properties, such as size and vesicle-formation concentration, which are very similar to common double-chain lipids; however, they show a propensity to form unilamellar aggregates, as well as a variety of different bilayered structures.

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In Situ Monitoring of a Heterogeneous Palladium-Based Polyketone Catalyst**

Wilhelmus P. Mul,* Heiko Oosterbeek,
Gerhard A. Beitel, Gert-Jan Kramer, and Eite Drent

In the early 1980s a class of very active palladium catalysts was discovered which allowed the synthesis of a perfectly alternating aliphatic polyketone ($n\,CH_2CH_2 + n\,CO \rightarrow [CH_2CH_2C(O)]_n$) in an efficient way.[1–3] These catalysts consist of a Pd^{II} center, a bidentate chelating ligand, and two weakly associated anions. The origin of the perfectly alternating nature of the copolymers has received ample attention, both in experimental[1, 3–7] and in theoretical studies.[8–10] The mechanism for copolymer chain growth involves two sequential propagation steps: migratory CO insertion into the Pd–alkyl bond of the growing polymer chain followed by migratory ethene insertion into the resulting Pd–acyl bond. There is consensus that double CO insertion does not occur for thermodynamic reasons, while double ethene insertion is kinetically hampered due to the higher affinity of Pd^{II} centers for CO over ethene. However, thus far all experimental mechanistic studies focused on copolymerization in solution, while under actual process conditions (slurry or gas-phase), the initially single-site Pd catalyst is heterogenized and resides on the surface or in the bulk of the copolymer.

While there are several analytical techniques for the in situ study of single-site catalysts in the liquid state,[11, 12] there is a lack of techniques to directly monitor catalysis at supported single-site catalysts.[13] Polarization modulation reflection absorption infrared spectroscopy (PM-RAIRS) is an adaptation of the well-known RAIRS technique for studying species adsorbed at metal surfaces with submonolayer sensitivity, allowing the detection of signals normally obscured by huge gas-phase absorptions.[14–16] We used PM-RAIRS to monitor CO/ethene copolymerization at the single-site Pd catalyst $[(dppp)Pd(CH_3)(OTf)]$ (**1**; dppp = 1,3-bis(diphenylphosphanyl)propane; OTf = OSO_2CF_3 = triflate) in the microcrystalline state (in the absence of any solvent), and focused on two aspects of the process: single insertion steps and copolymer growth.

Single insertion steps could be observed by alternately exposing the catalyst to CO and ethene atmospheres. Starting from **1**, sequential addition and removal of CO, ethene, and CO led to the stepwise formation of the six-membered

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[*] Dr. W. P. Mul, H. Oosterbeek, Dr. G. A. Beitel,[+]
Prof. Dr. G.-J. Kramer, Prof. Dr. E. Drent
Shell Research and Technology Centre, Amsterdam
P.O. Box 38000, 1030 BN Amsterdam (The Netherlands)
Fax: (+31) 20-630-2930
E-mail: pim.w.p.mul@opc.shell.com

[+] Current address:
Ferroelectric Technologies, Memory products
Infineon Technologies AG, MP ETF
Otto-Hahn-Ring 6, 81730 Munich (Germany)

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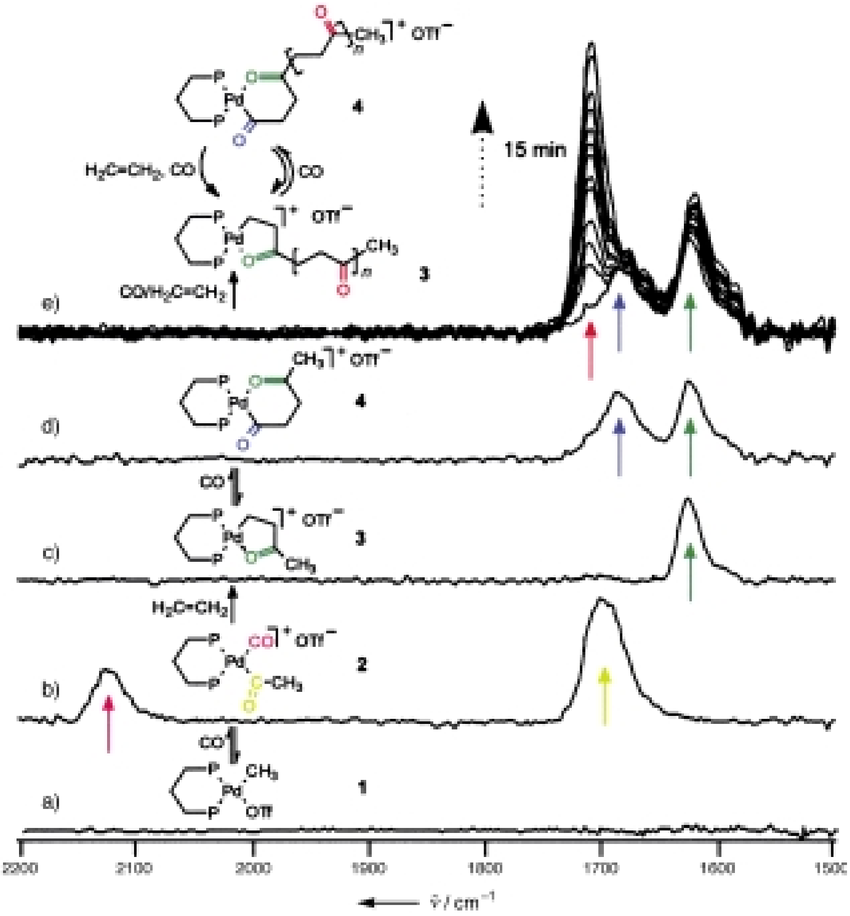


Figure 1. In situ PM-RAIR spectra of a sample of microcrystalline **1** a) at room temperature, b) under 500 mbar of CO, c) under 2 mbar of CO and 333 mbar of ethene, d) under subsequent exposure to 750 mbar CO, and e) during subsequent polymerization under 666 mbar of CO/ethene (1/1; evolution of the spectrum at 15 min intervals). For clarity the phenyl groups in dppp have been omitted.

palladacycle **4** (Figure 1 a–d). The PM-RAIR spectrum of microcrystalline **1** is featureless in the selected frequency range (Figure 1 a). Upon exposure of this species to 500 mbar of CO at room temperature, two new IR bands appear at 2125 and 1695 cm^{-1}, indicating the formation of [(dppp)Pd{C(O)CH$_3$}(CO)](OTf) (**2**, Figure 1 b). The IR band at 2125 cm^{-1} corresponds to a cationic Pd–carbonyl moiety and the one at 1695 cm^{-1} to a Pd–acyl group, formed by CO insertion into the Pd–methyl bond.[17] This reaction is reversible, just as in solution:[12, 18] After removal of CO the parent complex is reformed. Upon gradual increase of the CO pressure above complex **1**, the Pd–carbonyl band initially developed somewhat faster than the Pd–acyl band, indicating the occurrence of the intermediate [(dppp)Pd(CO)CH$_3$]$^+$ in significant amounts, in line with observations in solution.[4, 18]

After reduction of the CO pressure to 2 mbar and addition of 333 mbar of ethene the spectrum shown in Figure 1 c was recorded. The appearance of a new IR band at 1625 cm^{-1} indicates the formation of the five-membered palladacycle **3** by ethene insertion into the Pd–acyl bond and the simultaneous coordination of the (now) ketonic carbonyl group to palladium.[19] The IR spectrum exhibits no features that can be ascribed to coordination of other ligands such as CO or triflate (see below) to the square-planar 16e Pd^{II} center.

Subsequently, the palladacycle **3** was exposed to 750 mbar of CO, resulting in the appearance of an IR band at 1690 cm^{-1}, while the band at 1625 cm^{-1} remained unaltered (Figure 1 d). This indicates the formation of **4** by CO insertion into the Pd–alkyl bond of the (opened) palladacycle **3**. Complex **4** contains both an acyl group (1690 cm^{-1}) and a chelating carbonyl moiety (1625 cm^{-1}). So, the chelating ketones of **3** and **4** cannot be distinguished from each other by IR spectroscopy. This second CO insertion is also reversible: Reduction of the CO pressure to 2 mbar leads to the gradual decrease ($t_{1/2} \approx 15$ min) of the acyl signal at 1690 cm^{-1}. The ratio between **3** and **4** proved to be related to the CO partial pressure. Surprisingly, and in contrast to the situation after the first CO insertion, exposure of **4** to 333 mbar of ethene did *not* change the spectrum, although the emergence of free ketone was expected. This suggested that ethene insertion into the Pd–acyl bond of **4** does not occur under these conditions. This was confirmed in a comparable experiment in which the even more weakly coordinating BF$_4^-$ anion was used instead of triflate. In this case CO removal from **4** was much slower ($t_{1/2} \approx 120$ min). Exposure of this relatively stable palladacycle to 333 mbar of ethene for several hours also did not result in the insertion of ethene into the Pd–acyl bond. Only in the presence of a substantial amount of CO did ethene insertion occur (see below), indicating that in this microcrystalline catalyst insertion of ethene is CO-assisted.

The coordination of the triflate anion could be monitored during the first few consecutive steps. It is known that noncoordinated (weakly ion paired) and coordinated triflate ions have distinctly different IR absorptions.[20] The low-frequency region of the spectra showed that triflate originally occupies the fourth coordination site in **1** (Figure 2 a), but is

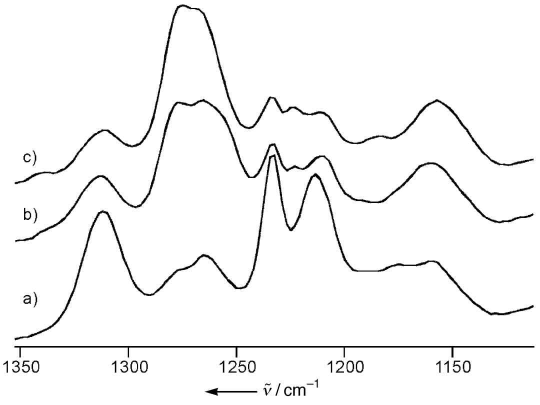
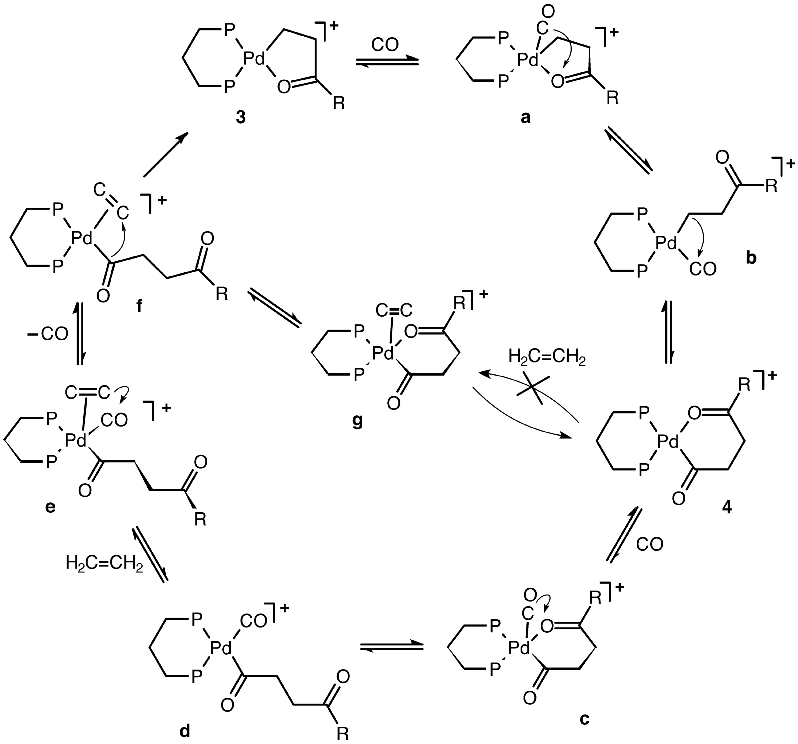


Figure 2. In situ PM-RAIR spectra of a sample of microcrystalline **1** a) at room temperature, b) under 500 mbar of CO, and c) under 2 mbar of CO and 333 mbar of ethene. Note the change from a coordinated (a) to a noncoordinated triflate anion (c).[20] Spectra a–c represent the low-frequency regions of the spectra shown in Figure 1 a–c.

"pushed aside" during the first monomer insertions until it is essentially noncoordinated in **3** (Figure 2c). The absorption signals for coordinated triflate reduced almost to zero. This implies that, at least initially, virtually all catalyst sites, also those located in the bulk of the microcrystalline solid, reacted with CO and ethene, because RAIRS detects all molecules with equal sensitivity.



Scheme 1. Proposed catalytic propagation cycle with observed (**3**, **4**) and proposed intermediates (**a**–**f**); R represents the growing polyketone chain; the phenyl groups in dppp have been omitted.

Copolymer growth could be followed in situ by exposing the Pd catalyst to a CO/ethene atmosphere (666 mbar) at room temperature, taking a mixture of **3** and **4** as a starting point. As polymerization proceeded, a signal at 1705 cm^{-1} developed (Figure 1e), which corresponds to the carbonyl groups of the growing polyketone chain. This growth process could be followed for days, during which the growth rate decreased gradually. During polymerization, the intensities of the signals for the Pd–acyl group at 1690 cm^{-1}, visible as a shoulder of the 1705 cm^{-1} peak, and for the chelating ketone(s) at 1625 cm^{-1} remained constant. This implies that the total abundance of and the ratio between **3** and **4** remained constant, and that both are resting states of the catalyst. No signal was observed in the 2100 cm^{-1} region, indicating the absence of an open-chain complex (**d** in Scheme 1), the main resting state for a Pd(phen)-based polyketone catalyst in solution (phen = 1,10-phenanthroline).[4] Labeling studies ($^{12}CO/^{13}CO$) showed that, in contrast to the initial CO and ethene insertion steps, during copolymerization only part of the catalyst sites actually contributed to polymer growth, the degree being related to sample preparation and reaction time.

The finding that during polymer growth ethene insertion into the Pd–acyl bond of **4** is CO-assisted is one of the most remarkable findings of this study. This has never been observed during studies in solution, nor evaluated theoretically.[8–10] It has been assumed that ethene will be able to readily displace the chelating ketone in **4** and insert subsequently to generate the five-membered palladacycle (**3**).[2] This has been confirmed experimentally in solution.[4] Insertion of ethene occurs by two discrete reaction steps: 1) substitution of the chelating ketone in **4** by ethene (**4**→**f**, Scheme 1) and 2) acyl migration to this ethene (**f**→**3**). The second step as such is facile in the microcrystalline state, since otherwise copolymerization would not have been achieved at all. Apparently, CO is required to enable a kinetically feasible reaction pathway for the first step. Taking into account that substitution reactions at square-planar Pd^{II} centers generally take place associatively,[5, 21] a feasible reaction pathway for the conversion of **4** into **f** can be derived. It is proposed that substitution of the chelating ketone in **4** by ethene occurs in two consecutive steps: associative substitution of the chelating ketone by CO (**4**→**c**→**d**) followed by associative substitution of this CO by ethene (**d**→**e**→**f**). Substitution of the chelating ketone by CO is more facile than by ethene as it is thermodynamically less hindered and because an incoming CO ligand can approach the crowded catalytic Pd center in an end-on fashion (**4**→**c**), while an incoming ethene ligand has to approach the catalyst in a sterically more demanding side-on way (**4**→**g**). Although substitution of CO by ethene is thermodynamically unfavorable,[4, 8, 10] the CO-coordinated Pd center in **d** is sterically less crowded than in the six-membered palladacycle **4**, thus facilitating the side-on approach of ethene required for (associative) CO displacement. In this way, a lower energy pathway becomes available for the formation of the ethene complex **f**, in which ethene can insert rapidly (**f**→**3**). Brookhart et al. showed that in solution opening of the six-membered palladacycle in $[(phen)Pd\{C(O)CH_2CH_2C(O)CH_3\}]^+$ by ethene and its subsequent insertion into the Pd–acyl bond are facile processes.[4] This might be related to the different type of ligand used—a phenantroline ligand is flat, leaving more space for ethene to approach the Pd center from an apical position—or to the presence of a solvent.

In conclusion, a dedicated spectroscopic technique (PM-RAIRS) has enabled us to directly monitor CO/ethene copolymerization at a microcrystalline palladium catalyst and to elucidate some intriguing molecular aspects of this process.

Experimental Section

The PM-RAIRS experiments were performed in a home-built cell which allows studies under gas pressures up to 1 bar.[16] Gold-coated silicon wafers (Topsil) were used as reflecting substrate. A sample of the catalyst $[(dppp)Pd(CH_3)(OTf)]$ (**1**) was prepared by placing a droplet of $[(dppp)Pd(CH_3)(CH_3CN)](OTf)$[7] in dichloromethane onto the gold-coated wafer. After drying, PM-RAIRS showed that the acetonitrile was evaporated (Figure 2a). Atomic force microscopy (AFM) measurements showed that the majority of the sample consisted of a regular island structure of microcrystals, with an average size of about 10 nm, each containing approximately 2.5×10^3 catalyst molecules. From the island density of about 4×10^{10} islands per cm^2, a coverage of 10^{14} molecules per cm^2 was estimated; this was supported by X-ray photoelectron spectroscopy (XPS) results (10^{14} Pd atoms per cm^2). The microcrystal size implies that roughly 35% of the catalyst molecules were located at the surface of the crystals.

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Induction of Lamellar Mesomorphic Structures in Columnar-Phase-Forming 1,3,5-Triazines through Charge-Transfer Interactions with Electron Acceptors**

Daniela Goldmann, Dietmar Janietz,*
Claudia Schmidt, and Joachim H. Wendorff

The molecular organization in thermotropic liquid-crystalline phases is predominantly associated with a rigid anisometric architecture of the constituent single molecules. Molecular self-organization may, however, also be effected by strong intermolecular forces between nonmesogenic molecules to give noncovalently bonded anisometric aggregates. The two principles can be combined by incorporating an intramolecular functionality into molecules with an anisometric shape.[1] This combination allows the control and manipulation of the structure formed by mesogens through directed intermolecular interactions with a second complementary component. Specific manipulations of columnar mesomorphic structures, for example, may arise from formation of donor–acceptor complexes[2] or from intermolecular hydrogen bonding[3] between two different individual molecules.

"Open-sided" core systems that have the capacity to form columnar phases of single components and also allow the docking of a second component to a molecular recognition site located in the inner core region (side-by-side interactions) are conceivable. Structure formation should then be possible for the same molecule through associations with electron-deficient counterparts through charge-transfer (CT) interactions perpendicular to the molecular periphery (face-to-face interactions) provided that the central part of the molecule coincidentally represents an electron donor (Figure 1). To realize this concept we have synthesized 2,4,6-triarylamino-1,3,5-triazines with long peripheral alkoxy groups and with an electron-rich polar group in the center.[7] The triazines substituted with six lipophilic side chains exhibit columnar mesophases in their pure state.[8] Furthermore, hydrogen bonding with complementary alkoxy-substituted benzoic acids gives rise to the control of the two-dimensional lattice symmetries[1, 9] and even induction of a hexagonal columnar mesophase.[10]

We report here mesomorphic assemblies of the hexagonal columnar (Col_{hd}) phase from sixfold alkoxy-substituted 2,4,6-triarylamino-1,3,5-triazines **1a**, **b**,[8] which act as electron

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[*] Priv.-Doz. Dr. D. Janietz, Dr. D. Goldmann
Fachbereich Chemie und Institut für Dünnschichttechnologie und Mikrosensorik
Universität Potsdam
Kantstrasse 55, 14513 Teltow (Germany)
Fax: (+49) 3328-46510
E-mail: janietz@rz.uni-potsdam.de

Dr. C. Schmidt, Prof. Dr. J. H. Wendorff
Institut für Physikalische Chemie und Wissenschaftliches Zentrum für Materialwissenschaften der Philipps-Universität Marburg (Germany)

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