones. The DEPT technique was applied to show that the signal in the case of propene/CO at 43.3 ppm is due to the methylene carbon atoms, while the peak at 38.9 ppm is the resonance of the methine carbon atoms. But in the case of butene/CO the resonance at 47.4 ppm is due to the methine carbon atoms, while the peak at 45.2 ppm is the resonance of the methylene carbon atoms. The integrated areas of the ^{13}C peaks of the carbonyl, main-chain CH and CH_2 , and side-chain CH_3 groups maintain a ratio of 1:1:1:1. Therefore, these high-molecular-weight propene/CO copolymers have the alternating structure. Also in the case of butene/CO copolymers, the integrated areas of the ^{13}C signals of the carbonyl, main-chain CH and CH_2 , and side-chain CH_2 and CH_3 functions show a ratio of 1:1:1:1:1. Therefore, these high-molecular-weight copolymers have an alternating structure. For the propene/butene/CO terpolymers, the integrated areas of the ^{13}C signals of the carbonyl and side-chain CH_3 groups of the propene/CO units and of the side-chain CH_3 groups of the butene/CO units show a ratio of 2:1:1. Therefore, also these high-molecular-weight terpolymers show an alternating arrangement of the monomeric building blocks.

Table 4. $^{13}\text{C}\{^1\text{H}\}$ -NMR (δ) of Polyketones without Undecenoic Acid Made by Catalyst 3c. CDCl_3 was Used as the Solvent

Polyketones	Carbonyl Group	Main-Chain CH	Main-Chain CH ₂	Side-Chain CH ₂	Side-Chain CH ₃
Propene/CO	211.0	38.9	43.3	-	15.0
Butene/CO	213.7	47.4	45.2	25.3	12.3
Propene/Butene/CO	211.9–211.2	46.0 ^a	44.0 ^a	23.5 ^a	10.5 ^a
		40.0 ^b	42.0 ^b	-	15.6 ^b

^a Butene/CO. ^b Propene/CO

2.4.2 Analysis of the Propene/CO, Butene/CO, and Propene/Butene/CO Microstructures Using Undecenoic Acid

Elemental analyses as well as IR and NMR spectroscopic investigations (Experimental Part) confirmed the incorporation of undecenoic acid in the aforementioned polyketones. Inverse gated $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were employed to determine the percentage of the undecenoic acid amount which is incorporated into the structure of the polymer. In the aforementioned polymerization process, performed by catalyst **3c**, the percentage of the incorporation of undecenoic acid is 13% in the case of the butene/CO, 7% in the case of the propene/CO, and only 3% in the case of propene/butene/CO copolymer.

The IR spectra of the propene/undecenoic acid/CO, butene/undecenoic acid/CO, and propene/butene/undecenoic acid/CO copolymers show a carbonyl stretching band centered at 1703 cm^{-1} , slightly broader than that found in the spectra of the propene/CO, butene/CO, and propene/butene/CO copolymers. Also there is a broad hydroxy stretching band of the undecenoic acid at 3284 cm^{-1} .

$^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3) spectra (Figures 9b-10b and Experimental Part) and the elemental analyses of the propene/CO and butene/CO polymeric materials confirm the incorporation of undecenoic acid in the polyketone backbone. As expected, only isolated undecenoic acid-derived units $[-\text{CH}_2\text{CHR}'\text{C}(=\text{O})\text{CH}_2\text{CHRC}(=\text{O})-$ with $\text{R}' = \text{CH}_3$, or CH_2CH_3 , $\text{R} = (\text{CH}_2)_8\text{COOH}$] are detected. The same analyses [$^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum (in CDCl_3) (see Figure 11b), elemental analyses] also confirmed the incorporation of undecenoic acid in the polyketone backbone of the terpolymer propene/butene/CO. The difference here are the undecenoic acid-derived units $[-\text{CH}_2\text{CHCH}_3\text{C}(=\text{O})\text{CH}_2\text{CHCH}_2\text{CH}_3-\text{C}(=\text{O})\text{CH}_2\text{CHRC}(=\text{O})-$ with $\text{R} = (\text{CH}_2)_8\text{COOH}$].

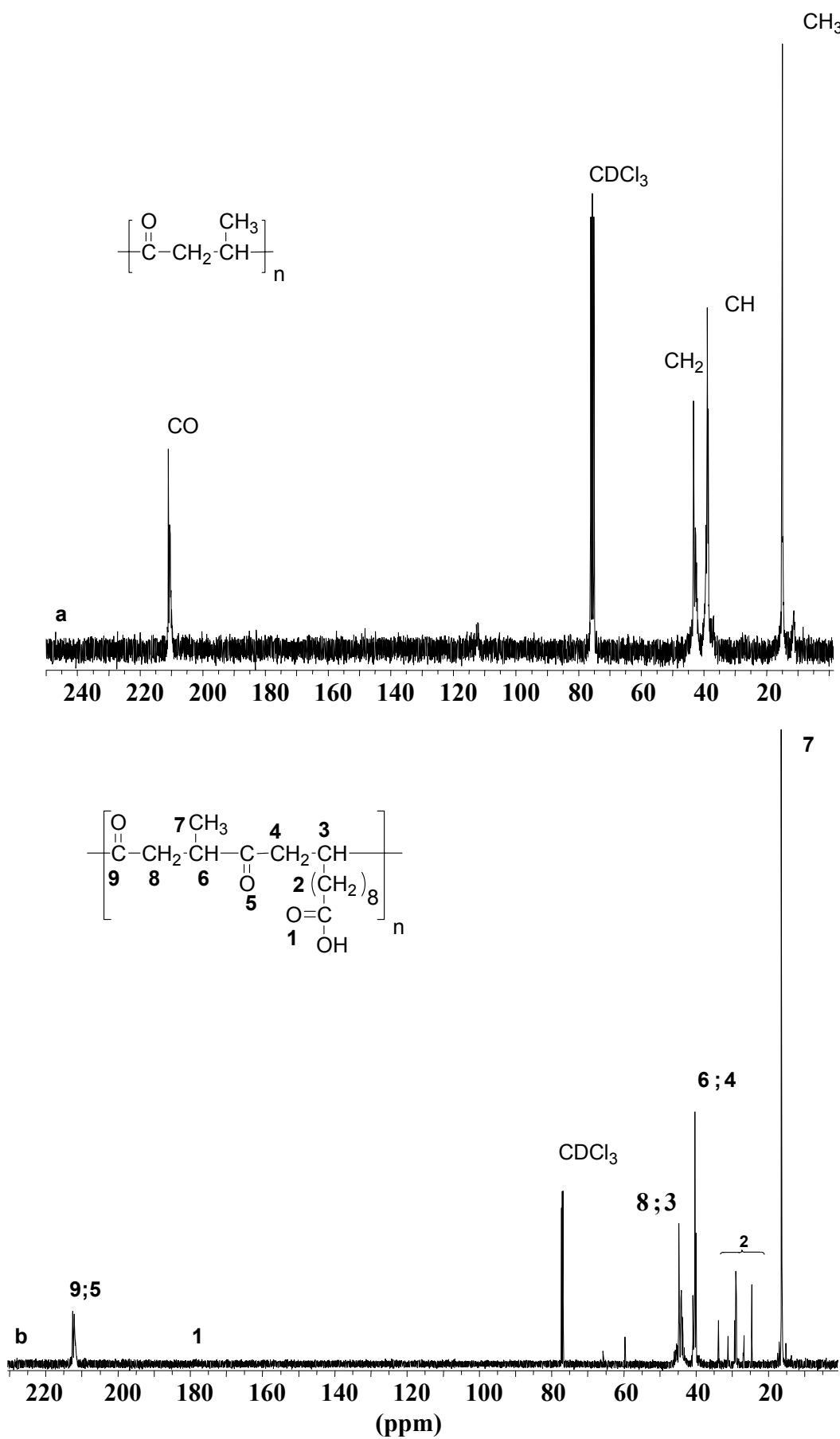


Figure 9. ^{13}C NMR Spectra of Propene/CO **(a)**. Propene/Undecenoic Acid/CO **(b)**

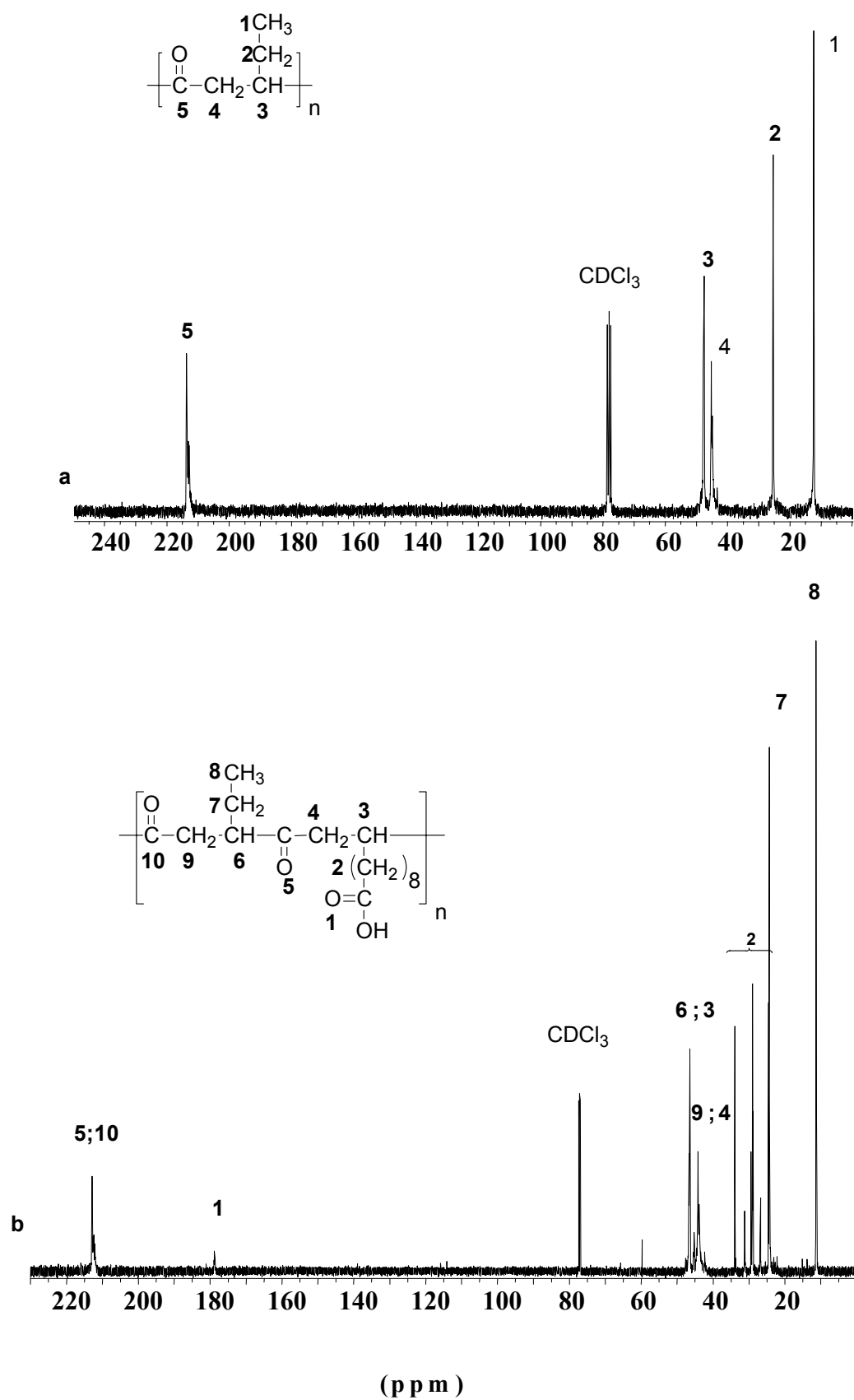


Figure 10. ^{13}C NMR Spectra of Butene/CO (a). Butene/Undecenoic Acid/CO (b)

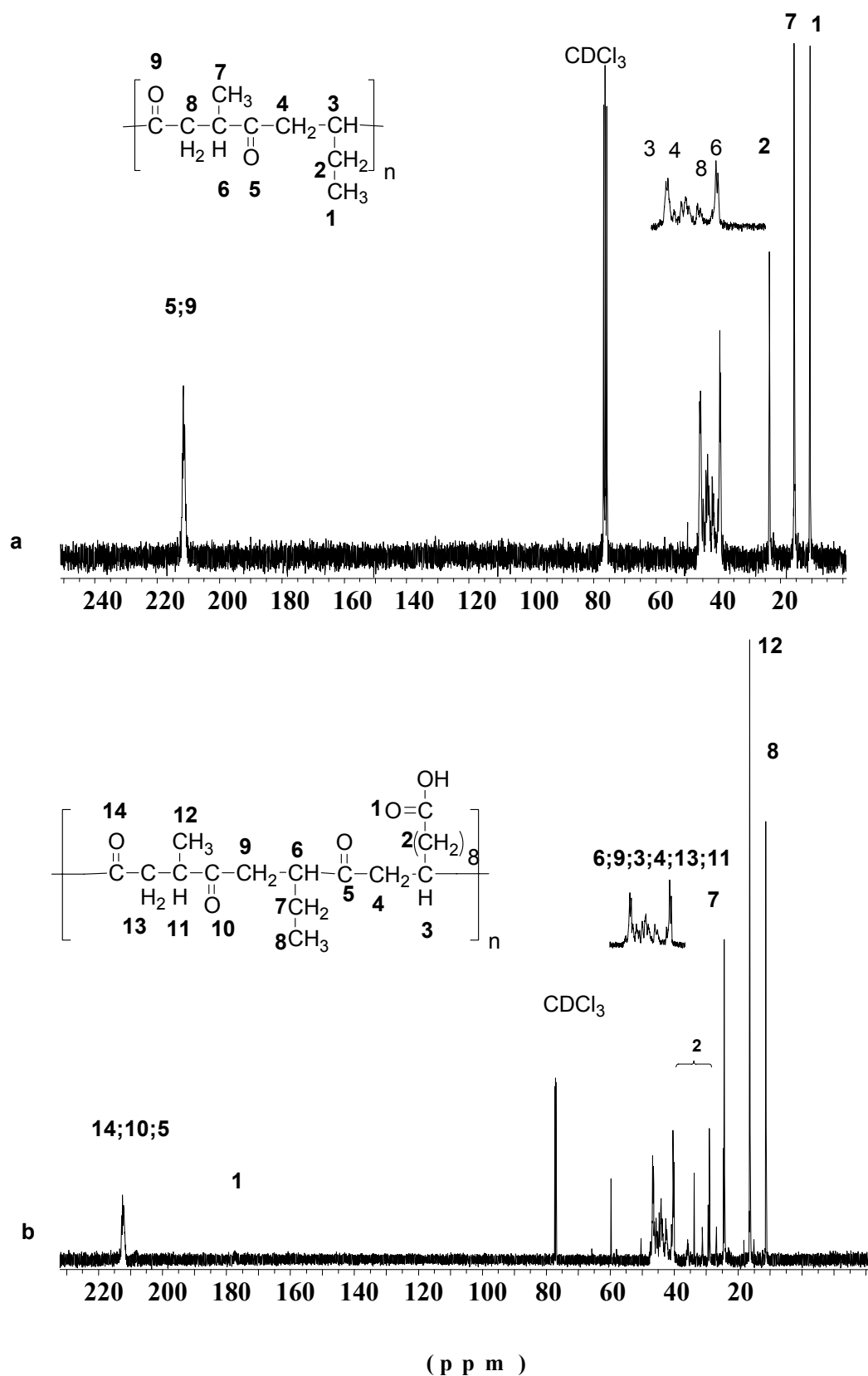


Figure 11. ^{13}C NMR Spectra of Propene/Butene/CO **(a)**. Propene/Butene/Undecenoic Acid/CO **(b)**

2.5 Conclusion

Three types of palladium complexes **3a-h** with hydroxyalkyl, phosphonate and amine substituents attached to the phosphorus donors were employed in the emulsion copolymerization of propene/CO, butene/CO, and propene/butene/CO. The presence of hydroxy groups in complex **3a** is responsible for the dark color of the dispersion, because alcoholic functions are known to reduce palladium(II) complexes to palladium(0). Such a reduction of palladium(II) was circumvented by using phosphonate and amine substituted diphosphine ligands of different length and steric demand. In the copolymerization of olefins with carbon monoxide using **3a-h** as catalyst precursors organic solvents can be replaced for the inexpensive, non-toxic and non-flammable reaction medium water. Depending on the chain-length of the phosphorus attached substituents in the catalysts **3a-h**, four variables for the propene/CO, butene/CO, and propene/butene/CO copolymers were controlled: (i) the regioregularity; (ii) the molecular weight, and (iii) the glass transition temperature and the melting point (T_g and T_m). Stable dispersions are obtained by introduction of undecenoic acid as a third or fourth monomer into the propene/CO, butene/CO, and propene/butene/CO copolymers and no phase separation, or the formation of a coagulum within ten weeks were observed. In these latices, hydrophilic carboxylic acid moieties covalently bound to the particle surface contribute to the stabilization. Using phase-transfer agents, namely methyl- β -cyclodextrin (W7 M 1.8) in the process of the co- and terpolymerization of hydrophobic monomers in the emulsion polymerization led to better results. Higher solids contents of the polyketones and a higher productivity of the catalysts were observed.

Experimental Section

1. General Comments

All experiments were carried out under an atmosphere of argon, if not stated otherwise. Dichloromethane was distilled from calcium hydride, diethyl ether, and THF from sodium-benzophenone, *n*-hexane from LiAlH₄, methanol from magnesium, and acetonitrile from P₄O₁₀. Palladium(II) acetate and allylamine were purchased from Acros and Fluka, respectively. Elemental analyses were carried out with an Elementar Vario El analyzer. The high resolution ¹H-, ¹³C{¹H}-, and ³¹P{¹H}-NMR spectra were measured relative to partially deuterated and deuterated solvent peaks, respectively, which are reported relative to TMS. ³¹P{¹H} spectra were measured relative to 85% H₃PO₄. Mass spectra were acquired on a Finnigan MAT 711A instrument modified by AMD and reported as mass/charge (*m/z*). IR spectra were recorded on a Bruker IFS 48 FTIR spectrometer. The alkenyl phosphonates CH₂=CH-(CH₂)_n-P(O)(OEt)₂ were obtained either from commercial suppliers (*n* = 0, 1) or prepared by literature methods (*n* = 2–4, 6).^{14,15} Also the diprimary phosphine CH₂(CH₂PH₂)₂,¹⁶ ligand **2a**,¹² and complex **3a**¹² were synthesized according to known specifications. Propene, 1-butene, and carbon monoxide were of polymer grade and generously provided by BASF Aktiengesellschaft and used without further purification. Methyl-β-cyclodextrin (W7 M 1.8) and the emulsifier Texapon[®] NSO (28%) were purchased from Wacker-Chemie GmbH and Henkel GmbH, respectively. Deionized water was degassed prior to use. Co- and terpolymerizations were carried out in a stainless steel autoclave (volumes 100 ml, 150 ml, respectively) equipped with a mechanical stirrer and a heating system (thermostate). The parameters, pressure, and stirring mechanism were measured, controlled, and recorded by a personal computer. Charging and venting steps were also

controlled and executed by a computer. Thus a high degree of reproducibility was guaranteed. The copolymer microstructures without undecenoic acid were analyzed by ^1H (250.13 MHz)- and $^{13}\text{C}\{^1\text{H}\}$ (62.9 MHz)-NMR spectroscopy on a Bruker DRX 250 at 20 °C using CDCl_3 as solvent. The copolymer microstructures using undecenoic acid were analyzed by ^1H (600.13 MHz)- and ^{13}C (150.9 MHz)-NMR spectroscopy on a Bruker AMX-600 MHz using CDCl_3 as solvent. IR spectra were recorded on a Bruker IFS 48 FTIR spectrometer. The determination of the glass transition temperatures and/or the melting points generally took place in accordance with DIN 53765 by means of a DSC820-instrument, Series TA8000 of Mettler Toledo. Glass transitions refer to the middle temperatures of the first heating cycle. Molecular weights were determined by means of gel permeation chromatography (GPC), using a set-up consisting of a Perkin-Elmer Series 10 HPLC pump, a Perkin-Elmer LC 90 UV detector, a PSS SDV linear XL column (eluent CHCl_3) with a pore size of 10 μm or a PSS PFG linear XL column (eluent 1,1,1,3,3,3-hexafluoroisopropanol containing 0.05 weight percentage of potassium trifluoroacetate) with a pore size of 7 μm . Dynamic light scatterings on dispersions were performed by means of an Autosizer IIC of Malvern instruments. The solid content of the polymer was carried out on a Sartorius Moisture Analyzer, model MA100/ MA50 .

2. Preparation of the Compounds

2.1 General Procedure for the Preparation of the Diphosphines 2b–h

In a quartz Schlenk tube 1,3-diphosphinopropane and a 10% excess of the corresponding olefin were magnetically stirred and the mixture was irradiated with ultraviolet light of a mercury high pressure lamp at 20°C. After 10 h, excess olefin was removed under reduced pressure. Further purification was not necessary (Scheme 5).

2.1.1 1,3-Bis[di(2-diethylphosphonatoethyl)phosphino]propane (2b)

1,3-Diphosfinopropane (600 mg, 5.55 mmol) and diethyl vinylphosphonate (4.0 g, 24.4 mmol) were reacted to give **2b** as a colorless air-sensitive oil (4.0 g, 95% yield). ^1H NMR (CDCl_3): $\delta = 1.27$ (t, $^3J_{\text{HH}} = 7.1$ Hz, 24H, OCH_2CH_3), 1.45–1.90 (m, 22H, $\text{CH}_2\text{CH}_2\text{P}((\text{CH}_2)_2)_2$), 4.01–4.07 (m, 16H, OCH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 16.8$ (d, $^3J_{\text{PC}} = 6.1$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 18.95 (dd, $^1J_{\text{PC}} = 16.2$, $^2J_{\text{PC}} = 6.7$ Hz, $\text{O}=\text{PCH}_2\text{CH}_2\text{P}$), 22.0 (dd, $^1J_{\text{PC}} = 140.5$, $^2J_{\text{PC}} = 13.8$ Hz, $\text{O}=\text{PCH}_2\text{CH}_2\text{P}$), 22.7 (s, $\text{CH}_2\text{CH}_2\text{P}$), 28.6 ($N^{17} = 26.3$ Hz, CH_2P), 62.0 (d, $^2J_{\text{PC}} = 6.7$ Hz, $\text{CH}_3\text{CH}_2\text{O}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = -22.0$ (t, $^3J_{\text{PP}} = 51.2$ Hz, 2P, PC_3), 32.3 (d, $^3J_{\text{PP}} = 51.2$ Hz, 4P, $\text{CP}(\text{O})(\text{OEt})_2$). IR (KBr, cm^{-1}): $\nu = 2981, 2934, 2908$ (CH_2), 1240 ($\text{P}=\text{O}$), 1028 ($\text{P}-\text{OEt}$). MS (FAB, 50°C): m/z 765.3 $[\text{M} + \text{H}]^+$. Anal. Calcd. for $\text{C}_{27}\text{H}_{62}\text{O}_{12}\text{P}_6$ (764.27): C, 42.41; H, 8.17. Found: C, 42.06; H, 8.51.

2.1.2 1,3-Bis[di(3-diethylphosphonatopropyl)phosphino]propane (2c)

1,3-Diphosfinopropane (600 mg, 5.55 mmol) and diethyl allylphosphonate (4.34 g, 24.4 mmol) were reacted to give **2c** as a colorless air-sensitive oil (4.3 g, 95% yield). ^1H NMR (CDCl_3): $\delta = 1.26$ (t, $^3J_{\text{HH}} = 7.1$ Hz, 24H, OCH_2CH_3), 1.4–1.8 (m, 30H, $\text{CH}_2\text{CH}_2\text{P}((\text{CH}_2)_3)_2$), 3.96–4.05 (m, 16H, OCH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 16.8$ (d, $^3J_{\text{PC}} = 6.1$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 19.52 (dd, $^1J_{\text{PC}} = 15.5$, $^3J_{\text{PC}} = 4.7$ Hz, $\text{O}=\text{P}(\text{CH}_2)_2\text{CH}_2\text{P}$), 27.5 (dd, $^1J_{\text{PC}} = 139.8$, $^3J_{\text{PC}} = 11.8$ Hz, $\text{O}=\text{PCH}_2(\text{CH}_2)_2\text{P}$), 28.0–28.6 (m, $\text{CH}_2\text{CH}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{P}=\text{O}$), 29.1 ($N^{17} = 21.6$ Hz, CH_2P), 61.7 (d, $^2J_{\text{PC}} = 6.7$ Hz, $\text{CH}_3\text{CH}_2\text{O}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = -32.0$ (s, 2P, PC_3), 32.4 (s, 4P, $\text{CP}(\text{O})(\text{OEt})_2$). IR (KBr, cm^{-1}): $\nu = 2981, 2932, 2907$ (CH_2), 1236 ($\text{P}=\text{O}$), 1029

(P-OEt). MS (FAB, 50°C): m/z 821.2 $[M + H]^+$. Anal. Calcd. for $C_{31}H_{70}O_{12}P_6$ (820.33): C, 45.37; H, 8.60. Found: C, 45.05; H, 8.86.

2.1.3 1,3-Bis[di(4-diethylphosphonatobutyl)phosphino]propane (2d)

1,3-Diphosphinopropane (600 mg, 5.55 mmol) and diethyl 3-butenylphosphonate (4.69 g, 24.4 mmol) were reacted to give **2d** as a colorless air-sensitive oil (4.7 g, 97% yield). 1H NMR (CD_3OD): δ = 1.26 (t, $^3J_{HH} = 7.1$ Hz, 24H, OCH_2CH_3), 1.4–1.8 (m, 38H, $CH_2CH_2P((CH_2)_4)_2$), 3.96–4.09 (m, 16H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 17.0 (d, $^3J_{PC} = 6.1$ Hz, CH_3CH_2O), 23.9 (s, CH_2CH_2P), 25.2 (dd, $^1J_{PC} = 11.8$, $^4J_{PC} = 5.1$ Hz, $O=P-(CH_2)_3CH_2P$), 26.8 (d, $^1J_{PC} = 140.1$ Hz, $O=PCH_2(CH_2)_3P$), 27.6–27.8 (m, $O=PCH_2CH_2-(CH_2)_2P$), 27.9–28.0 (m, $O=P(CH_2)_2CH_2CH_2P$), 30.1 ($N^{17} = 22.9$ Hz, CH_2P), 60.5 (d, $^2J_{PC} = 6.1$ Hz, CH_3CH_2O). $^{31}P\{^1H\}$ NMR (CD_3OD): δ = -33.2 (s, 2P, PC_3), 33.0 (s, 4P, $CP(O)(OEt)_2$). IR (KBr, cm^{-1}): ν = 2981, 2934, 2907, 2872 (CH_2), 1246 ($P=O$), 1053 ($P-OEt$). MS (FAB, 50°C): m/z 877.2 $[M + H]^+$. Anal. Calcd. for $C_{31}H_{70}O_{12}P_6$ (876.4): C, 47.94; H, 8.97. Found: C, 47.62; H, 9.40.

2.1.4 1,3-Bis[di(5-diethylphosphonatopentyl)phosphino]propane (2e)

1,3-Diphosphinopropane (600 mg, 5.55 mmol) and diethyl 4-pentenylphosphonate (5.03 g, 24.4 mmol) were reacted to give **2e** as a colorless air-sensitive oil (5.07 g, 98% yield). 1H NMR ($CDCl_3$): δ = 1.03 (t, $^3J_{HH} = 7.1$ Hz, 24H, OCH_2CH_3), 1.1–1.5 (m, 46H, $CH_2CH_2P-((CH_2)_5)_2$), 3.69–3.8 (m, 16H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 15.9 (d, $^3J_{PC} = 6.1$ Hz, CH_3CH_2O), 21.5–21.6 (m, $CH_2CH_2P((CH_2)_3CH_2CH_2)_2$), 24.8 (dd, $^1J_{PC} = 13.5$, $^5J_{PC} = 6.7$ Hz, $O=P(CH_2)_4CH_2P$), 24.9 (d, $^1J_{PC} = 140.1$ Hz, $O=PCH_2(CH_2)_4P$), 26.4 (d, $^2J_{PC} = 12.1$,

O=P(CH₂)₃CH₂CH₂P), 31.4–31.8 (m, CH₂CH₂P((CH₂)₂CH₂(CH₂)₂)), 60.8 (d, ²J_{PC} = 6.1 Hz, CH₃CH₂O). ³¹P{¹H} NMR (CDCl₃): δ = -30.7 (s, 2P, PC₃), 33.3 (s, 4P, CP(O)(OEt)₂). IR (KBr, cm⁻¹): ν = 2981, 2934, 2907, 2869 (CH₂), 1244 (P=O), 1053 (P–OEt). MS (FAB, 50°C): *m/z* 933.2 [M + H]⁺. Anal. Calcd. for C₃₉H₈₆O₁₂P₆ (932.45): C, 50.21; H, 9.29. Found: C, 49.80; H, 9.19.

2.1.5 1,3-Bis[di(6-diethylphosphonatohexyl)phosphino]propane (2f)

1,3-Diphosphinopropane (600 mg, 5.55 mmol) and diethyl 5-hexenylphosphonate (5.4 g, 24.4 mmol) were reacted to give **2f** as a colorless air-sensitive oil (5.4 g, 99% yield). ¹H NMR (CDCl₃): δ = 1.45–1.52 (m, 24H, OCH₂CH₃), 1.6–1.9 (m, 54H, CH₂CH₂P((CH₂)₆)₂), 4.16–4.27 (m, 16H, OCH₂CH₃). ¹³C{¹H} NMR (CDCl₃): δ = 16.8 (d, ³J_{PC} = 6.1 Hz, CH₃CH₂O), 22.49–22.91 (m, CH₂CH₂P((CH₂)₄CH₂CH₂)₂), 25.9 (d, ¹J_{PC} = 140.1 Hz, O=PCH₂(CH₂)₅P), 26.03 (d, ¹J_{PC} = 12.1 Hz, O=P(CH₂)₅CH₂P), 27.4 (d, ²J_{PC} = 10.8 Hz, O=P(CH₂)₄CH₂CH₂P), 30.7 (d, ³J_{PC} = 16.8 Hz, O=P(CH₂)₃CH₂(CH₂)₂P), 31.1–31.4 (m, CH₂CH₂P((CH₂)₃CH₂(CH₂)₂)₂), 61.7 (d, ²J_{PC} = 6.1 Hz, CH₃CH₂O). ³¹P{¹H} NMR (CDCl₃): δ = -30.3 (s, 2P, PC₃), 33.6 (s, 4P, CP(O)(OEt)₂). IR (KBr, cm⁻¹): ν = 2980, 2930, 2907, 2864 (CH₂), 1241 (P=O), 1024 (P–OEt). MS (FAB, 50°C): *m/z* 989.5 [M + H]⁺. Anal. Calcd. for C₃₁H₇₀O₁₂P₆ (988.52): C, 52.22; H, 9.58. Found: C, 51.76; H, 9.69.

2.1.6 1,3-Bis[di(8-diethylphosphonatooctyl)phosphino]propane (2g)

1,3-Diphosphinopropane (600 mg, 5.55 mmol) and diethyl 7-octenylphosphonate (6.1 g, 24.4 mmol) were reacted to give **2g** as a colorless air-sensitive oil (5.9 g, 97% yield). ¹H NMR (CDCl₃): δ = 1.08–1.15 (m, 24H, OCH₂CH₃), 1.28–1.58 (m, 70H, CH₂CH₂P((CH₂)₈)₂),

3.8–3.9 (m, 16H, OCH₂CH₃). ¹³C{¹H} NMR (CDCl₃): δ = 16.7 (d, ³J_{PC} = 6.1 Hz, CH₃CH₂O), 22.4–22.6 (m, CH₂CH₂P((CH₂)₆CH₂CH₂)₂), 25.8 (d, ¹J_{PC} = 140.1 Hz, O=PCH₂(CH₂)₇P), 26.1 (d, ¹J_{PC} = 12.1 Hz, O=P(CH₂)₇CH₂P), 27.36 (d, O=P(CH₂)₂CH₂(CH₂)₅P), 28.69–29.6 (m, O=P(CH₂)₅CH₂CH₂CH₂P), 30.7 (d, ⁴J_{PC} = 16.84 Hz, O=P(CH₂)₃CH₂(CH₂)₄P), 31.3–31.7 (m, CH₂CH₂P((CH₂)₃CH₂(CH₂)₄)₂), 61.5 (d, ²J_{PC} = 6.1 Hz, CH₃CH₂O). ³¹P{¹H} NMR (CDCl₃): δ = -30.6 (s, 2P, PC₃), 33.6 (s, 4P, CP(O)(OEt)₂). IR (KBr, cm⁻¹): ν = 2980, 2926, 2854 (CH₂), 1248 (P=O), 1030 (P–OEt). MS (FAB, 50°C): *m/z* 1101.4 [M + H]⁺. Anal. Calcd. for C₃₁H₇₀O₁₂P₆ (1100.6): C, 55.62; H, 10.07. Found: C, 55.11 H, 9.59.

2.1.7 1,3-Bis[di(3-aminopropyl)phosphino]propane (2h)

1,3-Diphosphinopropane (600 mg, 5.55 mmol) and allylamine (1.4 g, 24.4 mmol) were reacted to give **2h** as a colorless air-sensitive oil (1.77 g, 95% yield). ¹H NMR (CDCl₃): δ = 0.85–1.13 (m, 22H, CH₂CH₂P(CH₂CH₂)₂), 2.25–2.32 (m, CH₂CH₂P((CH₂)₂CH₂NH₂)₂). ¹³C{¹H} NMR (CDCl₃): δ = 24.9 (t, ²J_{PC} = 13,81 Hz, CH₂CH₂P), 26.7 (d, ¹J_{PC} = 12.1 Hz, CH₂CH₂P(CH₂(CH₂)₂NH₂)₂), 31.6 (^N17 = 23.6 Hz, CH₂CH₂P), 32.4 (d, ²J_{PC} = 12.1 Hz, CH₂CH₂P(CH₂CH₂CH₂NH₂)₂), 46.02 (d, ³J_{PC} = 11.45 Hz, CH₂CH₂P((CH₂)₂CH₂NH₂)₂). ³¹P{¹H} NMR (CDCl₃): δ = -30.2 (s). IR (KBr, cm⁻¹): ν = 3355, 3278 (NH), 2923, 2854 (CH₂), 1072 (C–N). MS (FAB, 50°C): *m/z* 337.3 [M + H]⁺. Anal. Calcd. for C₁₅H₃₈N₄P₂ (336.3): C, 53.55; H, 11.38; N, 16.65. Found: C, 53.18; H, 11.69; N, 16.10.

2.2 General Procedure for the Preparation of the Palladium(II) Complexes 3b–h

To a stirred solution of palladium(II) acetate in 50 ml of acetonitrile a solution of **2b–h** in 50 ml of dichloromethane was added at 25°C. Subsequently the solvents were

removed under reduced pressure. Finally the complexes **3b–h** were precipitated from dichloromethane with *n*-hexane and dried in vacuo (Scheme 5).

2.2.1 Diacetato{1,3-bis[di(2-diethylphosphonatoethyl)phosphino]propane}palladium (II) (**3b**)

2b (363 mg, 0.475 mmol) was reacted with palladium(II) acetate (107 mg, 0.475 mmol) to give **3b** as an orange oil (399 mg, 85% yield). ^1H NMR (CDCl_3): $\delta = 1.22\text{--}1.33$ (m, 24H, OCH_2CH_3), 1.5–2.6 (m, 28H, $\text{CH}_2\text{CH}_2\text{P}(\text{CH}_2\text{CH}_2)_2$), 3.99–4.1 (m, 16H, OCH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 16.8$ (d, $^3J_{\text{PC}} = 6.1$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 19.9–20.1 (m, $\text{O}=\text{PCH}_2\text{-CH}_2\text{P}$), 20.7 (d, $^1J_{\text{PC}} = 140.8$, $\text{O}=\text{PCH}_2\text{CH}_2\text{P}$), 21.1 (s, $\text{CH}_2\text{CH}_2\text{P}$), 23.8 (s, CH_3CO_2^-), 30.3 (s, CH_2P), 62.4–62.7 (m, $\text{CH}_3\text{CH}_2\text{O}$), 177.3 (s, CH_3CO_2^-). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 22.1$ (X-Part of an $[\text{A}_2\text{X}]_2$ spin-pattern, 2P, PC_3), 30.0 (A-Part of an $[\text{A}_2\text{X}]_2$ spin pattern, 4P, $\text{CP}(\text{O})(\text{OEt})_2$). IR (KBr, cm^{-1}): $\nu = 2982, 2931, 2908$ (CH_2), 1238 ($\text{P}=\text{O}$), 1028 ($\text{P}-\text{OEt}$), $\nu_s = 1403$ (CH_3CO_2^-), $\nu_{\text{as}} = 1576$ (CH_3CO_2^-). MS (FAB, 50°C): m/z 929.0 $[\text{M} - \text{OAc}]^+$. Anal. Calcd. for $\text{C}_{31}\text{H}_{68}\text{O}_{16}\text{P}_6\text{Pd}$ (988.2): C, 37.64; H, 6.93. Found: C, 37.26; H, 6.81.

2.2.2 Diacetato{1,3-bis[di(3-diethylphosphonatopropyl)phosphino]propane}palladium (II) (**3c**)

2c (845 mg, 1.03 mmol) was reacted with palladium(II) acetate (231 mg, 1.03 mmol) to give **3c** as an orange oil (915 mg, 84% yield). ^1H NMR (CDCl_3): $\delta = 1.26$ (m, 24H, OCH_2CH_3), 1.6–2.1 (m, 30H, $\text{CH}_2\text{CH}_2\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2)_2$), 3.96–4.1 (m, 16H, OCH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 16.8$ (d, $^3J_{\text{PC}} = 6.1$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 18.1 (d, $^3J_{\text{PC}} = 5.4$ Hz, $\text{O}=\text{P-CH}_2\text{CH}_2\text{CH}_2\text{P}$), 19.4 (s, $\text{CH}_2\text{CH}_2\text{P}$), 23.9 (s, CH_3CO_2^-), 25.4–26.2 (m, $\text{CH}_2\text{CH}_2\text{PCH}_2\text{-}$

CH₂CH₂P=O), 26.7 (d, $^1J_{\text{PC}} = 139.8$ Hz, O=PCH₂CH₂CH₂P), 27.6–27.8 (m, CH₂P), 62.0 (m, CH₃CH₂O), 177.3 (s, CH₃CO₂⁻). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 14.3$ (s, 2P, PC₃), 31.7 (s, 4P, CP(O)(OEt)₂). IR (KBr, cm⁻¹): $\nu = 2984, 2932, 2908$ (CH₂), 1238 (P=O), 1028 (P–OEt), $\nu_{\text{s}} = 1403$ (CH₃CO₂⁻), $\nu_{\text{as}} = 1576$ (CH₃CO₂⁻). MS (FAB, 50°C): m/z 985.2 [M – OAc]⁺. Anal. Calcd. for C₃₅H₇₆O₁₆P₆Pd (1044.3): C, 40.22; H, 7.33. Found: C, 39.77; H, 7.76.

2.2.3 Diacetato{1,3-bis[di(4-diethylphosphonatobutyl)phosphino]propane}palladium (II) (3d)

2d (1385 mg, 1.58 mmol) was reacted with palladium(II) acetate (355 mg, 1.58 mmol) to give **3d** as an orange oil (1513 mg, 87% yield). ^1H NMR (CDCl₃): $\delta = 1.26$ (t, $^3J_{\text{HH}} = 7.1$ Hz, 24H, OCH₂CH₃), 1.48–2.0 (m, 36H, CH₂CH₂P(CH₂CH₂CH₂)₂), 3.95–4.07 (m, 16H, OCH₂CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 16.8$ (d, $^3J_{\text{PC}} = 6.1$ Hz, CH₃CH₂O), 19.7 (s, CH₂CH₂P), 23.8 (s, CH₃CO₂⁻), 24.2–24.5 (m, O=PCH₂CH₂CH₂CH₂P), 25.2 (d, $^1J_{\text{PC}} = 140.8$ Hz, O=PCH₂(CH₂)₃P), 25.4 ($N^{17} = 22.2$ Hz, O=P(CH₂)₃CH₂P), 25.5 (s, O=PCH₂CH₂CH₂CH₂P), 32.1 (s, CH₂P), 62.0 (m, CH₃CH₂O), 177.3 (s, CH₃CO₂⁻). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 15.3$ (s, 2P, PC₃), 32.5 (s, 4P, CP(O)(OEt)₂). IR (KBr, cm⁻¹): $\nu = 2983, 2931, 2908$ (CH₂), 1252 (P=O), 1031 (P–OEt), $\nu_{\text{s}} = 1402$ (CH₃CO₂⁻), $\nu_{\text{as}} = 1577$ (CH₃CO₂⁻). MS (FAB, 50°C): m/z 1041.2 [M – OAc]⁺. Anal. Calcd. for C₃₉H₈₄O₁₆P₆Pd (1100.3): C, 42.53; H, 7.69. Found: C, 42.15; H, 7.62.

2.2.4 Diacetato{1,3-bis[di(5-diethylphosphonatopentyl)phosphino]propane}palladium**(II) (3e)**

2e (556 mg, 0.597 mmol) was reacted with palladium(II) acetate (134 mg, 0.597 mmol) to give **3e** as an orange oil (566 mg, 82% yield). ^1H NMR (CD_3CN): $\delta = 1.45$ (t, $^3J_{\text{HH}} = 7.1$ Hz, 24H, OCH_2CH_3), 1.7–2.3 (m, 52H, $\text{CH}_2\text{CH}_2\text{P}((\text{CH}_2)_5)_2$), 4.2–4.3 (m, 16H, OCH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN): $\delta = 15.5$ (d, $^3J_{\text{PC}} = 6.1$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 19.2–19.8 (m, $\text{CH}_2\text{CH}_2\text{P}$), 22.1 (d, $^2J_{\text{PC}} = 4.7$, $\text{O}=\text{PCH}_2\text{CH}_2(\text{CH}_2)_3\text{P}$), 23.3 (s, CH_3CO_2^-), 24.0 (s, $\text{O}=\text{P}(\text{CH}_2)_3\text{CH}_2\text{CH}_2\text{P}$), 24.2 (d, $^1J_{\text{PC}} = 139.5$ Hz, $\text{O}=\text{PCH}_2(\text{CH}_2)_4\text{P}$), 24.6 ($N^{17} = 30.32$ Hz, $\text{O}=\text{P}(\text{CH}_2)_4\text{CH}_2\text{P}$), 30.9–31.4 (m, $\text{CH}_2\text{CH}_2\text{P}$), 33.6 (d, $^3J_{\text{PC}} = 16.8$ Hz, $\text{O}=\text{P}(\text{CH}_2)_2\text{CH}_2(\text{CH}_2)_2\text{P}$), 60.7 (d, $^2J_{\text{PC}} = 6.1$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 174.8 (s, CH_3CO_2^-). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN): $\delta = 17.3$ (s, 2P, PC_3), 33.1 (s, 4P, $\text{CP}(\text{O})(\text{OEt})_2$). IR (KBr, cm^{-1}): $\nu = 2981, 2932, 2908$ (CH_2), 1244 ($\text{P}=\text{O}$), 1026 ($\text{P}-\text{OEt}$), $\nu_{\text{s}} = 1402$ (CH_3CO_2^-), $\nu_{\text{as}} = 1577$ (CH_3CO_2^-). MS (FAB, 50°C): m/z 1097.5 $[\text{M} - \text{OAc}]^+$. Anal. Calcd. for $\text{C}_{43}\text{H}_{92}\text{O}_{16}\text{P}_6\text{Pd}$ (1156.4): C, 44.62; H, 8.01. Found: C, 44.23; H, 8.49.

2.2.5 Diacetato{1,3-bis[di(6-diethylphosphonatehexyl)phosphino]propane}palladium**(II) (3f)**

2f (732 mg, 0.740 mmol) was reacted with palladium(II) acetate (166 mg, 0.740 mmol) to give **3f** as an orange oil (781 mg, 87% yield). ^1H NMR (CDCl_3): $\delta = 1.1$ (t, $^3J_{\text{HH}} = 7.1$ Hz, 24H, OCH_2CH_3), 1.2–1.7 (m, 60H, $\text{CH}_2\text{CH}_2\text{P}((\text{CH}_2)_6)_2$), 3.8–3.9 (m, 16H, OCH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 22.2$ (d, $^3J_{\text{PC}} = 6.1$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), 25.2–25.8 (m, $\text{CH}_2\text{CH}_2\text{P}$), 22.6 (d, $^2J_{\text{PC}} = 4.7$, $\text{O}=\text{PCH}_2\text{CH}_2(\text{CH}_2)_4\text{P}$), 29.2 (s, CH_3CO_2^-), 29.9 (s,

O=P(CH₂)₄CH₂CH₂P), 31.01 ($N^{17} = 30.32$ Hz, O=P(CH₂)₅CH₂P), 31.1 (d, $^1J_{PC} = 140.8$ Hz, O=PCH₂(CH₂)₅P), 35.8 (d, $^3J_{PC} = 16.8$ Hz, O=P(CH₂)₃CH₂(CH₂)₂P), 36.3–36.5 (m, CH₂-CH₂P((CH₂)₃CH₂(CH₂)₂)₂), 67.2 (d, $^2J_{PC} = 6.1$ Hz, CH₃CH₂O), 182.0 (s, CH₃CO₂⁻). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 15.1$ (s, 2P, PC₃), 33.2 (s, 4P, CP(O)(OEt)₂). IR (KBr, cm⁻¹): $\nu = 2981$, 2934, 2908 (CH₂), 1240 (P=O), 1028 (P-OEt), $\nu_s = 1402$ (CH₃CO₂⁻), $\nu_{as} = 1577$ (CH₃CO₂⁻). MS (FAB, 50°C): m/z 1153.1 [M - OAc]⁺. Anal. Calcd. for C₄₇H₁₀₀O₁₆P₆Pd (1212.5): C, 46.52; H, 8.31. Found: C, 46.44; H, 8.29.

2.2.6 Diacetato{1,3-bis[di(8-diethylphosphonatoctyl)phosphino]propane}palladium

(II) (3g)

2g (661 mg, 0.600 mmol) was reacted with palladium(II) acetate (135 mg, 0.600 mmol) to give **3g** as an orange oil (677 mg, 85% yield). ^1H NMR (CDCl₃): $\delta = 1.26$ (t, $^3J_{\text{HH}} = 7.1$ Hz, 24H, OCH₂CH₃), 1.5–1.9 (m, 76H, CH₂CH₂P((CH₂)₈)₂), 3.98–4.1 (m, 16H, OCH₂CH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 16.8$ (d, $^3J_{PC} = 6.1$ Hz, CH₃CH₂O), 22.5–22.7 (m, CH₂CH₂P((CH₂)₆CH₂CH₂)₂), 23.9 (s, CH₃CO₂⁻), 24.6 (s, O=P(CH₂)₂CH₂(CH₂)₅P), 25.6 ($N^{17} = 32.3$ Hz, O=PCH₂(CH₂)₆CH₂P), 25.9 (d, $^1J_{PC} = 140.8$ Hz, O=PCH₂(CH₂)₇P), 29.2–29.3 (m, O=P(CH₂)₅CH₂CH₂CH₂P), 30.7 (d, $^4J_{PC} = 16.8$ Hz, O=P(CH₂)₃CH₂(CH₂)₄P), 31.3–31.6 (m, CH₂CH₂P((CH₂)₃CH₂(CH₂)₄)₂), 61.7 (d, $^2J_{PC} = 6.1$ Hz, CH₃CH₂O), 177.0 (s, CH₃CO₂⁻). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃): $\delta = 14.4$ (s, 2P, PC₃), 33.7 (s, 4P, CP(O)(OEt)₂). IR (KBr, cm⁻¹): $\nu = 2980$, 2928, 2855 (CH₂), 1243 (P=O), 1030 (P-OEt), $\nu_s = 1369$ (CH₃CO₂⁻), $\nu_{as} = 1620$ (CH₃CO₂⁻). MS (FAB, 50°C): m/z 1265.0 [M - OAc]⁺. Anal. Calcd. for C₅₅H₁₁₆O₁₆P₆Pd (1324.6): C, 49.83; H, 8.82. Found: C, 49.30; H, 8.72.

2.2.7 Diacetato{1.3-bis[di(3-aminopropyl)phosphino]propane}palladium(II) (**3h**)

2h (547 mg, 0.615 mmol) was reacted with palladium(II) acetate (138 mg, 0.615 mmol) to give **3h** as a yellowish oil (775 mg, 85% yield). ^1H NMR (CDCl_3): $\delta = 1.8\text{--}2.1$ (m, 28H, $\text{CH}_2\text{CH}_2\text{P}(\text{CH}_2\text{CH}_2)_2$), 2.7–3.0 (m, $\text{CH}_2\text{CH}_2\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 18.8$ (s, $\text{CH}_2\text{CH}_2\text{P}$), 20.2–20.9 (m, $\text{CH}_2\text{CH}_2\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2$), 25.1 (s, CH_3CO_2^-), 25.8 (s, $\text{CH}_2\text{CH}_2\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2$), 41.9 (s, $\text{CH}_2\text{CH}_2\text{P}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)$), 177.8 (s, CH_3CO_2^-). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 1.1$ (s). IR (KBr, cm^{-1}): $\nu = 3355$, 3278 (NH), 2927, (CH_2), 1078 (C–N), $\nu_s = 1398$ (CH_3CO_2^-), $\nu_{\text{as}} = 1570$ (CH_3CO_2^-). MS (FAB, 50°C): m/z 501.2 [$\text{M} - \text{OAc}$] $^+$. Anal. Calcd. for $\text{C}_{19}\text{H}_{44}\text{N}_4\text{O}_4\text{P}_2\text{Pd}$ (560.2): C, 40.68; H, 7.91; N, 9.99. Found: C, 40.55; H, 7.82; N, 9.51.

3. General Procedure for the Copolymerization and Terpolymerization

The copolymerization was carried out with and without undecenoic acid for comparative studies.

3.1 Copolymerization of Propene/CO, Butene/CO, and Propene/Butene/CO with Undecenoic Acid

The copolymerization was carried out in a mechanically stirred steel autoclave (100 ml for the copolymer, 150 ml for the terpolymer), equipped with a heating/cooling jacket, and the temperature being controlled automatically by means of a sensor dipping into the reaction

mixture. The total volume in each experiment is approximately 43 ml. This volume consists of the following: 10 μmol of complexes **3a-h** and 12 ml (1.9 mmol) of HBF_4 (1%) were added to a mixture of 30 ml of water, 0.15 g (28%) of texapon, 0.15 g of methyl- β -cyclodextrin (W7 M 1.8), and 1.0 g (5.4 mmol) of undecenoic acid. The process of copolymerization was carried out by stirring the previous mixture with proper monomer (propene: 15 g, 0.357 mol or butene: 20 g, 0.357 mol) at 60°C and under CO pressure of 60 bar. In the case of the terpolymers propene/butene/CO the mixture consisted of 15 g of propene and 20 g of butene under the same conditions of temperature and pressure. At the end of the reaction period, the reaction mixture was cooled down to room temperature and the unreacted monomers were vented. The polymer latices were filtered through a funnel with glass wool prior to further workup and analysis. To isolate the precipitated polymers, the latices were added to an excess of methanol and the polyketones were collected by filtration and washed with methanol and dried in a vacuum. The solids content was generally determined by the following procedure: approximately 1 g of the aqueous copolymer dispersion (the crude product of the polyketone) was applied to an aluminium crucible with an inside diameter of approximately 3 cm. This crucible is then put in a special furnace (a Sartorius Moisture Analyzer, model MA100/MA50) at 130°C and 10 mbar (absolute). Two separate measurements were carried out for each experimental run and their average value has been considered.

3.1.1 Butene/Undecenoic Acid/CO Copolymer

Colorless solid. ^1H NMR (CDCl_3): δ = 4.69 (s, COOH), 2.85 (m, $\text{C(O)CH}_2\text{CHR-}$), $\text{C(O)CH}_2\text{CH(CH}_2\text{CH}_3)$), 2.74 (m, $\text{C(O)CH}_2\text{CHRC(O)CH}_2\text{CH(CH}_2\text{CH}_3)$), 2.57 (m, C(O)-), $\text{CH}_2\text{CHRC(O)CH}_2\text{CH(CH}_2\text{CH}_3)$), 2.55 (m, $\text{C(O)CH}_2\text{CHRC(O)CH}_2\text{CH(CH}_2\text{CH}_3)$), 2.41 (m, CH_2COOH), 2.21 (s, $\text{CH}_2(\text{CH}_2)_7\text{COOH}$), 1.45–1.50 (m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$), 1.38 (m, $\text{CH}_2\text{CH}_2\text{COOH}$), 1.22 (m, $\text{CH}_2(\text{CH}_2)_6\text{COOH}$), 1.16 (m, $\text{C(O)CH}_2\text{CHRC(O)CH}_2\text{CH-}$

(CH₂CH₃), 0.74 (s, C(O)CH₂CHRC(O)CH₂CH(CH₂CH₃)). ¹³C{¹H} NMR (CDCl₃): δ = 212.1–212.8 (s, C(O)CH₂CHRC(O)CH₂CH(CH₂CH₃)), 178.8 (s, COOH), 46.7 (m, C(O)CH₂CHRC(O)CH₂CH(CH₂CH₃)), 46.4 (m, C(O)CH₂CHRC(O)CH₂CH(CH₂CH₃)), 44.1 (m, C(O)CH₂CHRC(O)CH₂CH(CH₂CH₃)), 43.8 (m, C(O)CH₂CHRC(O)CH₂CH(CH₂CH₃)), 33.8 (s, CH₂COOH), 31.1 (s, CH₂(CH₂)₇COOH), 29.3–28.8 (m, (CH₂)₄(CH₂)₂COOH), 26.7 (s, CH₂CH₂COOH), 24.5 (s, CH₂(CH₂)₆COOH), 24.3 (s, C(O)CH₂CHRC(O)CH₂CH(CH₂CH₃)), 11.2 (s, C(O)CH₂CHRC(O)CH₂CH(CH₂CH₃)). IR (KBr, cm⁻¹): ν = 3284 (br, COOH), 1703 (vs, C=O). Anal. Calcd. for (C₁₇H₂₈O₄)_n (296.4): C, 68.89; H, 9.52. Found: C, 68.92; H 9.34.

3.1.2 Propene/Undecenoic Acid/CO Copolymer

Colorless solid. ¹H NMR (CDCl₃): δ = 4.92 (s, COOH), 2.97 (m, C(O)CH₂CHRC(O)CH₂CH(CH₃)), 2.87 (m, C(O)CH₂CHRC(O)CH₂CH(CH₃)), 2.47 (m, C(O)CH₂CHRC(O)CH₂CH(CH₃)), 2.45 (m, C(O)CH₂CHRC(O)CH₂CH(CH₂CH₃)), 2.31 (s, CH₂COOH), 2.3 (s, CH₂(CH₂)₇COOH), 1.44–1.76 (m, CH₂CH₂CH₂CH₂CH₂CH₂COOH), 1.25 (m, CH₂CH₂COOH), 1.2 (m, CH₂(CH₂)₆COOH), 0.97 (s, C(O)CH₂CHRC(O)CH₂CH(CH₃)). ¹³C{¹H} NMR (CDCl₃): δ = 211.6–212.8 (s, C(O)CH₂CHRC(O)CH₂CH(CH₃)), 178.2 (COOH), 44.6 (m, C(O)CH₂CHRC(O)CH₂CH(CH₃)), 43.3 (m, C(O)CH₂CHRC(O)CH₂CH(CH₃)), 40.32 (m, C(O)CH₂CHRC(O)CH₂CH(CH₃)), 40.0 (m, C(O)CH₂CHRC(O)CH₂CH(CH₃)), 33.8 (s, CH₂COOH), 31.2 (s, CH₂(CH₂)₇COOH), 29.4–28.8 (m, (CH₂)₄(CH₂)₂COOH), 26.8 (s, CH₂CH₂COOH), 24.5 (s, CH₂(CH₂)₆COOH), 16.4 (s, C(O)CH₂CHRC(O)CH₂CH(CH₃)). IR (KBr, cm⁻¹): ν = 3284 (br, COOH), 1703 (vs, C=O). Anal. Calcd. for (C₁₆H₂₆O₄)_n (282.4): C, 68.06; H, 9.28. Found: C, 67.30; H 8.46.

3.1.3 Propene/Butene/Undecenoic Acid/CO Copolymer

Colorless solid ^1H NMR (CDCl_3): $\delta = 4.8$ (s, COOH), 2.83 (m, $\text{C}(\text{O})\text{CH}_2\text{CHR}-\text{C}(\text{O})\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 2.74 (m, $\text{C}(\text{O})\text{CH}_2\text{CHRC}(\text{O})\text{CH}_2\text{CH}(\text{CH}_3)-\text{C}(\text{O})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 2.44–2.51 (m, $\text{C}(\text{O})\text{CH}_2\text{CHRC}(\text{O})\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 2.42 (m, $\text{C}(\text{O})\text{CH}_2\text{CHRC}(\text{O})\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 2.3 (m, CH_2COOH), 2.2 (s, $\text{CH}_2(\text{CH}_2)_7\text{COOH}$), 1.45 (m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$), 1.38 (m, $\text{CH}_2\text{CH}_2\text{COOH}$), 1.24 (m, $\text{CH}_2(\text{CH}_2)_6\text{COOH}$), 1.15 (m, $\text{C}(\text{O})\text{CH}_2\text{CHRC}(\text{O})\text{CH}_2\text{CH}(\text{CH}_3)-\text{C}(\text{O})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 0.92 (s, $\text{C}(\text{O})\text{CH}_2\text{CHRC}(\text{O})\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 0.74 (s, $\text{C}(\text{O})\text{CH}_2\text{CHRC}(\text{O})\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 211.8$ – 212.8 (s, $\text{C}(\text{O})\text{CH}_2\text{CHRC}(\text{O})\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 177.4 (s, COOH), 47.3 (m, $\text{C}(\text{O})\text{CH}_2\text{CHRC}(\text{O})\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 46.7 (m, $\text{C}(\text{O})\text{CH}_2\text{CHRC}(\text{O})\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 44.1 (m, $\text{C}(\text{O})\text{CH}_2\text{CHRC}(\text{O})-\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 42.6 (m, $\text{C}(\text{O})\text{CH}_2\text{CHRC}(\text{O})\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{O})-\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 40.24 (m, $\text{C}(\text{O})\text{CH}_2\text{CHRC}(\text{O})\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 39.96 (m, $\text{C}(\text{O})\text{CH}_2\text{CHRC}(\text{O})\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 33.7 (s, CH_2COOH), 31.2 (s, $\text{CH}_2(\text{CH}_2)_7\text{COOH}$), 29.3–28.8 (m, $(\text{CH}_2)_4(\text{CH}_2)_2\text{COOH}$), 26.7 (s, $\text{CH}_2\text{CH}_2\text{COOH}$), 24.6 (s, $\text{CH}_2(\text{CH}_2)_6\text{COOH}$), 24.3 (s, $\text{C}(\text{O})\text{CH}_2\text{CHRC}(\text{O})\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 16.3 (s, $\text{C}(\text{O})\text{CH}_2\text{CHRC}(\text{O})\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 11.2 (s, $\text{C}(\text{O})\text{CH}_2\text{CHRC}(\text{O})\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$). IR (KBr, cm^{-1}): $\nu = 3286$ (br, COOH), 1703 (vs, C=O). Anal. Calcd. for $(\text{C}_{21}\text{H}_{34}\text{O}_5)_n$ (366.5): C, 68.82; H, 9.35. Found: C, 68.58; H 9.26.

3.2 Copolymerization of the Propene/CO, Butene/CO, and Propene/Butene/CO without Undecenoic Acid

Copolymerization without using undecenoic acid was carried out exactly as previously described but using catalyst **3c** instead.

3.2.1 Butene/CO Copolymer

Colorless solid. ^1H NMR (CDCl_3): $\delta = 2.81$ (s, $\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 2.63 (m, $\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 1.30–1.47 (m, $\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 0.80 (s, $\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 212.8$ – 213.7 (s, $\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 47.4–48.7 (s, $\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 44.9–45.2 (s, $\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 25.3 (s, $\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 12.3 (s, $\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$). IR (KBr, cm^{-1}): $\nu = 1705$ (vs, C=O). Anal. Calcd. for $(\text{C}_5\text{H}_8\text{O})_n$ (84.1): C, 71.39; H, 9.58. Found: C, 70.91; H 9.63.

3.2.2 Propene/CO Copolymer

Colorless solid. ^1H NMR (CDCl_3): $\delta = 2.94$ (s, $\text{C(O)CH}_2\text{CH}(\text{CH}_3)$), 2.51 (s, $\text{C(O)CH}_2\text{CH}(\text{CH}_3)$), 1.01 (s, $\text{C(O)CH}_2\text{CH}(\text{CH}_3)$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 210.5$ – 210.9 (s, $\text{C(O)CH}_2\text{CH}(\text{CH}_3)$), 42.3–43.3 (s, $\text{C(O)CH}_2\text{CH}(\text{CH}_3)$), 38.5–39.3 (s, $\text{C(O)CH}_2\text{CH}(\text{CH}_3)$), 14.95 (s, $\text{C(O)CH}_2\text{CH}(\text{CH}_3)$). IR (KBr, cm^{-1}): $\nu = 1705$ (vs, C=O). Anal. Calcd. for $(\text{C}_4\text{H}_6\text{O})_n$ (70.1): C, 68.55; H, 8.63. Found: C, 66.94; H 8.59.

3.2.3 Propene/Butene/CO Copolymer

Colorless solid. ^1H NMR (CDCl_3): $\delta = 2.7\text{--}3.0$ (m, $\text{C(O)CH}_2\text{CH}(\text{CH}_3)\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$) $\delta 2.3\text{--}2.7$ (m, $\text{C(O)CH}_2\text{CH}(\text{CH}_3)\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), $1.3\text{--}1.5$ (m, $\text{C(O)CH}_2\text{CH}(\text{CH}_3)\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 0.99 (s, $\text{C(O)CH}_2\text{CH}(\text{CH}_3)\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 0.82 (s, $\text{C(O)CH}_2\text{CH}(\text{CH}_3)\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 211.2\text{--}211.9$ (s, $\text{C(O)CH}_2\text{CH}(\text{CH}_3)\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), $39.2\text{--}40.0$ (m, $\text{C(O)CH}_2\text{CH}(\text{CH}_3)\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), $41.5\text{--}41.9$ (m, $\text{C(O)CH}_2\text{CH}(\text{CH}_3)\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), $42.9\text{--}43.9$ (m, $\text{C(O)CH}_2\text{CH}(\text{CH}_3)\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$) $44.9\text{--}45.9$ (m, $\text{C(O)CH}_2\text{CH}(\text{CH}_3)\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 23.5 (s, $\text{C(O)CH}_2\text{CH}(\text{CH}_3)\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 15.6 (s, $\text{C(O)CH}_2\text{CH}(\text{CH}_3)\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$), 10.5 (s, $\text{C(O)CH}_2\text{CH}(\text{CH}_3)\text{C(O)CH}_2\text{CH}(\text{CH}_2\text{CH}_3)$). IR (KBr, cm^{-1}): $\nu = 1705$ (vs, C=O). Anal. Calcd. for $(\text{C}_9\text{H}_{14}\text{O}_2)_n$ (154.2): C, 70.10; H, 9.15. Found: C, 69.13; H 9.16.

4. X-ray Structural Determination of **3a**

Single crystals of **3a** were obtained by slow diffusion of diethyl ether into a concentrated solution of **3a** in dichloromethane. The crystal was mounted on a glass fiber and transferred to a P4 Siemens diffractometer, using graphite-monochromated Mo- K_α radiation. The lattice constants were determined by 25 precisely centered high-angle reflections and refined by least-squares methods. The structure was solved by direct methods¹⁸ and refined by full-matrix least-squares on F^2 using SHELXTL-97.¹⁹ All non-hydrogen atoms were refined anisotropically (based on F^2). Hydrogen atoms were placed in calculated positions. The final cell parameters and specific data collection parameters for **3a** are summarized in Table 5.

Table 5. Summary of Crystallographic Data and Parameters for Data Collection and Refinement of 3a

	1a
Formula	C ₃₁ H ₆₆ O ₉ P ₂ Pd
Formula weight	751.18
Color	colorless plates
Crystal dimensions (mm)	0.4 x 0.15 x 0.05
Crystal system	Triclinic
Space group	P $\bar{1}$
<i>a</i> (Å)	11.777(3)
<i>b</i> (Å)	12.423(10)
<i>c</i> (Å)	13.787(3)
α (°)	73.98(3)
β (°)	85.46(2)
γ (°)	71.29(4)
<i>V</i> (Å ³)	1836.3(16)
<i>Z</i>	2
<i>d</i> _{calcd} (g cm ⁻³)	1.359
<i>T</i> (°C)	-100
<i>F</i> (000) (e)	800
μ (Mo–K α) (mm ⁻¹)	0.639
Scan type	ω
θ limits (°)	2.03–27.49

Table 5. Continuation

Data collected: h, k, l	$\pm 10, \pm 15, \pm 17$
No. of reflections measured	14306
No. of unique data with $I \geq 2\sigma(I)$	4420
No. of variables	403
GOF	0.954
R_1^a	0.0503
wR_2^b	0.0940

$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. $^b wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{0.5}$.

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Summary

The objective of this thesis was the development of stable dispersions for aqueous polyketone latices on the basis of the copolymers propene/undecenoic acid/CO, butene/undecenoic acid/CO, and propene/butene/undecenoic acid/CO. Therefore, attention has been focused on the design of new water-soluble palladium(II) catalysts for the production of stable polymer latices with (i) high solids contents, (ii) high molecular weights, (iii) particle sizes in the range between 50 and 500 nm, and (iv) glass transition temperatures with values below room temperature.

In the first chapter of this thesis the synthesis and characterization of novel diphosphine ligands and their palladium(II) complexes is described. The diphosphines $R_2P(CH_2)_3PR_2$ [$R = (CH_2)_nP(O)(OEt)_2$, $n = 2-6, 8$; $(CH_2)_nOH$, $n = 6$; $(CH_2)_nNH_2$, $n = 3$] were obtained by heating $P(OEt)_3$ with 1,3-dibromopropane according to a Michaelis-Arbuzov reaction, followed by reduction of the resulting diphosphate with $LiAlH_4$ in diethyl ether to give $H_2P(CH_2)_3PH_2$. An excess of the corresponding olefin $CH_2=CH-(CH_2)_n-X$ ($X = OH$, $n = 4$; $P(O)(OEt)_2$, $n = 0-4, 6$; NH_2 , $n = 1$) was photochemically hydrophosphinated with the diprimary phosphine $H_2P(CH_2)_3PH_2$ over night. This convenient synthesis is nearly quantitative and simplifies the purification of the products. Purification is achieved by removing excess alkene under reduced pressure. The alkenyl phosphonates $CH_2=CH-(CH_2)_n-P(O)(OEt)_2$ were obtained either from commercial suppliers ($n = 0, 1$) or prepared by literature methods ($n = 2-4, 6$). All diphosphines resulted as colorless, air-sensitive, and oily products. They are soluble in water and chlorinated hydrocarbons like dichloromethane and chloroform. Upon reaction of palladium(II) acetate with these hydroxyalkyl, phosphonate and aminophosphine ligands in a 1 : 1 mixture of dichloromethane and acetonitrile at room temperature the corresponding diacetatodiphosphinepalladium(II) complexes $(R_2P(CH_2)_3PR_2)Pd(OAc)_2$ [$R = (CH_2)_nP(O)(OEt)_2$, $n = 2-6, 8$; $(CH_2)_nOH$, $n = 6$;

$(\text{CH}_2)_n\text{NH}_2$, $n = 3$] could be isolated. They are soluble in water, alcohols, and in organic solvents of medium polarity and offer an easy way to generate catalytically active precursor species in one step by addition of excess Brønsted acid to a solution in water. The structure of the complex $(\text{R}_2\text{P}(\text{CH}_2)_3\text{PR}_2)\text{Pd}(\text{OAc})_2$ [$\text{R} = (\text{CH}_2)_6\text{OH}$] additionally was investigated by an X-ray structural analysis. All diphosphine ligands and their palladium(II) complexes were characterized by means of MS, IR, and NMR spectroscopy. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of the phosphonate ligand $\text{R}_2\text{P}(\text{CH}_2)_3\text{PR}_2$ [$\text{R} = (\text{CH}_2)_2\text{P}(\text{O})(\text{OEt})_2$] and its palladium(II) complex $(\text{R}_2\text{P}(\text{CH}_2)_3\text{PR}_2)\text{Pd}(\text{OAc})_2$ [$\text{R} = (\text{CH}_2)_2\text{P}(\text{O})(\text{OEt})_2$] display two signals in a 2 : 1 ratio, assigned to the phosphonate and phosphine substituents. A marked shift and significant change of the multiplicity in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra for the phosphine group in this ligand from a triplet ($\delta = -22$) to a multiplet at $\delta = 22$ upon reaction of palladium(II) acetate with $\text{R}_2\text{P}(\text{CH}_2)_3\text{PR}_2$ [$\text{R} = (\text{CH}_2)_2\text{P}(\text{O})(\text{OEt})_2$] have been observed.

The second part of this thesis is devoted to the catalytic activity of these palladium(II) complexes for the copolymerization of α -olefins with carbon monoxide. Indeed the diacetatodiphosphinepalladium(II) complexes $(\text{R}_2\text{P}(\text{CH}_2)_3\text{PR}_2)\text{Pd}(\text{OAc})_2$ proved to be highly active catalysts for the co- and terpolymerization of several α -olefins with carbon monoxide in the presence of excess HBF_4 . Latices of aliphatic polyketones (propene/undecenoic acid/CO, butene/undecenoic acid/CO, and propene/butene/undecenoic acid/CO copolymers) prepared by a transition metal catalyzed polymerization are described for the first time. These aqueous polyketone latices exhibit high solids contents of up to 23% and high molecular weights of up to $6.3 \times 10^4 \text{ g mol}^{-1}$ at narrow polydispersities ($M_w/M_n \approx 2$). Also they are produced at rates similar to the commercial process performed in methanol. Stable dispersions are obtained by the introduction of undecenoic acid as a third or fourth comonomer and no phase separation, or the formation of a coagulum within ten weeks were observed. In these latices, hydrophilic carboxylic acid moieties covalently bound to the particle surface contribute to stabilization. In addition, for practical applications it is desirable

to find routes to set the T_g values significantly below room temperature. The introduction of 5–10% (wt/wt) of undecenoic acid to the olefin during the polymerization process indeed resulted in markedly decreased T_g values from room temperature to -2°C . With glass transitions being below room temperature, α -olefin/CO copolymers are well suited for the formation of films. In contrast to elastic materials obtained with **(dppp)Pd**, complexes $(\text{R}_2\text{P}(\text{CH}_2)_3\text{PR}_2)\text{Pd}(\text{OAc})_2$ produce non-elastic thermoplastics. The α -olefin/CO copolymer latices exhibit particle sizes between 60 and 224 nm, which are in the desirable range for latex applications.

The co- and terpolymerization of hydrophobic monomers in the emulsion polymerization in the presence of methyl- β -cyclodextrin (W7 M 1.8) as a phase transfer agent enables the production of higher solids contents of the polyketones and a higher productivity of the catalysts. Water-insoluble molecules become water-soluble by treatment with aqueous solutions of cyclodextrins. The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra (in CDCl_3) of the propene/CO, butene/CO, and propene/butene/CO copolymers, respectively, show only a single peak for the carbonyl group and this gives an indication that perfectly head-to-tail regioregular polyketones have been formed. Complexes $(\text{R}_2\text{P}(\text{CH}_2)_3\text{PR}_2)\text{Pd}(\text{OAc})_2$ [$\text{R} = (\text{CH}_2)_n\text{P}(\text{O})(\text{OEt})_2$; $n = 6, 3$] are highly active catalysts in the copolymerization of butene/undecenoic acid/CO, propene/butene/undecenoic acid/CO, and propene/undecenoic acid/CO, respectively, with productivities of up to 1.0×10^4 ($\text{mol}(\text{substr}) \times \text{mol}(\text{Pd})^{-1}$).

Generally the molecular weight of α -olefin/CO copolymers increase significantly as the chain length of the monomers decreases. Depending on the chain-length of the phosphorus attached substituents in the palladium catalysts $(\text{R}_2\text{P}(\text{CH}_2)_3\text{PR}_2)\text{Pd}(\text{OAc})_2$, four variables for the propene/CO, butene/CO, and propene/butene/CO copolymers can be controlled: (i) the regioregularity, (ii) the molecular weight, (iii) the glass transition temperature, and the melting point (T_g and T_m). This indicates clearly that the steric properties of the catalyst

control the molecular weights and the microstructure (e.g. the regioregularity) of the copolymers. The conformational flexibility of the four P-bonded hydroxyalkyl, phosphonate, or amine substituents combined with their steric demand and amphiphilic character generate a kind of hydrophobic catalytic pocket in the environment of the metal center in which aliphatic substrate molecules and the growing polymer chain nicely fit.

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