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Control of Molecular Weight in α-Olefin−Carbon Monoxide Alternating Copolymerization. A Way to High Molecular Weight Propene−Carbon Monoxide Thermoplastic Elastomers

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The copolymers of olefins with carbon monoxide are of considerable interest from different viewpoints. These include the low price of the monomers and the ease with which the carbonyl groups can be chemically modified to other classes of functionalized polymers.

In recent years several groups have reported on the Pd(II)-catalyzed alternating copolymerization of olefins with carbon monoxide. The reactions are performed at various reaction temperatures in aqueous media or in a variety of organic solvents that usually consist of methanol which serves as activator.[1−8] These reports show that the dicationic complex $[Pd(dppp)(NCMe)_2](BF_4)_2$ (**1**, dppp = 1,3-bis(diphenylphosphino)propane) is so far the most active catalyst for the alternating propene/CO copolymerization reaction.[4] Analysis of the previously isolated, amorphous propene/CO copolymers using this particular catalyst precursor and methanol as activator showed moderate to low molecular weights ($M_w \leq 5 \times 10^4$ at 50 °C).[9]

We report here that a considerable increase in molecular weight (Table 1) is observed by decreasing the activator concentration or by using the well-defined dicationic diaquapalladium(II) complex $[Pd(dppp)(OH_2)_2](BF_4)_2$ (**2**).[10] These high molecular weight propene/CO copolymers are thermoplastic elastomers if the molecular weight exceeds $M_w \approx 1 \times 10^5$. Stress−strain experiments show that their behavior resembles that of vulcanized natural rubber.

Results and Discussion. The copolymerization reactions were carried out in CH_2Cl_2 at room temperature with **1** or **2** as catalyst precursor. Methanol and water were used in different concentrations for activation of **1**. No polymerization reaction was observed without addition of methanol or water (Table 1). Decreasing the amount of added methanol from 2 mL to 0.25 mL resulted in an increase of M_w from 3.6×10^4 to 2.3×10^5 (Table 1, runs 2 and 3). A similar effect was observed when water was used instead of methanol. However, H_2O shows a trend to lower activity. At high water concentrations (Table 1, run 11) no polymerization activity can be observed and solid palladium is formed, probably in a Wacker-analogous reaction.[11] Interestingly, the water concentration is also affecting 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.[12] The molecular weight distributions of the polyketones are in the range expected for single-site catalyst species. All polymer products with molecular weights above 1×10^5 show the properties of thermoplastic elastomers.

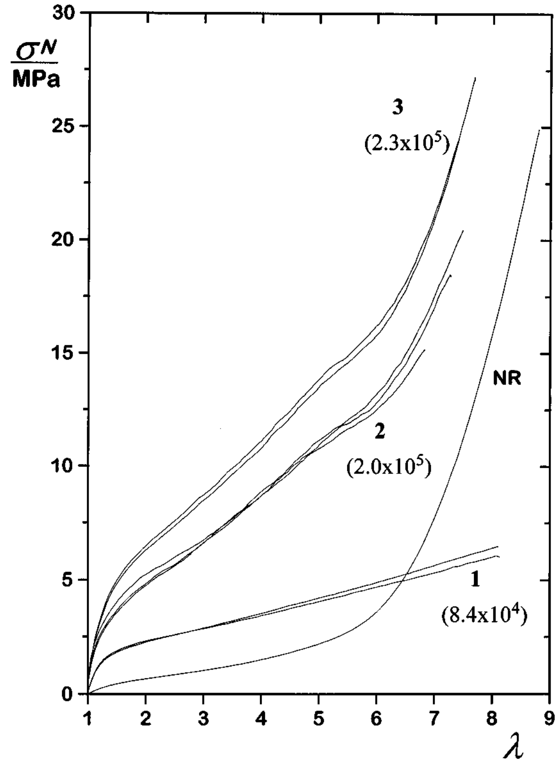

Figure 1. Stress−strain behavior of high molecular weight propene/CO copolymers (**1**, $M_w = 8.4 \times 10^4$; **2**, $M_w = 2.0 \times 10^5$; **3**, $M_w = 2.3 \times 10^5$) and of a vulcanized natural rubber (NR) (σ_n, nominal stress; λ, extension ratio).

Characterization of the copolymers was accomplished by IR, ^1H, and ^{13}C NMR spectroscopy, by DEPT (distortionless enhancement by polarization transfer), and by elemental analysis. The IR and NMR spectra were similar to those of the propene/CO copolymers reported previously.[1] A strong IR absorption ($CDCl_3$ or as film) at 1707 cm^{-1} was ascribed to the poly(1,4-ketone) carbonyl group.[13] The ^1H NMR ($CDCl_3$) spectrum of the copolymers exhibited three broad resonances at 2.89−3.14 ppm (2H), 2.27−2.51 ppm (1H), and 1.01−1.09 ppm (3H) corresponding to the CH_2, CH, and CH_3 groups, respectively. The ^{13}C NMR ($CDCl_3$) spectrum showed resonances at 215.8, 211.9, 207.7, 44.7, 40.4, and 16.5 ppm. The first three resonances are due to carbonyl groups flanked by head−head, head−tail, and tail−tail propene units and the latter are attributed to the CH, CH_2, and CH_3 groups, respectively. The integrated areas of carbonyl, main-chain CH_2 and CH, and the side chain CH_3 peaks maintain a ratio of 1:1:1:1. Therefore, these high molecular weight copolymers consist of alternating CO− and propene units. This observation is also supported by elemental analysis results.

Dissolving the propene/CO copolymers (Mw ≥ to 1×10^5) in CH_2Cl_2 or $CHCl_3$ followed by slow evaporation of the solvent leads to the formation of highly elastic, transparent films. Dissolving and precipitation are reversible processes and do not alter the physical properties of the polymers. A comparison of the stress−strain behavior of propene/CO copolymers of different molecular weights with that of a vulcanized natural rubber (NR) shows that the lower molecular weight products (e.g. **1**, Figure 1) do not have elastic properties. The material is relatively soft and can be stretched with low nominal forces (σ_N) until it breaks. At higher molecular weights the stress−strain curves resemble those of chemically cross-linked natural rubbers. The

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Table 1. Polymerization Results (Solvent: CH_2Cl_2, 50 mL)

run	cat. (activator)	amt of activ, mL	activ/Pd[a]	M_w (M_w/M_n)	activity[c]	H−T units,[d] %	elastomer
1	**1** (MeOH)	0	0		0		
2		0.25	140	2.3×10^5 (2.02)	55.5	55	yes
3		2.0	1100	3.6×10^4 (2.35)	62.9	60	no
4		50.0	27000	5.0×10^3 (1.68)	11.8	43	no[e]
5	**1** (H_2O)	0	0		0		
6		0.001	1.2	1.1×10^5 (3.25)	10.4	52	yes
7		0.125	150	2.7×10^5 (1.76)	86.6	53	yes
8		0.25	300	2.0×10^5 (1.87)	51.9	56	yes
9		0.5	600	8.4×10^4 (2.25)	27.0	62	no
10		2.0	2500	1.3×10^4 (1.21)	3.5	67	no
11		25	30000		0		
12	**2**	0	2	2.2×10^5 (1.85)	27.0	53	yes

[a] Activ/Pd: mole ratio of activator to palladium. [b] M_w (M_w/M_n) measured by GPC (relative to polystyrene). [c] Activity in g of copolymer × (g of Pd × $h)^{-1}$. [d] H−T units: regioregularity in mol % of head−tail units. [e] Viscous liquid.

samples **2** and **3** (Figure 1) can be stretched to a nominal extension (λ) of 6−7 with a higher strength compared to a typical rubber material. At higher extensions σ_N increases exponentially, indicating the stress−strain properties of typical elastomers.

Recently, it has been demonstrated for atactic polypropene[14] that homopolypropene elastomers 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 cross-linking by crystallization. DSC investigations show that there are also crystalline domains in the high molecular weight CO/alkene copolymers (Figure 1: sample **2** $T_g \cong 15$ °C, $T_m \cong 45$ and 90 °C; sample **3** $T_g \cong 23$ °C, $T_m \cong 106$ °C), which could be responsible for the elastic properties. This hypothesis is supported by some preliminary X-ray diffraction investigations, which allow us to estimate the degree of crystallinity to about 30%. However, it will be the subject of further investigations to find out to which extent entanglements and >CO−>CO dipolar interactions of the polar polyketones contribute to the development of the elastic properties.

Activation of Pd(II) complexes is accomplished either by using methanol as cocatalyst or by addition of small amounts of water. Excess methanol and water act as chain-transfer reagents (Table 1), indicated by a decrease of molecular weight of the polymer products. In order to introduce a minimum amount of activator, we prepared the stable diaqua-complex **2**, which is active without further addition of water or methanol (Table 1). **2** also leads to thermoplastic elastomers.

Experimental Section. Catalyst **1** is prepared as described previously.[4] Reagent grade chemicals were used as received unless otherwise stated. CH_2Cl_2 was distilled from CaH_2. Methanol was treated with sodium methoxide/dimethyl terephthalate and then distilled. Molecular weights and molecular weight distributions were measured by GPC relative to polystyrene standards. IR spectra were recorded on a Bruker IFS66V spectrometer. The mechanical measurements were performed on a Zwick 1445 tensile machine at room temperature. The specimens ($9 \times 2 \times 0.5$ mm^3) were extended at 10 mm/min. Other physical measurements were carried out with the equipment specified previously.[15]

High Molecular Weight Copolymers. A solution containing 0.045 mmol of the Pd(II) complex in CH_2Cl_2 (50 mL) and (complex **1**) the desired amount of activator (cf. Table 1) was placed in a 300 mL steel autoclave which was then charged with propene (14 g) and with carbon monoxide (52 bar). The reaction mixture was stirred at 25 °C for 30 h. At the end of this period, the remaining gases were vented off and the reaction was quenched by addition of methanol. The solvents were evaporated, and the resulting product was purified by adding CH_2Cl_2 (200 mL) followed by filtration over a short pad of silica gel in order to remove catalyst residues. Slow evaporation of the solvent gave the colorless copolymers.

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