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# High molecular weight 1-olefin/carbon monoxide copolymers: a new class of versatile polymers

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The moderate electrophilicity of palladium(II)-phosphine catalysts compared to those of zirconocene dichlorides makes them more tolerant toward a variety of polar functionalities of olefinic monomers. This allows use of Pd(II) complexes as catalysts for the copolymerization of olefins with readily available polar monomers, like acrylic acid derivatives or carbon monoxide. In particular, developments during the recent years have opened the way to a new and broad family of high molecular weight 1-olefin/CO co- and terpolymers. These 1,4-polyketone materials show interesting and easily variable properties which can be tuned from insoluble, highly crystalline to thermoplastic elastic. The latter polymers resemble in some cases flexible PVC and even vulcanized natural rubbers.

**Keywords:** catalysis, copolymerization, 1-olefin/carbon monoxide copolymers, Pd(II) complexes, thermoplastic elastomers, surface polarity

## 1. Introduction

Single-site, homogeneous group IV metallocene-based catalysts are currently of great scientific and industrial interest [1–4]. Worldwide research activities on such systems have led to convincing improvements of poly(1-olefin) materials as well as to an understanding of basic reaction mechanisms responsible for the growth of a stereoregular polymer chain at a metal center. However, this catalyst generation allows only the use of a limited number of polar monomers bearing sterically hindered functionalities due to the sensitivity of early transition metal complexes to electron-donating functional groups [5–7]. Thus, copolymers of technically important polar monomers with ethene are exclusively produced by radical polymerization routes in high-pressure processes [8]. The corresponding 1-olefin copolymers are not accessible by this technique. Related polymer architectures have been achieved by applying grafting reactions of acrylates onto isotactic polypropene. Controlled copolymerization of ethene or propene with polar olefins such as cheap acrylates, their derivatives and vinyl ethers is still a long-standing goal in polyolefin engineering, since copolymers of this type might endow a new generation of materials with remarkably high adhesive, dyeing and moisture adsorption properties[1].

Recently, palladium(II)-based catalysts were found to be capable of copolymerizing ethene or propene with readily available acrylic monomers to branched, high molecular weight products [12,13][2]. The reaction proceeds in a manner similar to the one described earlier by Fink and coworkers. These authors reported on nickel(II) complexes bearing sterically crowded ligand systems, that perform the polymerization of 1-olefins by a sequence of combined insertion/$\beta$-hydride elimination steps leading to 2,$\omega$-linked polyolefins [17,18].

A second family of linear polymers comprising ethene or simple 1-olefins and carbon monoxide is also accessible by Pd(II)-phosphine complexes. Most of the research has been focused on the copolymerization of carbon monoxide with ethene [19–23] or with 1-olefins such as propene and styrene [24–27]. The resulting ethene/CO copolymers are white crystalline solids with a high melting temperature ($T_m \approx 260\,^\circ$C) which are difficult to process and not amenable to an easy characterization. Terpolymers containing small amounts of propene/CO (P/CO) units show reduced melting transitions and a much more favorable behavior in blow-molding or in extrusion applications. This new group of crystalline polymers has been developed by Shell and is right now on the edge of commercialization under the trade name of CARILON®. Possible fields of application reach from PET- or Nylon-6-substitutes to new fiber materials, which might find their way into tire production [28]. The alternating propene-CO copolymers prepared by different catalyst systems exhibited moderate to low molecular weights ($M_w \leqslant 5 \times 10^4$ g/mol) [29,30], whereas the reaction of carbon monoxide with the higher 1-olefins pro-

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[1] A first success in this direction was recently achieved by using rare earth transition metal compounds. Lanthanide complexes were applied to prepare block copolymers comprising a polyethene and a polar polyacrylate or polyester moiety. In this reaction ethene is first polymerized by a samarocene complex. The second block is introduced by a consecutive group-transfer polymerization of methyl methacrylate or by ring-opening polymerization of a lactone, cf. [9–11].

[2] For related approaches: (a) A claim for a Pd(II)-catalyzed copolymerization of ethene and methyl methacrylate to give low molecular weight products was published in [14]. However, no detailed product characterization is given. (b) Klabunde et al. reported on copolymerization experiments of ethene with polar monomers. All trials with methyl methacrylate or vinyl acetate failed. Only comonomers with at least two $CH_2$-spacers between the vinyl unsaturation and the functional group led to copolymer products; cf. [15]. (c) Ester group containing norbornene derivatives are polymerized by (allyl)Pd(II) complexes; cf. [16].

ceeds with poor productivity and leads only to oligomeric products [22,31–33].

## 2. Catalysts and processes for the production of 1,4-polyketones

In the late 1940s, almost coincident to the development of the low-pressure process for the production of polyolefins, Reppe and Magin at BASF [34] discovered the nickel-catalyzed copolymerization of carbon monoxide and ethene to give strictly alternating copolymers [20,35,36]. Due to the inexpensive and easily available monomers, some interest was focused on these polymers. Hopes were directed toward the development of photodegradable and biodegradable materials based on the presence of the reactive carbonyl groups in the backbone [37–39] and on other types of functional polymers derived from the polyketones by chemical modification of the carbonyl groups [9,40,41].

Different synthetic methods were developed for the copolymerization of carbon monoxide with olefins. In addition to the insertion polymerization catalyzed by transition metal complexes, the initiation by radicals [42,43] and $\gamma$-rays [44,45] gives branched ethene/CO-materials, with a low to moderate CO content. The metal-catalyzed copolymerization reaction occurs at a significantly lower pressure and at ambient temperatures. The resulting polymers have a strictly alternating structure combined with a relatively high molecular weight, whereas the radical polymerization at elevated pressures affords $\alpha,\beta$-dicarbonyl units by a consecutive incorporation of two CO-monomers and leads hence to thermally labile products [20,35,36].

Nickel was the first transition metal used to catalyze the copolymerization of CO and ethene [34]. The catalyst ($K_2Ni(CN)_4$) produced low-melting oligomers of ethene and CO in addition to diethyl ketone and propionic acid. In the last decades, a number of group VIII transition metal compounds were reported as catalysts. Cobalt- [46] and rhodium- [47–49] based complexes showed some activity for the formation of low molecular weight ethene-CO alternating copolymers and oligomers. Palladium(II) systems were first disclosed by Gough in 1967 [50]. However, these palladium(II) dichloride complexes bearing monodentate phosphine ligands give low yields, even under drastic reaction conditions (250 °C, 200 MPa). Also Pd(II)-salts, like chlorides and cyanides, afforded only low yields of oligomers [51–55]. In the early 1980s, Sen et al. [56,57] reported that dicationic palladium(II) complexes of monodentate tertiary phosphines together with weakly coordinating acetonitrile ligands and non-coordinating tetrafluoroborate counter ions, produce ethene-CO copolymers at low pressure and ambient temperatures. The break-through for an industrial application came in 1984, when Drent [58] discovered that bidentate tertiary phosphine chelating ligands give ethene-CO copolymers with high activities under relatively mild reaction conditions (90 °C, 4–6 MPa).

The enhanced activity of the bidentate chelates, which is most pronounced for 1,3-bis(diphenylphosphino)propane (dppp), can be attributed to the cis-coordination of these ligands in square-planar Pd(II)-complexes. This forces also the growing polymer chain and the coordinated monomer into a cis-arrangement, which is a prerequisite for migratory insertion reactions. Monodentate phosphines, like triphenylphosphine afford the formation of cis- and trans-isomers, thus decreasing the chance for insertion reactions to occur (figure 1) [20,59].

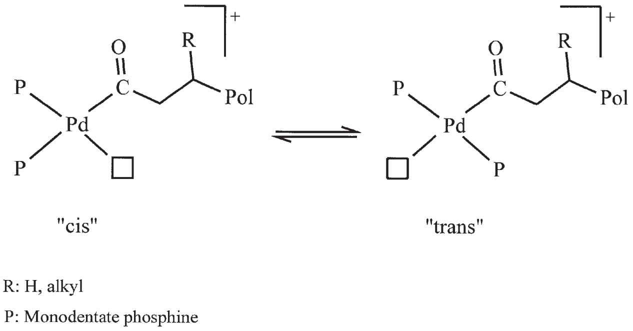

Figure 1. Cis/trans-isomers of monodentate diphosphine complexes.

## 3. Complex activation and formation of the first high molecular weight propene-carbon monoxide (P/CO) copolymers

Several research groups proposed that the initiation step in the copolymerization reaction can take place through an insertion of propene into a Pd-hydride- or Pd-alkyl-bond formed by reaction with an activator, like methanol or water [19–22,24–27,31]. However, no chemically consistent way for such a reaction was given. Based on the homopolymerization of norbonene by Pd(II)-complexes and

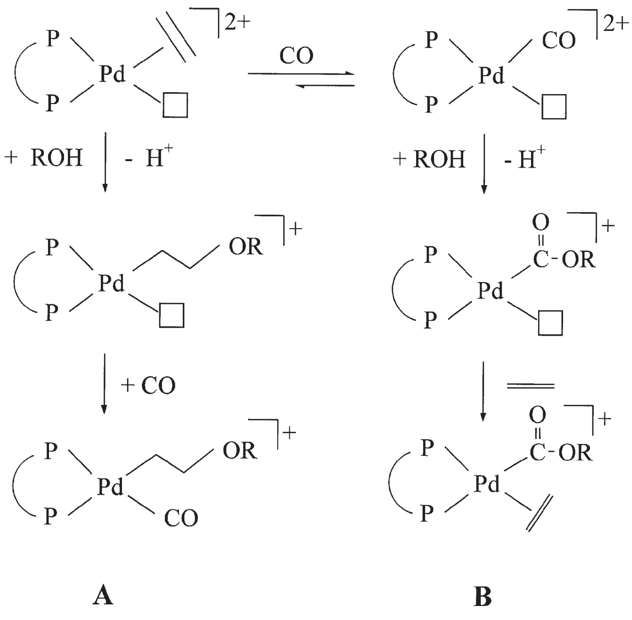

Figure 2. The activation of dicationic Pd(II)-complexes: nucleophilic addition of ROH to a coordinated olefin (**A**) or to a coordinated CO molecule (**B**).

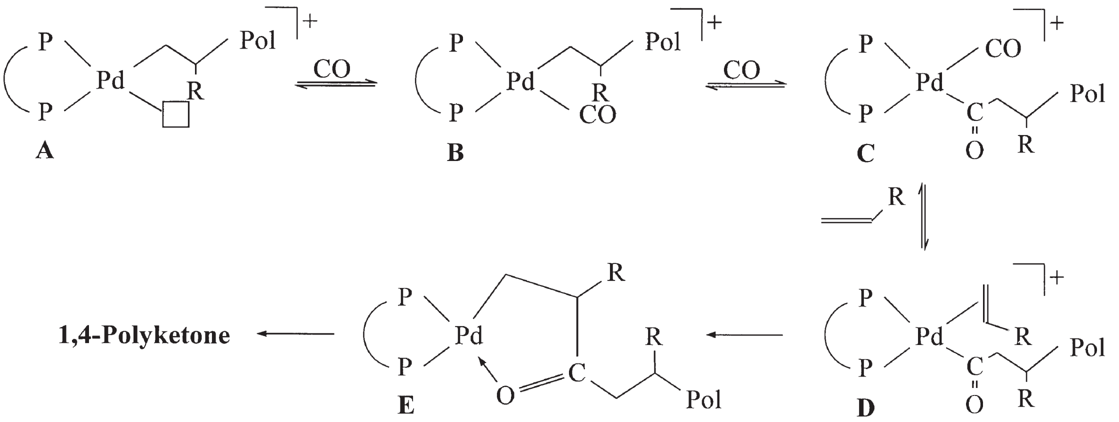

Figure 3. Formation of alternating CO/1-olefin copolymers by successive migratory insertion reactions of carbon monoxide and an olefin.

on the formation of solid Pd(0) at higher water concentrations in alkene/CO-copolymerization reactions, we speculated earlier [60] on a Wacker-analogous activation reaction (cf. figure 2), where the initial Pd–C-bond results from nucleophilic attack of an HOR-group (R = H, $CH_3$) to a coordinated olefin (figure 2(A)) or to carbon monoxide (figure 2(B)). Ester end groups of this type have been observed before [20,61].

Chain propagation towards the formation of 1,4-polyketones involves the alternating insertion of carbon monoxide and of the alkene monomer into a preformed polymer chain (figure 3) [19,20,24,25,62]. Due to the higher stability of the Pd(II)–CO-bond compared to the $\pi$-alkene complex, the coordination and migratory insertion of carbon monoxide into a Pd-alkyl species is faster than the alkene insertion [63], which is the rate limiting step in this polymerization reaction. Since double CO-insertion seems to be energetically unfavored [64,65] a strictly alternating copolymer results.

Based on this polymerization mechanism, an excess of activator (methanol, water) should act as chain transfer agent leading to the observed low molecular weight P/CO-copolymers by reaction with the sensitive Pd-alkyl- and Pd-acyl-intermediates (figure 4) [20,61].

We checked this hypothesis by varying the amount of methanol or water used to activate dicationic complexes, like $[Pd(dppp)(NCCH_3)_2](BF_4)_2$ (**1**, figure 5). A decrease in the methanol concentration afforded the formation of the first high molecular weight P/CO-copolymers, with $M_w$ up to $3 \times 10^5$ g/mol (table 1) [66]. A similar effect was observed when water was used instead of methanol. Application of the well-defined dicationic palladium(II)-complexes **2** or **3** [67] minimizes the activator amount, so that these complexes can be considered as self-activating, single-component catalysts. At high water concentrations (table 2, run 7) no polymerization activity can be observed and solid palladium is formed, supporting our hypothesis of Wacker-analogous reaction sequences [68,69]. Interestingly, the water concentration also affects the regioselectivity of the catalyst. An increase of the activator to palladium ratio leads to higher concentrations of regioregular head-tail units in the polymer products[3].

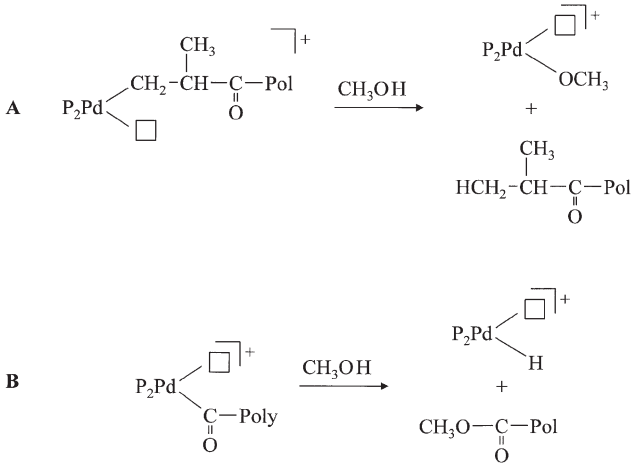

Figure 4. Methanol as chain termination agent.

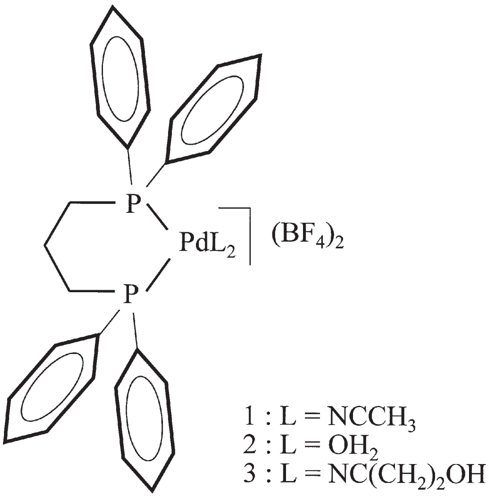

Figure 5. Dicationic palladium(II) complexes (**1**, L = acetonitrile) and single-component, self-activating species (**2**, **3**, L = $OH_2$, $NC(CH_2)_2OH$).

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[3] The influence of the $H_2O$/Pd(II) ratio on the regioselectivity of the catalyst is not yet understood. One possible explanation could be that water is present during the polyinsertion reaction.

Table 1
Propene/CO polymerization results using MeOH as activator [a].

| Entry | Cat. | MeOH (ml) | MeOH/Pd[b] | $M_w$[c] (g/mol) | $M_w/M_n$[c] | Activ.[d] | H-T-units[e] (%) | Elastomer |
|---|---|---|---|---|---|---|---|---|
| 1 | **1** | 0 | 0 | – | – | 0 | – | – |
| 2 | | 0.25 | 140 | $2.3 \times 10^5$ | 2.02 | 55.5 | 55 | yes |
| 3 | | 2.0 | 1100 | $3.6 \times 10^4$ | 2.35 | 62.9 | 60 | no |
| 4 | | 50.0 | 27000 | $5.0 \times 10^3$ | 1.68 | 11.8 | 43 | no[g] |
| 5 | **2** | 0 | 0 | $2.2 \times 10^5$ | 1.85 | 27.0 | 53 | yes |
| 6 | **3** | 0 | 0 | $1.1 \times 10^5$ | 2.49 | 10.4 | n.d.[f] | yes |
| 7 | **3** | 0.25 | 300 | $2.8 \times 10^5$ | 3.11 | 5.0 | n.d. | yes |

[a] Polymerization conditions: $T_p$, 25 °C; time, 48 h; solvent, $CH_2Cl_2$, 100 ml.
[b] MeOH/Pd: mol-ratio of activator to palladium.
[c] $M_w$ ($M_w/M_n$) measured by GPC (rel. to polystyrene).
[d] Activity in g-copolymer × (g Pd × h)$^{-1}$.
[e] H-T-units: regioregularity in mol% of head-tail units.
[f] n.d.: not determined.
[g] Viscous liquid.

Table 2
Propene/CO polymerization results using $H_2O$ as activator [a].

| Entry | $H_2O$ (ml) | $H_2O$/Pd[b] | $M_w$[c] (g/mol) | $M_w/M_n$[c] | Activ.[d] | H-T-units[e] (%) | Elastomer |
|---|---|---|---|---|---|---|---|
| 1 | 0 | 0 | – | – | 0 | – | – |
| 2 | 0.001 | 1.2 | $1.1 \times 10^5$ | 3.25 | 10.4 | 52 | yes |
| 3 | 0.125 | 150 | $2.7 \times 10^5$ | 1.76 | 86.6 | 53 | yes |
| 4 | 0.25 | 300 | $2.0 \times 10^5$ | 1.87 | 51.9 | 56 | yes |
| 5 | 0.5 | 600 | $8.4 \times 10^4$ | 2.25 | 27.0 | 62 | no |
| 6 | 2.0 | 2500 | $1.3 \times 10^4$ | 1.21 | 3.47 | 67 | no |
| 7 | 10 | 30000 | – | – | 0 | – | – |

[a] Polymerization conditions: catalyst **1**; $T_p$, 25 °C; time, 48 h; solvent, $CH_2Cl_2$, 100 ml.
[b] Activ./Pd: mol-ratio of activator to palladium.
[c] $M_w$ ($M_w/M_n$) measured by GPC (rel. to polystyrene).
[d] Activity in g-copolymer × (g Pd × h)$^{-1}$.
[e] H-T-units: regioregularity in mol% of head-tail units.

Table 3
Influence of the monomer composition on the molecular weight of propene/carbon monoxide copolymers [a].

| Entry | CO (MPa) | $C_3$ (g) | $M_w$ (g/mol) | $M_w/M_n$ | Yield (g) |
|---|---|---|---|---|---|
| 1 | 0.91 | 40 | $3.9 \times 10^4$ | 1.36 | 1.0 |
| 2 | 1.41 | 40 | $2.4 \times 10^5$ | 1.64 | 7.0 |
| 3 | 5.09 | 40 | $2.0 \times 10^5$ | 1.89 | 16 |
| 4 | 10.2 | 40 | $1.9 \times 10^5$ | 2.26 | 4.5 |
| 5 | 5.09 | 80 | $4.3 \times 10^5$ | 2.03 | 35.0 |

[a] Polymerization conditions: catalyst **1**; $T_p$, 25 °C; time, 48 h; solvent, $CH_2Cl_2$, MeOH (0.25 ml).

Activity and molecular weight of the polymer products depend sensitively on the CO-pressure and on the ratio of both monomers (table 3). An increase of the CO-concentration relative to [$C_3$] leads first to enhanced molecular weights and to improved yields. After reaching a maximum (table 3, entries 2 and 3) a further increase of the CO-pressure gives reduced molecular weights and causes also lower activities, presumably by forcing the active species into resting states (cf. figure 3(C)) or even by the formation of Pd(0) [70]. However, by a careful choice of the reaction conditions we were able to produce P/CO-copolymers with $M_w$ up to $4.3 \times 10^5$ g/mol[4].

### 3.1. Properties of the high molecular weight propene-CO copolymers

Dissolving the propene/CO copolymers in $CH_2Cl_2$ or $CHCl_3$ followed by slow evaporation of the solvent leads to the formation of highly flexible, transparent films. A comparison of the stress-strain behavior of propene/CO-copolymers of different molecular weight with a vulcanized natural rubber (NR) shows, that products of $M_w \leqslant 1 \times 10^5$ g/mol (e.g., figure 6, **1**) do not have flexible or elastic properties. The material is relatively soft and can be stretched with low nominal forces ($\sigma_N$) until it breaks. At higher molecular weights the stress-strain curves start to resemble those of chemically crosslinked natural rubbers. Samples with $M_w \approx 2 \times 10^5$ g/mol (figure 6, *entry*

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[4] The effect of temperature on polymerization was only studied briefly, since an increase of the polymerization temperature to 80 °C leads to a dramatically reduced molecular weight ($2.3 \times 10^5$ g/mol at 25 °C to $1.3 \times 10^3$ g/mol at 80 °C).

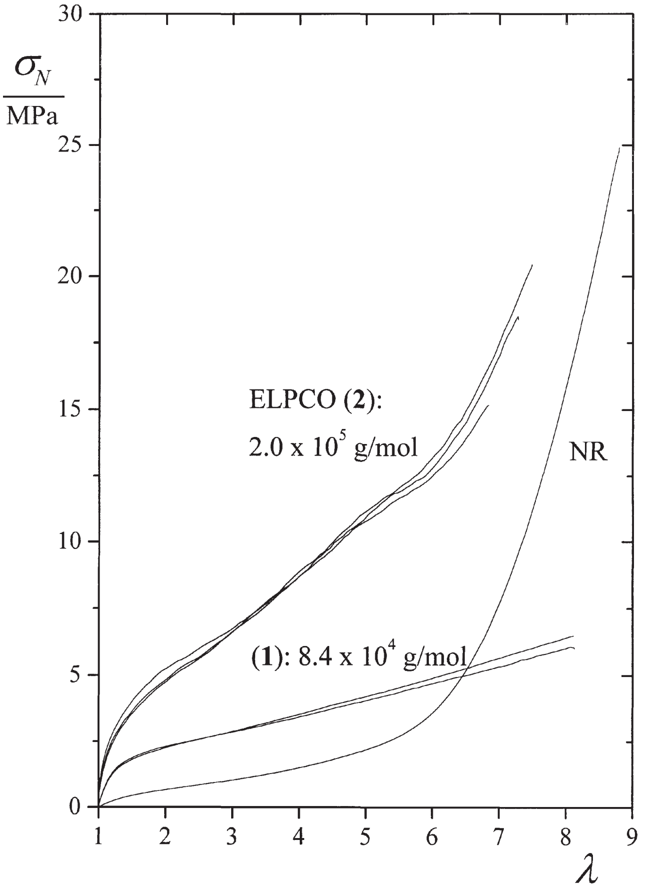

Figure 6. Stress-strain behavior of propene-CO copolymers (**1**, $M_w = 8.4 \times 10^4$ g/mol; **2** (ELPCO) $M_w = 2.0 \times 10^5$ g/mol) and of a polyisoprene (NR) ($\sigma_n$, nominal stress; $\lambda$, extension ratio).

*2*) can be stretched to a nominal extension ($\lambda$) of 6–7 with a higher strength compared to a typical rubber material. At higher extensions $\sigma_N$ increases exponentially, indicating the stress-strain properties of typical flexible polymers with low crystallinity.

Recently it has been demonstrated that homopolypropene elastomers [71] are accessible by increasing the molecular weight. At a certain chain length the probability for ordered segments, even in atactic polymers, is high enough to cause the formation of a three-dimensional network by crystallization. DSC-investigations show that there are also crystalline domains in the high molecular weight CO/alkene copolymers (table 6: sample 2: $T_g = 15\,°C$; $T_m = 50\,°C$), which could be responsible for the elastic properties. This hypothesis is supported by X-ray diffraction investigations, which allow to estimate the degree of crystallinity to about 30%. Furthermore, entanglements and CO–CO-dipolar interactions of the polar polyketones might contribute to the development of the elastic properties.

The thermal behavior of the high molecular weight polymers was studied as a function of storage time [72]. A glass transition ($T_g$) at 19.8 °C and a clear melting transition at 50.1 °C was observed for a copolymer with $M_w = 1.0 \times 10^5$ g/mol, after storing the DSC sample for six weeks at room temperature. This behavior is even more pronounced after another 5 weeks of storage ($T_g = 24.2\,°C$, $T_m = 51.8\,°C$). A comparison of stress-strain measurements for different molecular weight polyketone samples prepared at room temperature with the same samples after pressing at 130 °C showed that the materials are stable at elevated temperatures and show the same flexible properties after cooling to ambient temperature.

Table 4
Barrier properties of ELPCO 200 [a].

| Materials | Permeability [a] 23 °C, 0% r.H. | | | Permeability 23 °C, 85% r.H. |
|---|---|---|---|---|
| | $N_2$ | $O_2$ | $CO_2$ | $H_2O$ |
| Polyamide | 2 | 12 | 42 | 15 |
| PVC | 7 | 30 | 160 | 2,5 |
| ELPCO 200 | 50 | 240 | 1200 | 51 |
| HDPE | 170 | 600 | 2600 | 0,3 |
| Polystyrene | 250 | 1000 | 5200 | 12 |
| LDPE | 570 | 2000 | 8600 | 1,1 |

[a] $P$ in $\frac{cm^3 \times 10^{-4}\ m}{m^2 \times d \times bar}$; film thickness: 19 $\mu$m.

The mechanical properties of the higher molecular weight propene/CO-copolymers ($M_w \approx 2 \times 10^5$ g/mol) resemble those of flexible PVC. For the use of this material in medical applications (e.g., blood bags, tube systems), the permeability and diffusion properties for the gases $N_2$, $O_2$, $CO_2$ and for gaseous water are important. Measurements on our polymers show, that most of the properties lie between HDPE and PVC (table 4). Interestingly, a higher penetration was observed only for $H_2O_{(g)}$, which is in the range of typical polyurethanes.

## 4. Ultrahigh molecular weight propene-ethene-CO elastomers

The influence of chain defects induced by incorporating small amounts of propene/CO (P/CO) units on solubility, crystallization and melting behavior of E/CO-copolymers has been previously studied [19,73]. The properties of these highly crystalline CARILON-terpolymers are still dominated by the E/CO units. Applying the dicationic palladium(II) complex **1** (figure 5) as catalyst precursor in $CH_2Cl_2$ at room temperature and an optimized amount of water as activator, soluble propene-ethene-CO terpolymers with ultrahigh molecular weights (up to $1.2 \times 10^6$ g/mol) are accessible (table 5) [74]. $^{13}$C-NMR spectra show three peaks, due to carbonyl groups flanked by head-head, head-tail and tail-tail propene monomers and another one is attributed to isolated E/CO carbonyl units [19], indicating the formation of a regio- and stereoirregular P/CO-copolymers containing randomly distributed E/CO-units. Only two resonances of carbonyl groups can be detected in the polymers consisting of about a 1 : 1-ratio of E/CO- to P/CO-units (table 5, *entries 2* and *3a*). These signals result from the two remaining regioisomers $–CH_2–CH_2–C(O)–CH(CH_3)–CH_2–$ and $–CH_2–CH_2–C(O)–CH_2–CH(CH_3)–$, which are expected for a nearly alternating arrangement of E/CO– and P/CO fragments.

Table 5
Terpolymerization results [a].

| Entry | Ethene in feed, (mol%) | Activ.[c] | $10^{-5}\ M_w$ (g/mol) | $M_w/M_n$ | E/CO in terpolymer [d] (mol%) | $T_g$ [e] (°C) | $T_m$ [e] (°C) | $X_c$ [e] (%) | Elastomer |
|---|---|---|---|---|---|---|---|---|---|
| *1* | 3.0 | 21.7 | 5.89 | 3.0 | 13.0 | 23.3 | –[f] | n.d.[g] | yes |
| *2* | 7.0 | 43.3 | 4.11 | 2.3 | 47.8 | 10.3 | –[f] | 30 | yes |
| *3a* | 13.0 | 21.7[b] | 5.28 | 2.3 | 50.0 | 10.3 | –[f] | 30 | yes |
| *3b* | 15.0 | 13.0[b] | 12.0 | 2.9 | 69.0 | 14.1 | 52.9 | n.d. | no |

[a] Catalyst **1**, MeOH/Pd mol-ratio = 300, solvent: $CH_2Cl_2$, 100 ml.
[b] $CH_2Cl_2$ soluble part.
[c] Activity in g-terpolymer × (g Pd × h)$^{-1}$.
[d] Calculation based on $^1H$ NMR spectra.
[e] $T_g$: glass transition temperature; $T_m$: melting temperature; $X_c$: degree of crystallinity.
[f] Broad melting peaks.
[g] n.d.: not determined.

Stress-strain experiments carried out on films of propene/ethene/CO-terpolymers show that by the incorporation of E/CO units along the P/CO-main chain, materials with variable mechanical properties can be prepared [67,74]. The terpolymers are elastomers (EPEC) or crystalline thermoplastics depending on the ethene content (figure 7). When the mol-ratio of E/CO to P/CO is about 50 mol%, the materials are thermoplastic elastomers. The polymers show a broad elastic plateau and high forces at the maximal extension. Above 50 mol% E/CO the polymers can be isolated as a crystalline powdery or as a fibrous material. These polymers (e.g., table 5, figure 7, *entry 3b*, E/CO = 69%) have ultrahigh molecular weights (up to $1.2 \times 10^6$ g/mol) while still being soluble in organic solvents such as $CH_2Cl_2$ and $CHCl_3$. Higher E/CO-contents lead to insoluble materials with properties resembling those of the CARILON® grades.

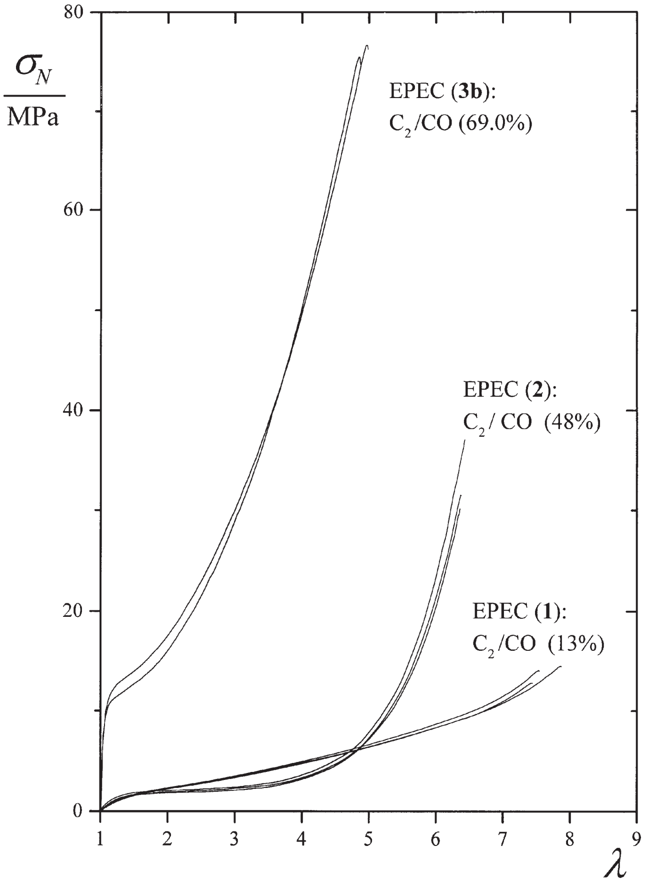

Figure 7. Stress-strain properties of high molecular weight propene-ethene-CO terpolymers (EPEC **1**, E-CO = 13 mol%, $M_w = 5.9 \times 10^5$ g/mol; EPEC **2**, E-CO = 48 mol%, $M_w = 4.1 \times 10^5$ g/mol; EPEC **3b**, E-CO = 69 mol%, $M_w = 12.0 \times 10^5$ g/mol).

The dynamic mechanical behavior of the elastomer consisting of a 1 : 1-ratio of E/CO to P/CO building units (table 5, *entry 2*) was determined by temperature and frequency depending investigations (figures 8 and 9). The complex shear compliance [$J^* = J' - iJ''$] was determined with a dynamic mechanical spectrometer [75]. The samples (thickness = 0.2–0.3 mm, area = 12 mm$^2$) were measured with stress amplitudes from 10 kPa at low temperatures to 1 kPa at high temperatures. Two temperature runs were performed with a heating rate of 1 K/min and a frequency of 1 Hz (figure 8). The first run shows after a glass transition (at about 10 °C) a small step in the compliance beginning at 35 °C that disappears at the second run. This behavior was also found in calorimetry and polarization microscopy and is due to the small crystalline domains present in the samples, depending on the thermal history as mentioned above [72]. After the second temperature run, mechanical spectra ($10^{-3}$–30 Hz) were taken at temperatures varying from 10 to 110 °C, to construct a mastercurve (figure 9). The glass process (at about 10 Hz) is followed by a rubbery plateau (1–$10^{-4}$ Hz) and viscous flow in the low frequency region. This behavior is typical for an amorphous, rubber-like polymer such as polyisoprene or SBR with high recoveries in stretching and releasing cycles [76,77].

## 5. Co- and terpolymerization of carbon monoxide with higher 1-olefins

The tolerance of the Pd(II)-phosphine catalysts toward carbon monoxide offers an important extension compared to pure polyolefins. As pointed out above, ethene/CO-copolymers are highly crystalline materials with melting transitions far above 200 °C. This demonstrates that the

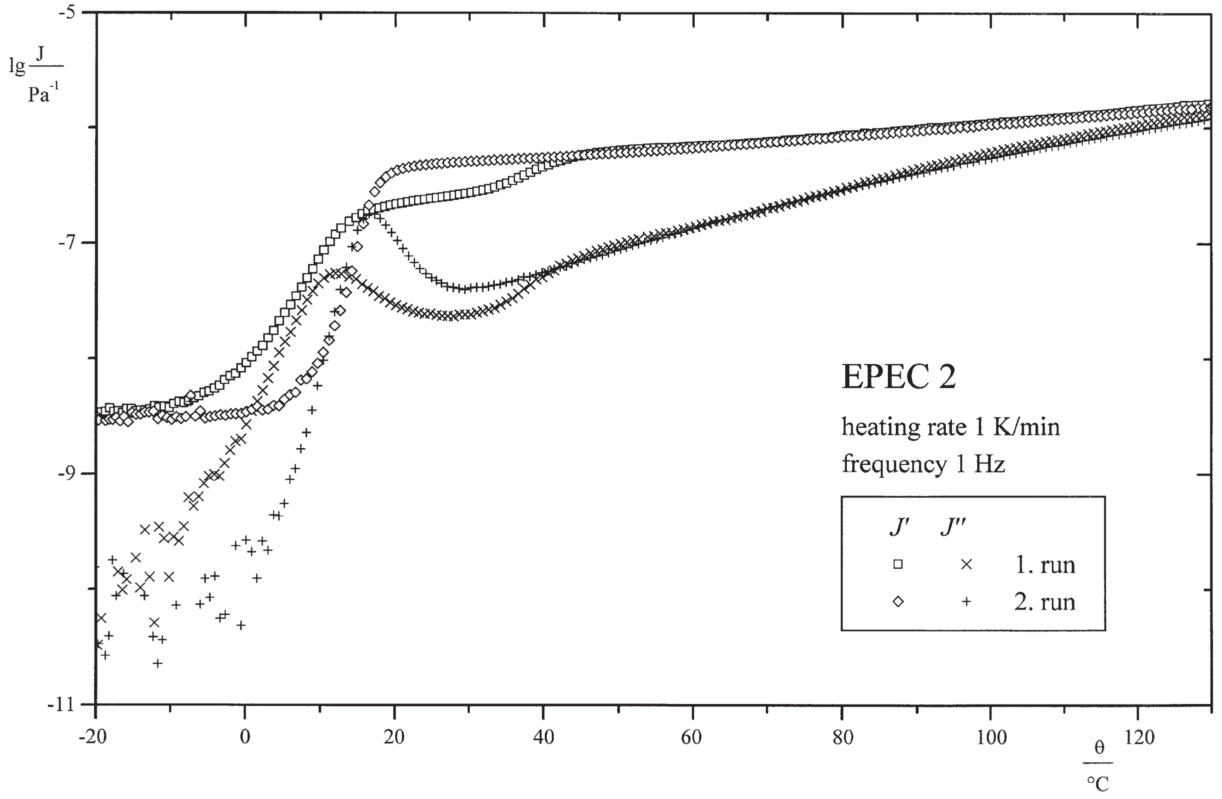

Figure 8. Shear compliance of the terpolymer EPEC **2** during two temperature runs.

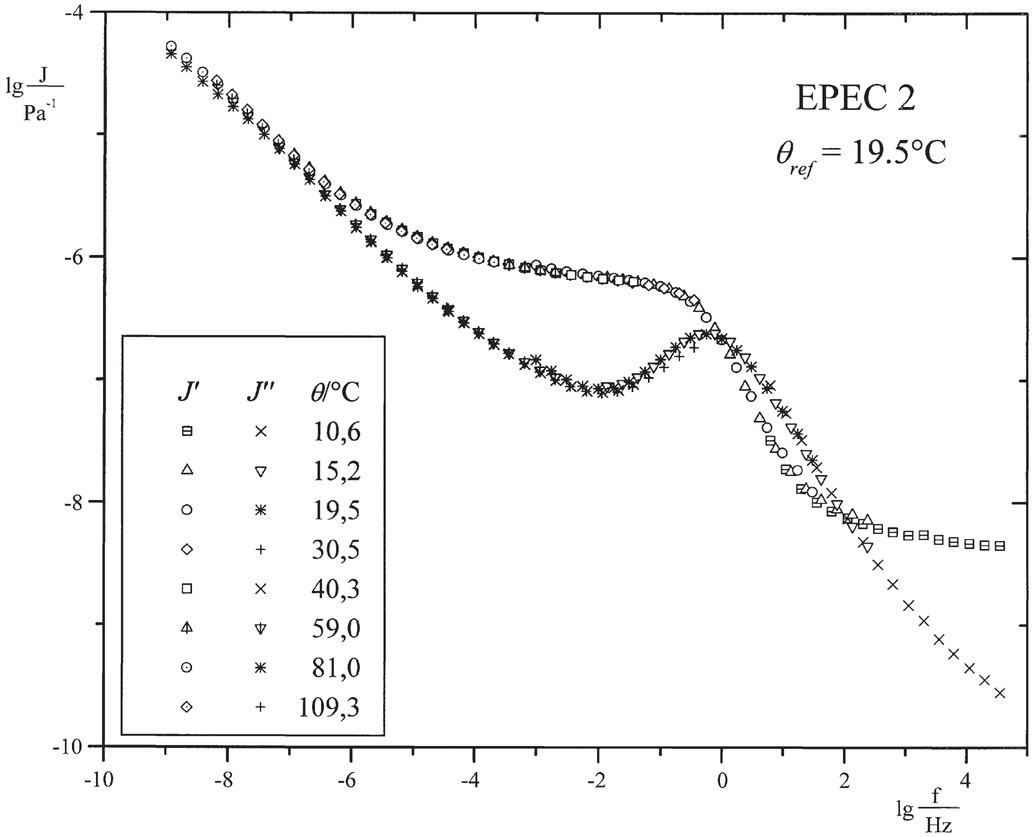

Figure 9. Mastercurve of the terpolymer EPEC **2**.

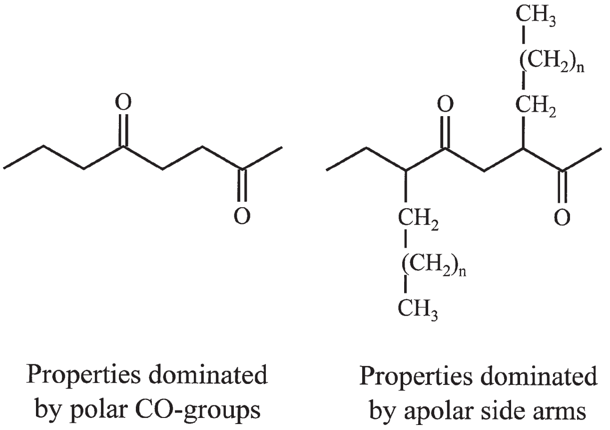

Figure 10. Influence of higher 1-olefin side groups on the polarity of CO/alkene copolymers.

properties of these copolymers are clearly dominated by the polar carbonyl groups (figure 10). An exchange of ethene by propene leads to polymers with a significantly reduced crystallinity, depending on the E/CO to P/CO-ratio and on the distribution of E/CO-units within a regio- and stereoirregular propene/CO-matrix. Accordingly, the properties of these materials can be conducted from hard to soft or from crystalline to flexible by a proper choice of the ethene/propene ratio. On the other hand, the polarity of the 1,4-polyketones, the structure of which resembles that of partly oxidized polyolefins, should also depend on the length of the 1-olefin alkyl side groups, so that the polarity of the polyketones should be controllable by application of higher 1-olefins.

Based on that background, we performed co- and terpolymerization experiments with carbon monoxide, ethene, propene and higher $\alpha$-olefins ranging from 1-hexene to 1-icosene (table 6, figure 11). It was speculated earlier, that

Table 6
Copolymerization results of carbon monoxide with various 1-olefins [a].

| Entry | Copolymer | $\alpha$-olefin | $M_w$ [b] (g/mol) | $M_w/M_n$ [b] | $T_g$ [d] (°C) | $T_m$ (°C), ($\Delta H_m$ (J/g)) [d] | Isolated yield (g) |
|---|---|---|---|---|---|---|---|
| 1 | Hx-CO | 1-hexane | $2.2 \times 10^4$ | 1.61 | 20.0 | 54.0 | 3.4 |
| 2 | Hp-CO | 1-heptene | $2.8 \times 10^4$ | 1.69 | −24.0 | −7.0 | 2.6 |
| 3 | Oc-CO | 1-octene | $2.9 \times 10^4$ | 1.76 | −33.0 | n.d.[e] | 2.5 |
| 4 | Dd-CO | 1-dodecene | $1.9 \times 10^4$ | 1.78 | −59.8 | n.d. | 1.6 |
| 5 | Hd-CO | 1-hexadecene | $2.3 \times 10^4$ | 1.68 | –[e] | 13.0 | 1.3 |
| 6 | Od-CO | 1-octadecene | $2.6 \times 10^{4}$ [c] | 1.53[c] | –[e] | 19.3, 32.2(103) | 8.5 |
| 7 | Ic-CO | 1-icosene | $2.1 \times 10^{4}$ [c] | 1.67[c] | –[e] | 28.9(51.0), 41.2(65.8) | 8.0 |

[a] Polymerization conditions: catalyst **1**; solvent, $CH_2Cl_2$ (100 ml); MeOH/Pd mol ratio, 140; polymerization temperature, room temperature; carbon monoxide, $82.0 \times 10^5$ Pa; olefin, 20 g; reaction time, 72 h.

[b] Measured by GPC (relative to polystyrene standards).

[c] Viscosimetry: Od-CO: $M_w(M_w/M_n) = 6.9 \times 10^4$ (1.88); Ic-CO: $M_w(M_w/M_n) = 5.7 \times 10^4$ (1.97).

[d] Glass transition temperature ($T_g$), melting temperature ($T_m$) and enthalpy of melting ($\Delta H_m$) of the second heating trace.

[e] n.d.: not detected.

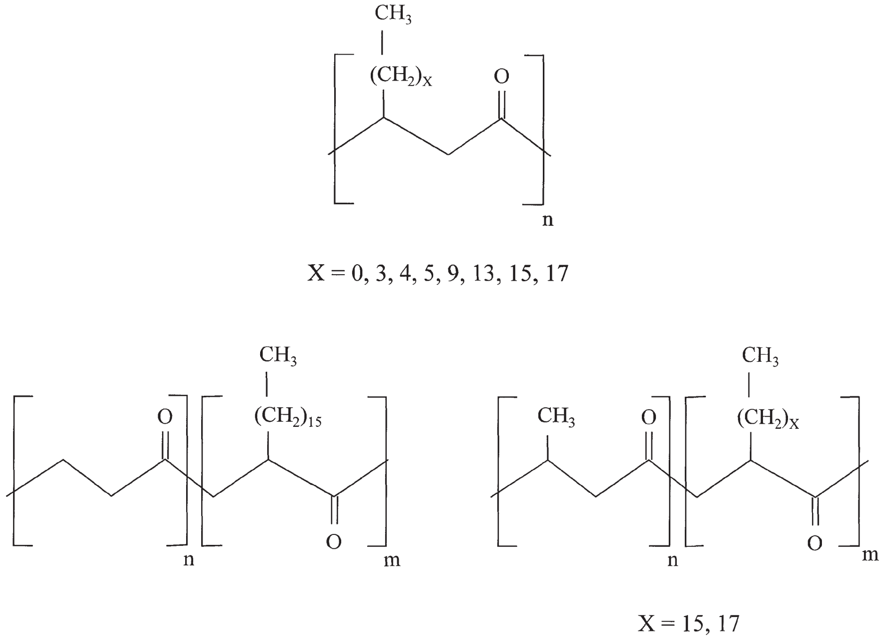

Figure 11. Composition of the present 1-olefin/CO copolymers and ethene or propene/higher 1-olefin/CO terpolymers.

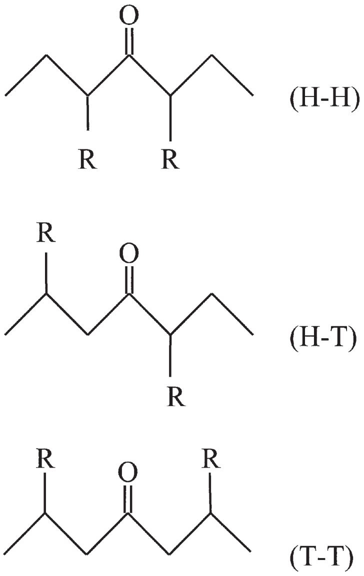

Figure 12. Regiochemistry of 1-olefin-CO copolymers (Head-Head (H-H), Head-Tail (H-T), and Tail-Tail (T-T)).

higher 1-olefins should not be suitable to undergo a copolymerization reaction with carbon monoxide due to their ability to be isomerized to internal olefins [22,78]. However, we have been able to prepare a variety of these polymers with moderate to high molecular weights and promising activities by following the same procedure described for the propene/CO-copolymers using the dicationic palladium(II) complex **1** as catalyst precursor [79].

In propene-CO copolymers, the resonances of the carbonyl groups, which appear in the $^{13}$C-NMR spectra between 207 and 215 ppm, are nicely separated and can be used to describe the catalyst regioselectivity by determination of the ratio of head-tail (H-T) to the sum of tail-tail (T-T) and head-head (H-H) olefin units that flank the carbonyl groups (figure 12). (For NMR data of corresponding structures cf. [19,31,66,74].)

However, a similar measurement is not possible for long chain branched copolymers of higher 1-olefins (e.g., 1-octadecene (Od) or 1-icosene (Ic)) due to the low intensity of those signals relative to that of $CH_2$ and $CH_3$ groups. Therefore, we performed a copolymerization experiment of 1-icosene with $^{13}$CO in order to determine the regioselectivity of catalyst **1** also in the case of higher 1-olefins. The $^{13}$C-NMR spectrum of Ic-$^{13}$CO shows intensive peaks of the carbonyl groups at 209.0–210.0 (H-H), 211.7–212.7 (H-T), 213.8–215.2 ppm (T-T), indicating about 55% regioregular H-T-connected units, which is in the same order as found for 1/methanol in propene/CO copolymerization experiments [66]. The DSC traces of Od-CO and Ic-CO copolymers show two melting temperatures (table 6) which can be attributed to side chain crystallization of the low regioregular copolymers. The presence of two peaks in the melting endotherm for these comb-like polymers is a behavior which is similar to that of paraffinic hydrocarbons that contain the same number of carbon atoms in the aliphatic chain [80,81]. For the previously described high molecular weight propene/ethene/CO-elastomers (figures 6 and 7) high glass transition temperatures ($T_g$) in the range of room temperature were observed [67,74]. We would like to attribute this effect to attractive dipolar interactions between the carbonyl groups. In order to guarantee the flexible or elastic properties also in low temperature applications it would be desirable to find routes for setting the $T_g$ to values significantly below room temperature. For conventional EPDM rubbers a decline of $T_g$ can be realized by

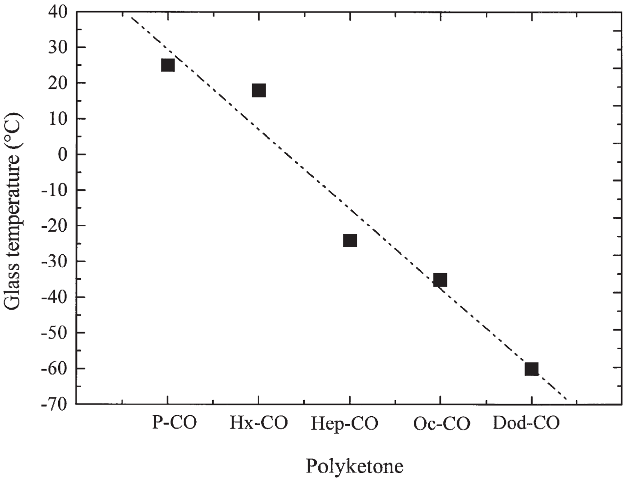

Figure 13. Influence of the side groups of 1-olefin/CO copolymers on the glass transition temperatures ($T_g$).

Table 7
Terpolymerization experiments [a].

| Entry | Terpolymer | Higher α-olefin in feed (g) | $M_w$ (g/mol) | $M_w/M_n$ | $T_g$[d] (°C) | $T_m$ (°C) ($\Delta H_m$ (J/g)) | Higher 1-olefin in terpolymer (mol% [f]) | Isolated yield (g) |
|---|---|---|---|---|---|---|---|---|
| 1 | OdPCO 1 | 5.0 | $1.63 \times 10^5$ | (1.84) | 19.3 | 81.0(20.7) | 13.0 | 8.0 |
| 2 | OdPCO 2 | 14.0 | $6.83 \times 10^4$ | (1.43) | −15.4 | 12.9(66.0) | 30.0 | 10.0 |
| 3 | IcPCO | 10.0 | $5.66 \times 10^4$ | (1.90) | n.d.[c] | 9.12(16.5); 33.0(118.0) | 21.0 | 2.0 |
| 4 | OdECO | 10.0 | –[b] | –[b] | n.d. | 84.52(24.9), 185(20.8) | –[b] | 5.5 |

[a] Polymerization conditions: catalyst **1**; solvent, $CH_2Cl_2$ (100 ml); MeOH/Pd-catalyst mol ratio, 140; polymerization temperature, room temperature; carbon monoxide, $82.0 \times 10^5$ Pa; propene, 40 g; ethene, $10.5 \times 10^5$ Pa; reaction time, 48 h.

[b] The polymer is insoluble.

[c] n.d.: not detected.

[f] Calculation based on $^1$H NMR spectra.

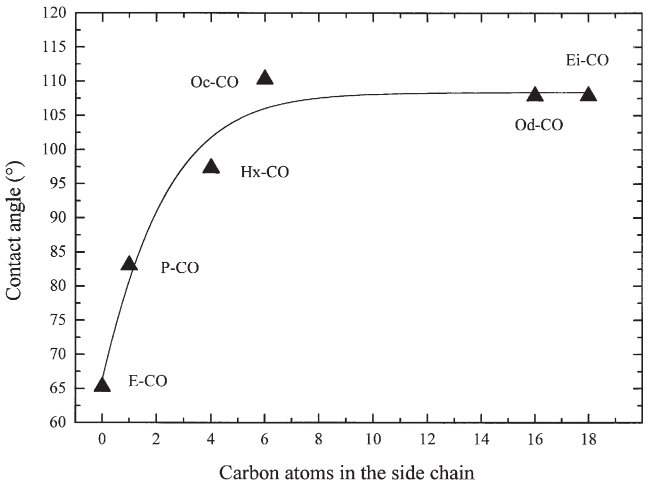

Figure 14. Sessile drop contact angles of water drops on films of a series of copolymers (ethene/CO (E-CO), propene/CO (P-CO), hexene/CO (Hx-CO), octene/CO (Oc-CO), octadecene/CO (Od-CO), icosene/CO (Ic-CO)).

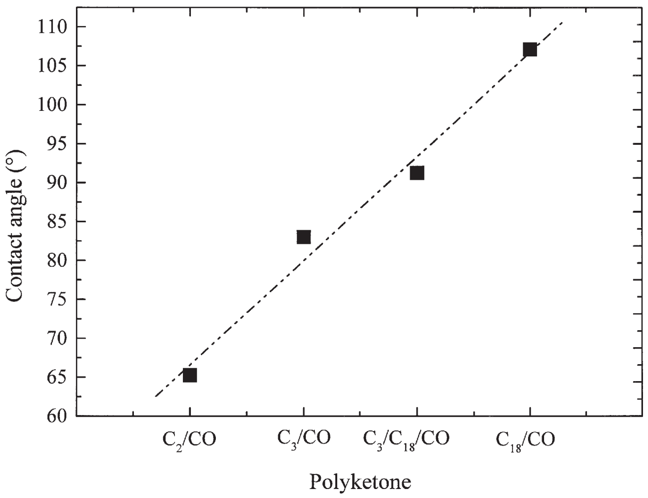

Figure 15. Control of surface polarity by terpolymerization ($C_3$/$C_{18}$/CO).

incorporating olefins with long side chains [82–84]. A similar decrease is observed for the co- and terpolymers of higher 1-olefins with carbon monoxide [79,85]. For the series of hexene-CO (Hx-CO), heptene-CO (Hp-CO), octene-CO (Oc-CO) and dodecene-CO (Dd-CO) copolymers, $T_g$ decreases from room temperature to almost $-60\,^\circ$C nearly linearly with the length of the side groups (table 7, figure 13), indicating a clear reduction of dipolar interactions by isolation of the carbonyl groups through the apolar side groups.

The same effect can also be achieved by terpolymerization of a higher 1-olefin with either ethene or propene and CO. Increasing the octadecene-CO content in a terpolymer with propene from 13 to 30 mol% leads to a decline of $T_g$ from about 19 to $-15.4\,^\circ$C (table 6, *entries 1 and 2*).

### 5.1. Contact angle measurements

Adaptation of bulk and surface polarity, especially of the surface hydrophilicity is one prerequisite for the design of biocompatible materials [86,87]. The polyketones consist just of carbon, hydrogen and oxygen, so that no harmful decomposition products are to be expected, even by an intensive contact with living systems, like with polyurethanes or polysilicones. They even contain no harmful plasticizers as in the case of flexible PVC, which are known to diffuse from the blood bag material into the stored blood. On the other hand these highly variable materials are accessible by a catalytic reaction from cheap and readily available feedstocks, so that they might offer an interesting basis for future applications in this field.

The ease with which the surface polarity can be varied by simply introducing different 1-olefin components is best demonstrated by contact angle measurements, performed on selected copolymers (E-, P-, Hx-, Hp-, Oc-, Od- and Ic/CO). The measurements on a drop of water located on the surface of copolymer films (“sessile-drop-technique”) show that the contact angles ($\theta$) depend sensitively on the amount and on the length of the alkyl branches (figure 14). An increase of the number of side chain carbon atoms from 0 (E/CO, $\theta = 65\,^\circ$) to 6 (Oc/CO) results in an increase of $\theta$ to $110.27\,^\circ$. At this length a maximum in the $\theta$-value is reached. A further increase from $C_6$ to $C_{18}$ (Ic-CO) has now effect on the surface polarity.

A similar effect can be achieved by terpolymerization of propene/CO with, e.g., 1-octadecene (table 7, *entry 1*, OdPCO 1, 13% Od/CO). A film cast from this polymer shows a contact angle of $\theta = 91.3\,^\circ$. This value is considerably higher than that of propene-CO ($\theta = 83.03\,^\circ$) but lower than the value for the octadecene-CO ($\theta = 107.14\,^\circ$) (figure 15).

## 6. Co- and terpolymerization of functionalized 1-olefins with carbon monoxide

The possibility to incorporate polar groups, like CO, into a polyolefin “backbone” adds a new dimension to the design of polymer properties by transition metal catalysts. This variability could be further improved by incorporating functional monomers. We focused in a first approach on co- and terpolymerization reactions of a benzo-15-crown-5-functionalized 1-olefin and propene, 1-hexene, 1-dodecene and 1-octadecene with carbon monoxide (figure 16) [88,89].

As the terpolymers with long 1-olefin side chains combine a relatively large hydrophobicity with low glass transition temperatures, these materials might offer an interesting alternative route toward new membrane materials. For these applications, the 1-olefin side chains introduce enough hydrophobicity to prevent fouling of the membrane, whereas the carbonyl groups in the polymer offer a significant polarity to assist ions in crossing the water/membrane boundary. Due to the lower reactivity of higher 1-olefins, a decrease in the molecular weight of the terpolymers consisting of the crown-ether-monomer and a second long 1-olefin was observed (table 8, **C12**, **C18**). However, terpolymerization of the crown-ether-substituted olefin with carbon

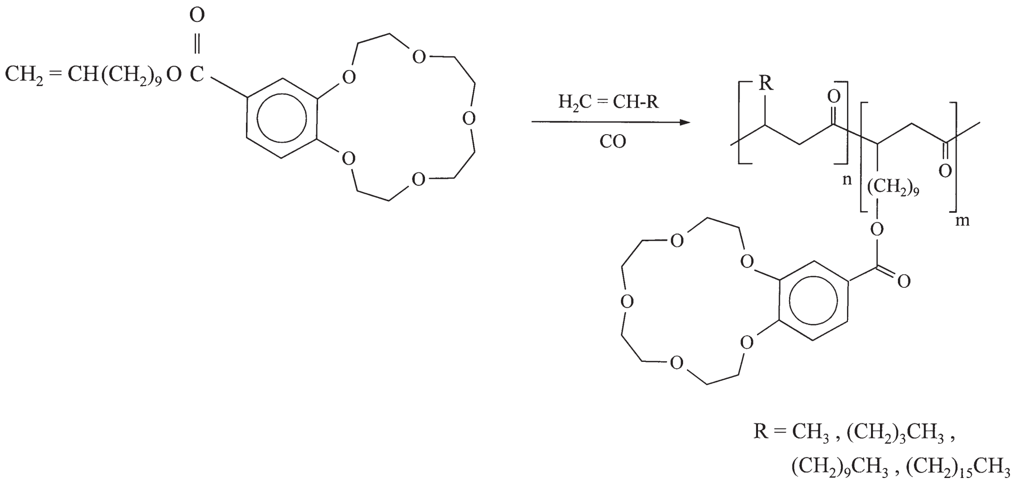

Figure 16. Terpolymerization of 4′-(undec-10-enylcarboxylate)benzo-15-crown-5 with different $\alpha$-olefins.

Table 8
Composition of crown-ether containing terpolymers.

| Polymer | $M_w$[a] (g/mol) | $M_w/M_n$[a] | $B_{15}C_5$ (mol%)[b] $^1$H NMR | $B_{15}C_5$ (mol%)[b] $^{13}$C NMR | $NaClO_4$-flux ($10^{-8}$ mol/m$^2$ s) | $T_g$[c] (°C) |
|---|---|---|---|---|---|---|
| **C3**[e] | 115000 | 2.1 | 0 | 0 | 0.15 | 20 |
| **C6** | 12800 | 1.5 | 5.4 | 4.7 | 0.36 | −18 |
| **C12** | 11000 | 2.0 | 4.4 | 4.3 | 0.30 | −76 |
| **C18** | 5300 | 1.8 | 9.6 | 9.0 | 0.21 | –[d] |

[a] Weight-average molecular weight ($M_w$) and the polydispersity ($M_w/M_n$) measured by GPC in chloroform (relative to polystyrene).
[b] $B_{15}C_5$: amount of benzo-15-crown-5 moieties (mol%).
[c] Onset-temperatures from the second heating run (10 K/min) as determined by DSC.
[d] No observable $T_g$.
[e] CO/propene copolymer for comparison; no crown-ether monomer added.

monoxide and shorter 1-olefins, like hexene (table 8, **C6**) gives higher molecular weight polymers which are suitable for film applications.

For **C6** and **C12** glass transitions could be observed at $-18\,°C$ and $-76\,°C$, respectively, which are lower than those of the corresponding copolymers hexene/CO ($T_g = 20\,°C$) and dodecene/CO ($T_g = -60\,°C$). The amorphous character of these polymers is in accordance with the relatively low regio- and stereoselectivity of the catalyst. **C18** displays a sharp melting transition at 17 °C. As side chain crystallization becomes more probable with increasing length of the 1-olefin, this transition might be ascribed to such an effect.

Ion-selective membranes were prepared by gel-crystallization of a dilute xylene-solution containing ultra-high molecular weight polyethylene (UHMW-PE) and the benzo-15-crown-5 substituted polyketones in a 1 : 1 mass ratio. On cooling, crystallization of the polyethylene causes gelation of the initially homogeneous solution. After evaporation of the solvent, a thin microporous polyethylene-support, encapsulating the receptor-substituted polyketone, remains. This gel crystallization approach is of great advantage as it allows a facile one-step incorporation of polymeric membrane materials into the UHMW-PE support. Furthermore, the resulting membranes can be easily drawn to yield extremely thin, mechanically stable films.

In order to establish their feasibility for membrane applications, the permeation of $NaClO_4$ across polymeric membranes containing the crown-ether functionalized polyketones was investigated. The $NaClO_4$-fluxes for the different terpolymers are presented in table 8. The covalent linkage of the benzo-15-crown-15 moieties to a polymer backbone guarantees a high life-time stability of these membranes.

A previous publication [90] has proved the existence of a percolation-threshold for the transport of alkali-metal perchlorates across membranes containing polysiloxane-bound benzo-15-crown-5 and calix[4]arene groups. The results were interpreted in terms of a phase-segregation between the receptor-moieties and the apolar polymer-backbone. Below the percolation-threshold (which is at $\sim$ 20 mol%) the benzo-15-crown-5 and calix[4]arene groups associate into isolated clusters, whereas at high degrees of substitution they form ion-conductive percolating paths transverse the membrane. The $NaClO_4$ fluxes at receptor contents below the percolation-threshold are more or less independent of the degree of substitution, and transport is assumed to take place by diffusion of the polymer-bound receptor-molecules or of clusters thereof. In contrast, at benzo-

15-crown-5 or calix[4]arene contents above the percolation threshold the $NaClO_4$-fluxes are high, because transport no longer takes place via diffusion but by a site-to-site jumping of the ions from one polymer-bound receptor-site to an adjacent one.

Although the benzo-15-crown-5 content is different for each of the terpolymers, it is well below the percolation-threshold within a region where the transport-rates are relatively independent of the degree of substitution of the polymers. Whereas the pure propene/CO-copolymers shows only a low $NaClO_4$ flux, increasing the length of the 1-olefin from hexene (**C6**) to 1-octadecene (**C18**) is accompanied by a continuous decrease in the $NaClO_4$-flux across the corresponding membranes. The $NaClO_4$ transport rates reflect the polarity of the membrane material, which is an important parameter for the partitioning of the salts from the aqueous phase into the membrane (table 8).

## 7. Conclusion

Ethene/CO-copolymers are the next generation of transition metal catalyzed polyolefins entering the market. Under the trade name of CARILON® they will find application in packaging as well as in the car and fiber industry due to their nylon-6 analogous properties. In the recent years the first high molecular 1-olefin/CO- co- and terpolymers have become accessible. The properties of this new class of materials, that are available in a catalytic reaction from cheap feedstocks, can be controlled from highly crystalline to soft and flexible and even to excellent elastomers which resemble flexible-PVC or natural rubbers. Moreover, the easy switch between hydrophilic and hydrophobic properties is one important factor for the development of biocompatible polymer systems, where questions of cell adhesion on surfaces are concerned. In this respect, the variable polyketones, which from an ecological perspective resemble the structure of partially oxidized polyolefins, might open the way to a new class of materials applicable in biologically active systems or as ultra-tough fibers.

Despite the fact, that CARILON® grades are already produced commercially, the palladium-phosphine catalysts are still not comparable to zirconocene dichlorides, especially with respect to activity. Future research has therefore to be directed to the search for new catalyst lead structures, that allow to compensate for the different coordination capabilities of carbon monoxide and alkene monomers.

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