Novel Linear and Branched Poly(1,4-ketone)-*b*-polyalcohol Block Structures through Control of the Catalyst Initiation Mechanism

Angela Mücke and Bernhard Rieger*

Anorganische Chemie II, Materials and Catalysis, Universität Ulm, D-89069 Ulm

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Introduction. The combination of apolar polyolefins with polar functions is still one of the major challenges in metal-catalyzed polymerization reactions. Besides the elegant work of Keim and Fink[1] in the 1980s and the recent success of Brookhart,[2] the alternating CO/alkene copolymerization reaction provides still an excellent route to such polar structures. We reported recently on the first high molecular weight CO/propene copolymers and on CO/ethene-CO/propene multiple block terpolymers[3] with interesting mechanical and surface properties, which added a new family of flexible and elastic polyketones to the long existing, highly crystalline CARILON and KETONEX thermoplastics.

It was a long standing hypothesis that the first catalyst initiation results from a nucleophilic attack of H_2O or of methanol to a CO ligand, which is coordinated to a dicationic Pd(II) complex fragment.[4] Methanol (Scheme 1, R = CH_3) is present as polymerization medium in the case of CARILON. However, due to the insolubility of the ethene/CO products and their high molecular weight, it was hardly possible to support this hypothesis by probing the existence of methyl ester chain ends.[5]

We report here on an approach to generate novel copolymer block structures by modifying the nature of the initiating alcohol. In addition to low molecular weight initiators to prove the suggested mechanism we use polymeric alcohols, such as PEG or PVA, which lead to linear PCO-*b*-PEG chains (Scheme 1, olefin = C_3H_6, R = PEG) or to branched $(PCO)_n$-*b*-PVA copolymers (R = PVA).

Results and Discussion. Our previous investigations were focused on the first high molecular weight (2×10^5), soluble propene/CO copolymers by optimizing the ratio of Pd(II) species to methanol.[6] However, also here the covalent linkage of the alcohol moiety to the PCO chain by an ester group (cf. Scheme. 1) was hard to prove. We now changed the activating agent from methanol to ethylene glycol monomethyl ether (Me-EG) and reduced the polymerization time to 24 h. This resulted in a PCO material having $M_w = 1.4 \times 10^5$ (entry 1).[7] A further reduction to 20 min, however, gave a product of $M_w = 4.4 \times 10^3$ (entry 2),[8,9] providing a suitable material for MALDI−TOF characterization (Figure 1).

Every peak (Figure 1A) can be analyzed according to the equation $M_{peak} = M^{ester} + nM^{repeat\ unit} + M^{keto} + M^{Na}$ (Figure 1B) and gives, after subtraction of one sodium atom (23) and *n* repeat units (70.091), the mass of one ester (M^{ester}: 103) and one keto (M^{keto}: 43)[10] end group per polymer chain. This demonstrates clearly that the Me-EG initiator is incorporated into each chain by a covalent ester linkage.[11,12]

Further support for this observation comes from NMR spectroscopy of the same sample. The resulting ^1H NMR spectra show signals of the glycol end group (Figure 1B: CH_3(1), 3.4; CH_2(2), 3.6; CH_2(3), 4.2 ppm) with the expected shift of CH_2(3) to lower field relative to free Me-EG (CH_2(3), 3.8 ppm). In addition, the peak for the ester carbonyl group (172.2 ppm) appears nicely separated from the CO signals of the PCO (212−215 ppm) in the ^{13}C NMR experiment.

This concept of incorporated alcohols enabled us to prepare novel PCO block copolymers by using polymeric initiators containing hydroxyl end and side groups (Table 1, entries 3−6: PEG, poly(ethylene glycol), M = 1000; PVA, poly(vinyl alcohol), $M_W = (9-10) \times 10^3$; 80% hydrolyzed). The formation of block copolymers instead of physical mixtures was demonstrated by preparative GPC experiments performed on the PCO−PEG sample.

Excess PEG (Figure 2D) could be separated from the main fraction, which was further separated into three parts (A, B, C). A NMR investigation proved PEG to be present in A, B, and C, identified by the typical signals of the PEG−CH_2 groups. The novel block copolymers gave homogeneous films (nonphase separation) due to the different relative block lengths (PCO, $M_W = 1.4 \times 10^5$; PEG, 1000), as indicated by TEM experiments. In comparison, physical mixtures of equivalent PCO and PEG chains of similar ratio separated spontaneously into two phases (cf. Supporting Information).

Application of the CH_2Cl_2-insoluble PVA initiator resulted in a soluble branched block copolymer product (Table 1, entries 4 and 5). The ratio of propene/CO to vinyl alcohol (VA) units is controllable by the polymerization time and is reflected by an investigation of the thermal properties of the reaction products. The high T_m of unmodified PVA (T_m > 300 °C; T_g = 41 °C) is reduced to 111 °C (T_g = 31 °C) at a ratio of VA/(propene/CO) = 1/19 (entry 4). A further increase to 1/37 leads to a material (entry 5: T_m = 76.9 °C; T_g = 23.4 °C) giving data similar to those of pure PCO ($T_m \cong 80$ °C; $T_g \cong 23$ °C).

Experimental Section. The Pd(II) complex, $[(dppp)Pd^{II}(CN-CH_3)_2](BF_4)_2$,[13] was synthesized according to literature known procedures. CH_2Cl_2 and ethylene glycol monomethyl ether from Fluka were dried over CaH_2. Poly(ethylene glycol) from Fluka was dissolved in dry toluene and the solvent of this solution was continuously dried over molecular sieve via a Soxhlet extractor. The polyalcohols from Aldrich were kept for 24 h at 60 °C under vacuum.

A mixture containing the Pd(II) complex (0.040 g, 0.051 mmol) and the initiator in CH_2Cl_2 (120 mL) was placed in a 300 mL mechanically stirred steel autoclave which was then charged for 0.5 h with propene at its equilibrium pressure and with carbon monoxide (60−80 bar). The reaction mixture was stirred at room temperature for the desired reaction time. At the end of this period, the remaining carbon monoxide and propene monomers were vented off and the reaction was quenched by addition of excess water. The solvents were evaporated and the resulting product was purified by chromatography over silica or Sephadex LH 20-100.

Methods. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX 500 or AC 200 spectrometer. Molecular weights and molecular weight distributions

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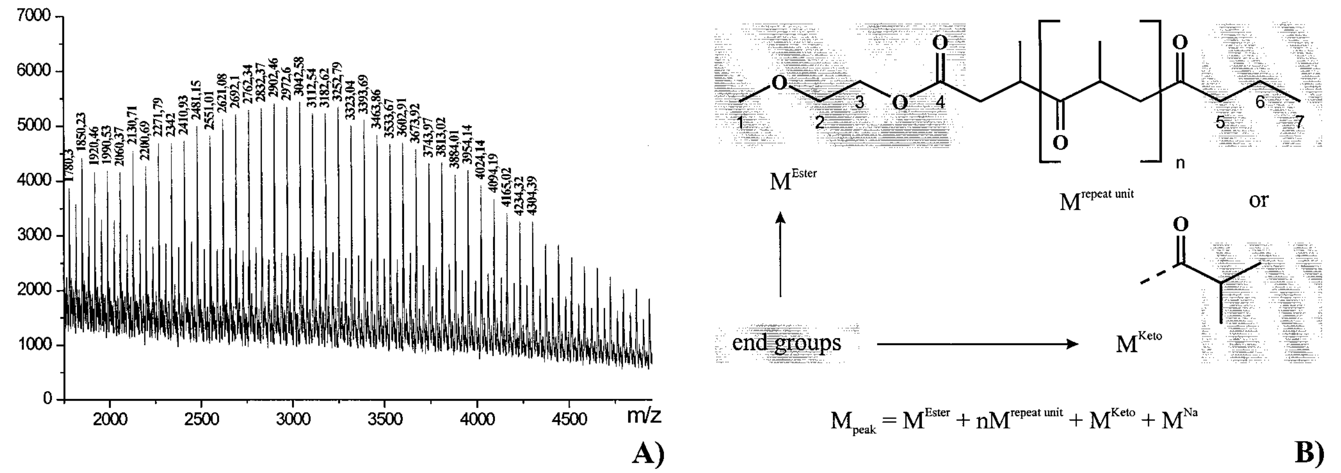

Figure 1. MALDI–TOF spectrum (A); end group characterization (B).

Scheme 1. Initiation Reaction by Alcohols

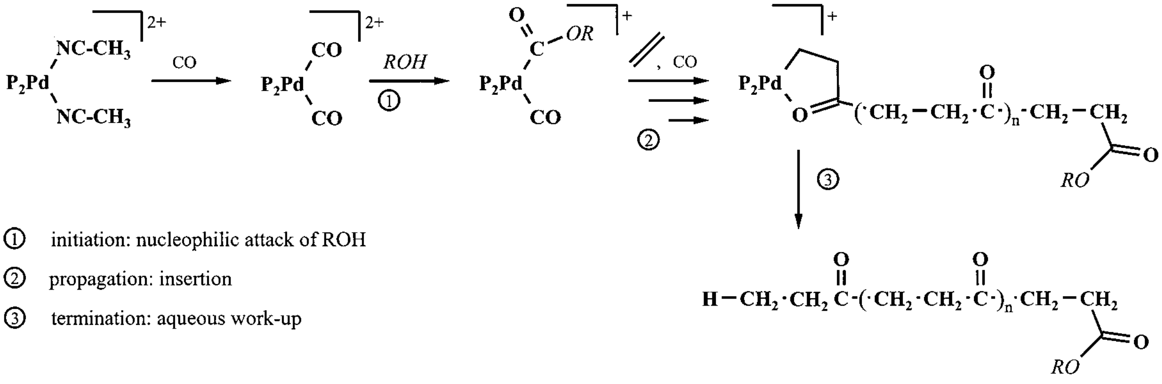

Table 1. Overview of the Initiators Used for Polymerization Reactions[a]

no.	initiator	initiator quantity	ratio initiator/catalyst	yield (g)	T_m (°C)	T_g (°C)	M_n/M_w $\times 10^{-3}$ [b]
1	CH_3–O–CH_2–CH_2–OH	0.53 mL	120	5.6	≅ 80	≅ 24	86/137
2[c]	CH_3–O–CH_2–CH_2–OH	40 mL	1250	1.0	≅ 80	≅ 24	3.8/4.4
3	poly(ethylene glycol) 1000	3.0 g	120	6.2	77.0	19.1	81/145
4	PVA 80% hydrolyzed, M_w 9000–10000	0.34 g	120	1.3	111.3	30.8	12/15[d]
5	PVA 80% hydrolyzed, M_w 9000–10000	0.34 g	120	2.6	76.9	23.4	17/25[d,e]

[a] Reaction conditions: 24 h; 40 mg of catalyst; 120 mL of dry dichloromethane; 60–80 bar CO, ca. 40 g of propene; at room temperature. [b] Molecular weight measured by GPC, in $CHCl_3$, relative to polystyrene. [c] 20 min, 240 mg of catalyst, 100 mL of dry dichloromethane.[d] In hexafluoro-2-propanol (HFIP), relative to polymethylmetacrylate.[13] [e] Reaction time extended to 48 h.

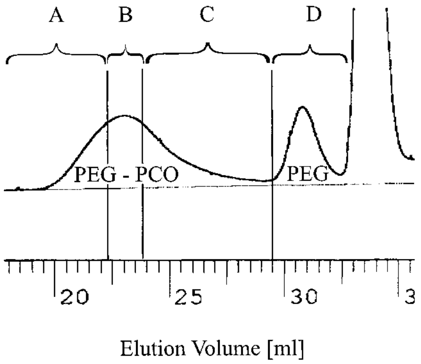

Figure 2. Fractionation of PEG–PCO by preparative GPC.

were measured by gel permeation chromatography (GPC) in dichloromethane relative to polystyrene standards or in hexafluoro-2-propanol relative to poly(methyl methacrylate) standards.[14] Preparative GPC experiments were performed in dichloromethane relative to polystyrene standards. TEM pictures were taken with a Philips CM-20 Super-Twin microscope (acceleration voltage, 200 kV; resolution, 0.23 nm). MALDI–TOF spectra were recorded with Bruker-Franzen REFLEX III, N2 laser (337 nm) with a DHB (2,5-dihydroxybenzoic acid) matrix.

Supporting Information Available: TEM pictures of a PEG 1000 + PCO mixture (phase separation); TEM pictures of the amorphous part of a PEG–PCO film (homogeneous block copolymer); NMR spectra of Me-EG started PCO (Table 1, entry2). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Keim, W.; Appel, R.; Storeck, A.; Krüger, C.; Goddard. R. *Angew. Chem.* **1981**, *93*, 91. (b) Fink, G.; Möhring, V. M. *Angew. Chem.* **1985**, *97*, 982.

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(3) Huhn, W.; Hollmann, F.; Hild, S.; Kriewall, T.; Rieger, B. *Macromol. Mater. Eng.* **2000**, *283*, 115.

(4) (a) Herrmann, A. W.; Cornils, B. *Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehen-*

sive Handbook in Two Volumes, VCH: Weinheim, Germany, 1996; Vol. 1, p 333. (b) An alternative initiation mechanism would include a CO insertion after formation of palladium alkoxy species, leading to the active palladium acyl compound. However, in our eyes, the mechanism outlined in Scheme 1 seems to be more likely due to the high CO excess and the low oxophilicity of Pd(II). (c) For other approaches, see the following patents: EP 0349084 B1 Shell 27.6.89; DE 19917920 A1 BASF 26.4.99.

(5) Short chains bearing keto and ester end groups resulting from chain transfer of already growing chains via methanol have been described before (Drent, E.; Budzelaar, H. M. *Chem. Rev.* **1996**, *96*, 663. Mul, W. P.; Drent, E.; Jansens, P. J.; Kramer, A. H.; Sonnemans, M. H. W. *J. Am. Chem. Soc.* **2001**, *123*, 5350).

(6) (a) Abu-Surrah, A. S.; Wursche, R.; Eckert, G. Pechold, W.; Rieger, B. *Macromolecules* **1996**, *29*, 4806. (b) Abu-Surrah, A. S.; Rieger, B. *Top. Catal.* **1999**, *7*, 165.

(7) Trials to produce a number of well-defined block-copolymer chains via transfer-to-activator remained unsuccessful. This can be attributed to the low tendency of the glycol initiators to act as chain transfer agents, due to their low acidity and increased molecular weight (relative to methanol). Therefore approximately one polymer chain was produced per Pd(II) atom (e.g., Table 1: entry 1, 52 μmol (40 mg) of Pd(II) catalyst leads to 60 μmol (5.6 g) of polymer product ($M^{\mathrm{GPC}} \approx 9 \times 10^4$); entry 2, 310 μmol (240 mg) of Pd(II) catalyst leads to 312 μmol (1.0 g) of polymer ($\mathrm{M}^{\mathrm{MALDI}} \approx 3.2 \times 10^3$)).

(8) The Me-EG/Pd(II) ratio was designed to guaranteed fast initiation. Spontaneous termination by β-hydride elimination was excluded previously (Huhn, W.; Hollmann, F.; Hild, S.; Kriewall, T.; Rieger, B. *Macromol. Mater. Eng.* **2000**, *283*, 115).

(9) This low molecular weight material could not be purified by column chromatography over silica. Pd(II) residues were separated via multiple SEC over Sephadex LH 20-100.

(10) The keto end group can occur in a linear and a branched form resulting from chain termination after 1,2- or 2,1-insertion of propene units (Figure 1B). NMR spectroscopy (^{1}H NMR, H^6, 1.6 ppm; ^{13}C, C^7, 13.8 ppm) shows the existence of the linear keto structure. The branched isomer is either not present or the characteristic peaks are superimposed by signals of the PCO chain.

(11) For example: M_{peak} (3533.7) $-$ M^{Na} (23) $-$ 48 $\times$ $M^{\text{repeat unit}}$ (48 $\times$ 70.091 = 3364.3) = ($M^{\mathrm{ester}} + M^{\mathrm{keto}} = 146.4$).

(12) The second underlying distribution results from Ag$^+$ ions, which were used for catalyst preparation.

(13) Synthesis: (dppp)PdCl$_2$ was converted to [(dppp)Pd$^{\mathrm{II}}$(CN$-$CH$_3$)$_2$](BF$_4$)$_2$ by reaction with AgBF$_4$ in acetonitrile. For characterization, see: Xu, F. Y.; Zhao, A. X.; Chien, J. C. W.; *Makromol. Chem.* **1993**, *194*, 2579

(14) The branched nature of the PCO-*b*-PVA hindered molecular weight determination by GPC using CH$_2$Cl$_2$ as eluent. Therefore GPC measurements were performed using hexafluoro-2-propanol (HFIP) as solvent.

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