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Highly active, recyclable catalyst for the manufacture of viscous, low molecular weight, CO-ethene-propene-based polyketone, base component for a new class of resins

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This paper is dedicated to Professor Kees Vrieze for our fruitful collaboration and his outstanding contributions to science

Abstract

A highly active, recyclable homogeneous palladium(II) catalyst is described for the manufacture of viscous, low molecular weight CO–ethene–propene-based polyketone (*Carilite Oligomer*), used for the manufacture of a new class of resins (*Carilite Resins*). The catalyst is composed of palladium acetate, and a sulfonated diphosphine ligand, bdompp-S (1,3-bis(di-(2-methoxy, 5-sulfona-tophenyl)phosphino)propane). In comparison with its non-sulfonated counterpart this catalyst not only exhibits a much more favourable partitioning coefficient in liquid–liquid separation of the polyketone product and solvent, but it also exhibits an approximately 2.5 times higher catalytic activity (up to 11.2 kg PK (g Pd)⁻¹ h⁻¹) in the manufacture of PK-PE-30 (polyketone terpolymer built up of CO, ethene and propene in a molar ratio of 100:30:70). A variety of salts were found to exert a positive influence on the activity of the catalyst. Possible origins of this 'salt-effect' are briefly discussed. The bdompp-S ligand was synthesised by sulfonation of bdompp using either a boric acid–oleum mixture or sulfuric acid as the sulfonation reagent. The product was isolated either as sodium-salt (bdompp-S[Na]₄·nNa₂SO₄), by extraction with methanol after neutralisation, or, in acidic, hydrated form (bdompp-S[H]₄·nH₂O), via a new and highly efficient procedure, i.e. cooling the reaction mixture after dilution with water. The X-ray crystal structure of bdompp-S[H]₄·nH₂O is discussed. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Carilite Resins is a new class of polyketone-based resins which are produced by alternating co- and terpolymerisation of carbon monoxide, ethene and propene, followed by chemical cross-linking (curing) [1,2]. Depending on the ratio between propene and ethene incorporated in the polymer backbone, the product consistency of the low molecular weight polyketone intermediate ($M_n \approx 1500-5000$), referred to as Carilite Oligomer, ranges from viscous flowing at room temperature for the ethene-free types, to waxy or melting solids at an ethene content of about 80 wt% (on total olefin content). These intermediates are closely related to Carilon Polymer, a family of semi-crystalline thermoplastics [3].

Owing to the presence of the ketone functions, the oligomer can be derivatized in various ways. Among these, the Paal-Knorr reaction has been developed as the basic curing chemistry. In this reaction two adjacent ketone moieties and a primary amino group are converted into a water-resistant pyrrole unit with the liberation of water (Scheme 1). Carilite Oligomer can be cured using a variety of di- or multi-functional amino-

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Scheme 1. Carilite curing chemistry.

based curing agents [2]. Further, a method has been developed in which Carilite is first converted into a poly-amino-pyrrole by reaction with a non-symmetrical di-amine at low temperature, followed by curing with another equivalent of Carilite at high temperature [2c]. The use of these stable, water-based poly-amino-pyrrole emulsions as intermediates prevents emission of volatile ingredients during curing. The Carilite–polyamine thermoset system can be used in various applications like foams, coatings, castings and adhesives. However, the use as glue for the manufacture of various wood composites is currently seen as the most promising outlet.

Like Carilon Polymer, CO-propene and COethene-propene-based Carilite Oligomer is manufactured in an organic solvent using a homogeneous palladium-based catalyst at a reaction temperature of 70-100 °C and pressures of typically up to 8.5 MPa (Scheme 2). The catalyst selected for the manufacture of Carilon Polymer at commercial scale is Pd- $(bdompp)X_2$ (bdompp = 1,3-bis(di-(o-methoxyphenyl)phosphino)propane, X = weakly or non-coordinating anion, e.g. triflate (OTf), tosylate (OTs), methylsulfonate (OMs), trifluoroacetate (TFA)). This catalyst is not only more active than the most prominent member of the first generation of CO-ethene copolymerization catalysts. $Pd(dppp)X_2$ (dppp = 1,3-(diphenylphosphino)propane), but also produces co- and terpolymers with a considerably higher molecular weight [3e,4].



This offers the advantage of producing PK-EP-6 with $M_{\rm n} = 52\,000$, one of the main commercial polyketone





grades, at a much higher rate than with $Pd(dppp)X_2$ [3e].^{2,3}

Initially, the catalyst applied in the production of Carilon Polymer, $Pd(bdompp)X_2$, was tested for the manufacture of Carilite Oligomer. However, modest performance of this catalyst, both in terms of activity and recyclability, prompted us to search for an alternative catalyst system that would substantially lower the contribution of the catalyst costs to the total manufacturing costs of the Carilite product. The use of a sulfonated, water-soluble diphosphine ligand was anticipated to lead to improved catalyst recycle efficiency [5]. In this paper, the synthesis and work-up of bdompp-S, the tetra-sulfonated analogue of bdompp, are described, as well as the performance (activity, recyclability) of the palladium-based catalysts derived for the manufacture of Carilite Oligomer.⁴ Recently, the manufacture of this catalyst and its excellent performance in the copolymerisation of CO and ethene in water (with rates up to 32 kg PK (g Pd)⁻¹ h⁻¹) was reported by Sheldon and coworkers [5d].

2. Experimental

2.1. General

All reactions were carried out under an inert atmosphere (nitrogen), unless stated otherwise, using standard Schlenk techniques. Sulfuric acid (95-97%) was purchased from Merck, boric acid from Aldrich and 27-33% sulfur trioxide solution in sulfuric acid from Fluka. The solvents used were p.a. All chemicals were

² Applied notation for perfectly alternating CO– α -olefin polyketones: PK-M₁M₂-*n*, in which M₁ and M₂ are abbreviations for the types of α -olefins incorporated in the co- or terpolymer chain (e.g. M = ethene (E), propene (P)), and *n*, the molar monomer index (*n* = (100·[M₂]/([M₁] + [M₂])), the percentage of M₂ (in mol%) on the total amount of α -olefin incorporated in the polymer backbone. For example, PK-E represents a copolymer build up of CO and ethene while PK-EP-6 represents a terpolymer build up of CO, ethene and propene in a molar ratio of 100:94:6.

³ The value for $M_{\rm n}$ was determined by GPC, and is given relative to the PMMA standards.

⁴ Most results described in this paper have been published in patent. See Ref. [1c].

used without further purification. 1,3-Bis(di-(*o*-methoxyphenyl)phosphino)no-propane (bdompp) was synthesised according to literature procedures [6,7].

The ¹H, ¹³C{¹H}, ¹⁹F and ³¹P{¹H} NMR spectra were measured at room temperature (r.t.) in Varian 300 and 400 MHz spectrometers, operating at 300.1 and 400.0 MHz for ¹H, at 75.5 and 100.6 MHz for ¹³C, and at 121.5 and 161.9 MHz, respectively, for ³¹P measurements. Deuterated solvents were used as internal reference, and the ³¹P data are given in δ units relative to triphenylphosphine (-6 ppm). Elemental analysis was performed at the Analytische Laboratorien, Lindar (Germany). The sulfate concentration in the sulfonated diphosphine products was determined with ion chromatography against a standard sulfate solution. ICconditions: DX100 (DIONEX), measured area (analogous) 0–1000 µS; column: AG9 (guard column) and AS4SC (separation column); eluent: 1.5 mM $HCO_3^{-}-1.2$ mM CO_3^{2-} demi-water. Detection was achieved conductometrically.

The CO-ethene-propene terpolymerisation reactions were carried out in a 350 ml, magnetically stirred AISI 316 steel batch autoclave.

2.2. Synthesis of bdompp-S[Na]₄

Orthoboric acid (3.2 g, 51.7 mmol) was dissolved in 30 ml of concentrated sulfuric acid (95-97%) and stirred until a homogeneous solution was obtained. After all boric acid had dissolved, 7.3 g (13.7 mmol) of bdompp was added in small portions. The reaction mixture was cooled to 0 °C and a solution of 30% oleum (150 ml) was added drop wise, while the temperature of the mixture was maintained between 0 and 5 °C.⁵ After the addition was complete, stirring was continued at ambient temperature for 48 h. The mixture was then hydrolysed by pouring it out on ice (400 g), neutralised by the addition of a 25 wt% solution of sodium hydroxide in water, and concentrated by the evaporation of water at 75 °C under vacuum until a white suspension was formed. Methanol (750 ml) was then added to the mixture, which was stirred for 15 min. The precipitate (Na₂SO₄) was removed by filtration. The product isolated after removal of the solvent under vacuum still contained a significant amount of Na₂SO₄. Therefore, a second extraction with methanol was carried out. After filtration and removal of the solvent under vacuum, a white product was obtained in a yield of 12.6 g. Elemental analysis indicated the product to consist of a mixture of bdompp-S[Na]₄ and hydrated Na₂SO₄. Based on this elemental analysis the

active matter content was calculated to be $36 \pm 4\%$ and the actual yield about 35%.

2.2.1. Spectroscopic data for bdompp-S[Na]₄

¹H NMR (D₂O): δ 7.71 (d, J = 12.9 Hz, 4H, H_{Ar}), 7.55 (d, J = 8.7 Hz, 4H, H_{Ar}), 6.9 (m, 4H, H_{Ar}), 3.63 (s, 12H, *OCH*₃), 2.20 (m, 4H, *CH*₂P), 1.44 (m, 2H, *CH*₂CH₂P); ³¹P NMR (D₂O): δ – 34.4 (s); ¹³C NMR (D₂O): δ 163.2 (d, $J_{CP} = 12.0$ Hz, C5), 135.6 (s, C2), 129.9 (d, $J_{CP} = 32.1$ Hz, C3 or C6), (d, $J_{CP} = 29.2$ Hz, C3 or C6), 124.4 (C4), 111.3 (d, $J_{CP} = 51.2$ Hz, C1), 56.0 (d, $J_{CP} = 54.4$ Hz, *OCH*₃), 25.5 (br, *CH*₂P), 21.5 (br, *CH*₂CH₂P). *Anal.* Found: C, 12.89; H, 2.81; P, 2.81; S, 15.42; Na, 17.92. Calc. for bdompp-S[Na]₄·7.6 Na₂SO₄·27 H₂O: C, 13.25; H, 2.94; P, 2.54; S, 15.18; Na, 18.06%.



2.3. Preparation of a bdompp-S[Na]₄-based catalyst

Palladium acetate (5.0 mg, 22 μ mol) and bdompp-S[Na]₄·7.6Na₂SO₄·27H₂O (65.9 mg, 25.2 μ mol) were dissolved in acetone (5 ml) at r.t., and then water (5 ml) was added. After 1 h, trifluoroacetic acid (10.1 mg, 88 μ mol) was added and a clear yellow solution was obtained, which was used as such to catalyse the copolymerization reaction described below.

2.4. Polymerization reaction using bdompp-S[Na]₄-based catalyst

The reactor was charged with 129 ml of a MeOH- $H_2O-HOAc-MeOAc$ mixture (45.4:29.5:5.3:19.6 v/v). After purging the reactor with nitrogen, it was charged with 60 g of propene and thereafter it was pressurised with 7 bar (0.7 MPa) of hydrogen gas and 1 bar (0.1 MPa) of carbon monoxide. The reactor was subsequently heated to 89 °C and charged further with 30 bar (3.0 MPa) of a 80:20 v/v CO-ethene mixture gas to give a total pressure of about 70 bar (6.9 MPa). After stabilization of temperature and pressure, all the bdompp-S[Na]₄-based catalyst made according to the procedure described above, was injected into the reactor to start the reaction. The catalyst injection system was flushed with 10 ml of acetone to ensure quantitative catalyst injection. The reactor temperature increased to 91 °C. The pressure was kept constant by the continuous addition of 80:20 v/v CO-ethene mixture gas. After 3 h the reaction was stopped. The flow

⁵ Reaction performed in accordance with the procedure(s) described in: EP 632 047 (to Hoechst, 1994), EP 704 450 (to Hoechst, 1996).

of mixture gas was stopped by blocking the gas supply and the reactor was cooled rapidly down to r.t., and then the remaining gases were vented until atmospheric pressure was obtained. The reaction mixture was collected and the solvent mixture was removed under reduced pressure at 70 °C. The isolated polymer was weighed and analysed for molecular weight (GPC) and ethene content (¹³C NMR). Reaction rate data were calculated on the basis of gas flow uptake and on the basis of average product weight and are summarised in Table 3.

2.5. Polymerization reaction using a bdompp-based catalyst

A catalyst was prepared by dissolving 5.0 mg (22 μ mol) of palladium acetate and 12.5 mg (0.23 μ mol) of bdompp in 10 ml of acetone. After 1 h, 10.1 mg (88 μ mol) of trifluoroacetic acid was added. The resulting clear yellow liquid was used to start an oligomerisation reaction according to the procedure described above, using this catalyst in place of the bdompp-S[Na]₄-based catalyst. Polymerisation rate and product data are given in Table 3.

2.6. Recycling experiments with catalyst bdompp-S[Na]₄

First, a polymerization reaction was carried out as described above for the bdompp-S[Na]₄-based catalyst. After 3 h the reaction was stopped by the steps taken in the following order: first, the flow of the mixture gas was stopped by blocking the gas supply; then the reactor was cooled down to r.t. and vented until atmospheric pressure was obtained. The reactor content was subsequently transferred to a separation funnel. After approximately 1 h the two phases were separated and weighed. The top layer was used to charge the reactor, the bottom layer was washed with the equilibrium MeOH-H₂O-HOAc-MeOAc solvent mixture (45.5:29.5:5.3:19.6 v/v), with a volume of V(wash) =V(reactor solvent) (129 ml) – V(top layer). This mixture of the bottom layer and the wash-solvent were allowed to settle and were separated after approximately 1 h. A second top layer and a bottom layer were formed. Both layers were weighed. The reactor was charged with both top layers. If necessary, the volume was brought to the initial solvent volume of 129 ml. The new bottom layer containing the polyketone product was transferred to a rotavapor. The solvents were removed at a reduced pressure of 1 mbar (0.1 kPa) at 70 °C and the isolated polymer was analysed for molecular weight and ethene content. The solvent mixture in the reactor was used to perform the same experiment again. However, this time no catalyst was injected. Two recycles were carried out by this method. The results of this experiment are labelled as Experiment A in Table 5.

A variant of this procedure involves injecting additional fresh catalyst into the system compensating for the loss of active catalyst during the recycle experiments. Again two recycles were performed by this method, 34 wt% of the fresh catalyst being added at the start of each recycle. The results are labelled as Experiment B in Table 5.

2.7. Synthesis of bdompp-S[H]₄

The bdompp (22.5 g, 42.3 mmol) was added in small portions to 110 ml of sulfuric acid and stirred for 24 h at r.t. The reaction mixture was then poured in 500 ml of water and after storage at 4 °C for 24 h, a white precipitate was formed. After filtration, the white solid was washed twice with 250 ml of methyl ethyl ketone. After drying for 3 h at 80 °C under vacuum, 33.6 g of bdompp-S[H]₄·8H₂O (90.0%) was obtained. No decomposition was shown by bdompp-S[H]₄·*n*H₂O (e.g. oxidation) when stored at ambient conditions for extended periods (>1 year). The solubility of bdompp-S[H]₄·*n*H₂O in water amounts to 280 g1⁻¹ (20 °C) and in methanol to 810 g1⁻¹ (20 °C).

2.7.1. Spectroscopic data for bdompp-S[H]₄

¹H-NMR (D₂O): δ 7.86 (dd, J = 8.8 Hz, J = 2.0 Hz, 4H, H₄), 7.74(dd, $J_{PH} = 14.8$ Hz, J = 2.0 Hz, 4H, H₆), 6.98 (dd, $J_{PH} = 5.5$ Hz, J = 8.8 Hz, 4H, H₃), 3.58 (s, 12H, OCH_3), 2.91 (m, 4H, CH_2P), 1.72 (m, 2H, CH_2CH_2P); ³¹P-NMR (D₂O): δ -5.6; ¹³C-NMR (D₂O): δ 163.5 (s, C2), 135.6 (d, $J_{CP} = 12.6$ Hz, C5), 134.9 (C4), 131.8 (C6), 112.9 (d, $J_{CP} = 61.2$ Hz, C3), 104.9 (d, $J_{CP} = 140$ Hz, C1), 56.8 (d, $J_{CP} = 59.6$ Hz, OCH_3), 19.0 (br, CH_2-P), 17.8 (br, CH_2CH_2P). Anal. Found: C, 37.29; H, 5.21; P, 6.01; S, 12.67. Calc. for bdompp-S[H]₄·8H₂O: C, 37.35; H, 4.98; P, 6.21; S, 12.87%; H₂SO₄-content (IC): 0.17 wt%.



2.8. Preparation of a bdompp- $S[H]_4$ -based catalyst

Palladium acetate (5.0 mg, 22 μ mol) and bdompp-S[H]₄.4H₂O (21.8 mg, 23.6 μ mol) were dissolved in acetone (5 ml) at r.t., and then water (5 ml) was added. After 1 h, trifluoroacetic acid (10.1 mg, 88 μ mol) was added and a clear yellow solution was obtained, which

Table 1

Crystal data and structure refinement parameters for bdompp- $S[H]_4{}^\prime n H_2O$

Empirical formula	$C_{31}H_{53}O_{26.5}P_2S_4$
Formula weight	1039.91
Crystal system	tetragonal
Space group (no.)	$I4_{(1)/acd}$ (no. 142)
Unit cell dimensions	
a (Å)	28.010(4)
<i>c</i> (Å)	24.021(5)
$V(Å^3)$	18846(5)
Ζ	16
Absorption coefficient (mm ⁻¹)	0.356
Reflections collected	38481
Independent reflections	$3087 [R_{int} = 0.1089]$
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.1339,$
	$wR_2 = 0.3723$
Goodness-of-fit on F^2 , S	1.498
Largest difference peak and hole (e \AA^{-3})	0.533 and -0.483

was used to catalyse the polymerization reaction described below. In addition, catalyst solutions were prepared to which 4.02, 6.12 or 8.00 mol NaOH per mole bdompp-S[H]₄ was added to neutralise the remained sulfonic acids groups of the ligand. In one case sodium sulfate (a constituent of the applied batch of bdomp-S[Na]₄) was added as well (see Table 4).

2.9. Polymerization reaction using bdompp- $S[H]_4$ -based catalyst

The polymerization reaction was carried out as described above for the bdompp-S[Na]₄-based catalyst, employing a hydrogen gas partial pressure of 4 bar instead of 7 bar. The results are summarised in Table 4.

2.10. Determination of partitioning coefficients

First, a sample of 129 g of Carilite Oligomer (PK-PE-30, $M_n = 2470$), synthesised with a (bdompp-S[Na]₄based catalyst was purified (for residual Pd) by mixing it with the solvent mixture consisting of 100 ml of methanol and 70 ml of methyl ethyl ketone to which a few drops of acetic acid were added and stirred overnight at 60 °C. After cooling the solution to r.t. 150 ml of water was added and the resulting two phases were separated. This procedure was repeated twice and the remaining solvent was removed under vacuum affording a sample of Carilite Oligomer ($M_n = 2560$) containing 2 ppm of palladium (ICP-MS). This sample was used to determine the partitioning coefficients for Pd-(bdompp)(TFA)₂ and Pd(bdompp-S[Na]₄)(TFA)₂.

The partitioning coefficients were determined by mixing Carilite Oligomer (± 5 g) with an exactly equal amount of the solvent mixture applied to the polymerizations described above, MeOH-H₂O-HOAcMeOAc mixture (45.4:29.5:5.3:19.6, v/v). This mixture was warmed in a centrifugation tube to 50 °C with vigorous stirring. Subsequently, one of the selected palladium catalysts was added in such an amount that $[Pd]_{mixture} = 500$ ppm and stirring at 50 °C was continued for 1.5 h. The solution was cooled to ambient temperature resulting in phase separation. Subsequently, the mixture was centrifuged for 30 min at 3000 rpm, resulting in the formation of two well-separated layers. These layers were separated, weighed, and [Pd] was determined by ICP-MS for both the top (solventrich) and bottom (Carilite-rich) layers. The results are given in Table 6.

2.11. Structure analysis of bdompp-S[H]₄·nH₂O

Crystal data and other details of the structure analysis are presented in Table 1. A colourless crystal of rod-like habit bdompp-S[H]₄·nH₂O of dimensions $0.13 \times 0.13 \times 0.50$ mm was mounted at the end of a glass fibre and held in place with silicone grease. All diffraction measurements were made at -100 °C in a Siemens SMART CCD area detector diffractometer, using graphite monochromated Mo Ka X-radiation $(\lambda = 0.71073 \text{ Å})$. Diffracted intensities were measured in a hemisphere of reciprocal space for $2\theta < 45^{\circ}$ by 0.3° width ω frames, a total of 1371 frames being measured. No decay over the period of data collection was observed. All data with $I > -3\sigma(I)$ were retained for use in structure refinement. An absorption and detector correction was applied on the basis of 2787 symmetry equivalent reflection intensities; effective transmission coefficients were in the 1.00-0.691 range.

Refinement of the zwitterion indicated significant disorder, notably manifested as large and highly anisotropic displacement parameters for the heavy atoms (e.g. S(1) and S(2)). The other space groups investigated did not give improved refinements. The water structure is not well defined and the water oxygens in the refined model have an occupancy sum equating to 10.5 molecules of water per molecule of zwitterion. The true occupancy of water in the crystal is probably lower than 10.5 since some of the oxygen sites are unrealistically close to one another (see below) and all show large displacement parameters. This is in accord with the other analytical data (which indicates an $8:1 \text{ H}_2\text{O}$ bdompp-S[H₄] ratio). Attempts to refine a model with lower occupancy oxygen positions led to significantly worse residuals and so the model presented was retained. Full occupancy oxygens are O(9, 10, 11, 13), while O(12) has occupancy 0.25 and O(14) and O(15) have occupancies of 0.5. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints (except where required by crystallographic symmetry). All hydrogen atoms were constrained to idealised geometries and



Scheme 3. Sulfonation of bdompp.

assigned fixed isotropic displacement parameter. Fullmatrix least-squares refinement of this model against F^2 converged to final residual indices⁶ given in Table 1. Final difference electron density maps showed no features of chemical significance. Selected bond lengths and bond angles are given in Table 2. Listings of the final atomic positional parameters for the non-hydrogen atoms, the derived bond lengths and inter-bond angles, and the anisotropic displacement parameters and hydrogen atomic parameters, respectively, have been deposited as a CIF file. All calculations were carried out using programs of the SHELXTL package [8]. Complex neutral-atom scattering factors were taken from Ref. [9].

3. Results and discussion

3.1. Synthesis, isolation and characterization of sulfonated bdompp

Bdompp was sulfonated using either a boric acidoleum mixture (Herrmann's method [10]) or sulfuric acid⁷ as the sulfonation reagent (Scheme 3). Complete and selective conversion of bdompp into the tetra-sulfonated product (bdompp-S) took place, depending on the reagent applied, within 4-24 h.⁸ Although the reaction is highly exothermic and temperature excursions of up to 60 °C were encountered, formation of phosphine oxides or other side products was not observed, even not when the reaction was performed under air, instead of under nitrogen. The applicability of sulfuric acid as a sulfonation reagent for *o*-methoxy substituted arylphosphines will stem from the electronic properties of the *o*-methoxy group. In electrophilic aromatic substitution reactions, the methoxy-group is a moderately activating, *ortho-para*-directing group.

Isolation of bdompp-S was achieved via two different procedures. After hydrolysis and neutralisation of the reaction mixture followed by the removal of water under vacuum, extraction of the residue with methanol gave the product containing a varying, but substantial amount of (hydrated) sodium sulfate (30-80 wt%; based on elemental analysis).9 The ligand bdompp- $S[Na]_4 \cdot x Na_2 SO_4 \cdot y H_2O$, was isolated in a yield of 20-35% and was characterised by ¹H, ¹³C and ³¹P NMR and elemental analysis. The presence of sodium sulfate in the product was undesired. After several attempts, a new, simple and efficient work up procedure was found. After hydrolysis of the reaction mixture, storage at 5 °C or below resulted in the precipitation of a white crystalline material.¹⁰ After filtration, washing with methyl ethyl ketone and drying, the product was isolated in acidic, hydrated form, bdompp-S[H]₄ $\cdot n$ H₂O (n = 8; based on elemental analysis), typically in a yield of 85-90%. The bis-zwitterionic product was characterised by ¹H, ³¹P and ¹³C NMR spectroscopy (Fig. 1). The occurrence of exclusive para-sulfonation (with respect to the *o*-methoxy substituent) was confirmed by H,H-COSY and C,H-COSY (PFG-HMQC techniques) and by X-ray diffraction.¹¹ The residual content of sulfuric acid in the product did not generally exceed 0.2 wt% (based on sulfate analysis by ion chromatography).

 $[\]overline{\left| \begin{array}{c} F_{\rm c} & WR_{\rm c} = [\Sigma w \Delta^2 / \Sigma w F_{\rm o}^{4}]^{0.5}; S = [\Sigma w \Delta^2 / ({\rm N-NV})]^{0.5}; R_{\rm 1} = \Sigma ||F_{\rm o}| - |F_{\rm c}|| / \Sigma |F_{\rm o}|; \quad \Delta = F_{\rm o}^2 - F_{\rm c}^2; \quad {\rm N=NO+restraints}; \quad w = [\sigma_{\rm c}^2 (F_{\rm o}^2) + (gP)^2]^{-1}; \quad \sigma_{\rm c}^2 (F_{\rm o}^2) = {\rm variance} \quad {\rm in} \quad F_{\rm o}^2 \quad {\rm due} \quad {\rm to} \quad {\rm counting} \quad {\rm statistics}, P = [{\rm max}(F_{\rm o}^2, 0) + 2F_{\rm c}^2]/3.$

⁷ Sulfonation of bdompp by sulfuric acid was also reported by Sheldon and coworkers [5d].

⁸ If the concentration of bdompp is too high (> 25%) while employing sulfuric acid as the sulfonation reagent, the reaction does not proceed completely. This is probably due to a gradual lowering of the acid concentration because of the generation of 1 mol of H_2O per mol of the sulfonic acid group generated. The concentration of H_2SO_4 must be higher than 92%; otherwise the sulfonation proceeds very slowly and incompletely or not at all. Incomplete conversion of bdompp can be overcome by the addition of some oleum (30%).

⁹ This problem is often encountered when sulfonated phosphines are isolated this way, but can be overcome by a proper choice of extraction solvent. See Ref. [5d].

¹⁰ Also at room temperature, the reaction mixture is over-saturated and the product crystallizes upon standing. However, cooling of the reaction mixture accelerates this process and improves the yield.

¹¹ The ³¹P NMR resonances of bdompp-S[H]₄ (-5.6 ppm), bdompp-S[Na]₄ (-34.4 ppm), bdompp (-36.6 ppm) and protonated bdompp, bdompp-[H]₂·2OTf (-4.5 ppm), clearly indicate the presence of bdompp-S[H]₄ in zwitterionic form, containing protonated phosphorus atoms.



Fig. 1. Zwitterionic bdompp-S[H]₄.

Further study revealed that bdompp-S[H]₄·nH₂O precipitates from water–sulfuric acid mixtures over a broad range of ratios (in high yield over the range of 3:1–10:1 v/v). Its limited solubility in water–sulfuric acid mixtures (~0.5 wt% at 4 °C) was quite unexpected regarding its high solubility both in pure water (28 wt% at 20 °C) and in concentrated sulfuric acid (>25 wt% at 20 °C). A possible explanation for this phenomenon is that over the given ratio, water–sulfuric acid mixtures are much more polar than the concentrated sulfuric acid or pure water as such, due to the high degree of dissociation of sulfuric acid (pK₁ 1.92) in water. As a result, the bis-zwitterionic, overall neutral,

Table 2

Selected bond lengths (Å) and bond angles (°) for bdompp-S[H]_4nH₂O

Bond lengths	
S(1)–O(2)	1.32(2)
S(1)–O(1)	1.37(2)
S(1)–O(3)	1.392(12)
S(1)–C(5)	1.745(13)
S(2)–O(5)	1.269(14)
S(2)–O(7)	1.38(2)
S(2)–O(6)	1.39(2)
S(2)-C(12)	1.63(2)
P(1)-C(3)	1.764(10)
P(1)-C(10)	1.766(14)
P(1)-C(2)	1.783(12)
C(1)–C(2)	1.516(14)
Bond angles	
O(2)–S(1)–O(1)	110(2)
O(2)–S(1)–O(3)	106.2(12)
O(1)–S(1)–O(3)	117(2)
O(2)–S(1)–C(5)	107.0(11)
O(1)–S(1)–C(5)	106.8(8)
O(3)–S(1)–C(5)	108.5(7)
O(5)-S(2)-O(7)	107(2)
O(5)-S(2)-O(6)	116.1(13)
O(7)–S(2)–O(6)	109.3(14)
O(5)-S(2)-C(12)	107.1(10)
O(7)–S(2)–C(12)	107.2(10)
O(6)–S(2)–C(12)	109(2)
C(3)–P(1)–C(10)	114.2(5)
C(3)–P(1)–C(2)	110.7(5)
C(10)-P(1)-C(2)	107.6(7)
C(2)-C(1)-C(2) ^a	107.2(13)

^a Symmetry transformations used to generate equivalent atoms: -y+5/4, -x+5/4, -z+1/4.



Fig. 2. Molecular structure of bdompp- $S[H]_4$ showing atom labelling scheme. All hydrogen atoms have been omitted for clarity.

diphosphine bdompp-S[H]₄ is a relatively apolar species in these highly polar mixtures and hence exhibits a limited solubility. Alternatively, it might be due to 'salting-out' of bdompp-S[H]₄, with $H_3O^+ \cdot HSO_3^-$ being the salt. This new, simple and unprecedented isolation procedure might be applicable to other sulfonated (di)phosphines as well.

3.2. X-ray crystal structure

The structure of zwitterionic $[H_2\{(2,5-C_6H_3(OMe)-(SO_3)\}_2PHCH_2CH_2CH_2PH\{(2,5-C_6H_3(OMe)-(SO_3)\}_2]$ · nH_2O , bdompp-S $[H]_4 \cdot nH_2O$, is shown in Fig. 2. The crystal structure consists of $[H_2\{2,5-C_6H_3(OMe)-(SO_3)\}_2PHCH_2CH_2CH_2PH\{(2,5 - C_6H_3(OMe)(SO_3)]$ molecules and water molecules. No hydrogen atoms were located in the X-ray analysis, as a result of the rather poor quality diffraction data obtained.¹² Crystals did not show any signs of loss of water from the structure during the lifetime of the experiment. Selected bond lengths and bond angles are given in Table 2.

Molecules of bdompp-S[H₄] lie at positions of the crystallographic twofold rotational symmetry (C_2) and therefore there is one crystallographically unique phosphorus in the structure. The P(CH₂)₃P chain therefore has an extended conformation as is expected for a (CH₂)₃ chain linking the two bulky centres [11]. Although the hydrogen at the tertiary phosphonium centre was not directly located its presence is clearly implied by the P–C and C–P–C angles [12] which are small and large, respectively, compared with the tertiary diarylphosphine species. In other respects the intramolecular geometry is unexceptional and not very

¹² Attempts to improve data quality by collection at lower (and room) temperature proved fruitless. All crystals examined gave similar low quality diffraction patterns with no useful intensity beyond $2\theta = 45^{\circ}$.



Fig. 3. Packing diagram of the structure of bdompp-S[H]₄·nH₂O viewed down the c axis.

reliably determined because of the disorder problems noted above.

The presence of a proton at each phosphorus implies that two of the four sulfonic acid groups per molecule of bdompp-S[H₄] are deprotonated (i.e. one of the two unique SO_3 groups in the crystal). It is not clear from the intramolecular geometry of bdompp-S[H₄] as to which sulfonate oxygen carries the remaining proton. The shortest interaction between full occupancy oxygens is O(1)…O(9) 2.51 Å. The other O…O contacts of < 3.1 Å involving SO₃ group oxygen atoms are: O(2)···O(10) 2.87 Å, O(3)···O(15) 2.15 Å*; O(5)···O(13) 3.01 Å; O(6)···O(11) 2.77 Å, O(7)···O(9) 2.92 Å, O(7)...O(10) 3.04 Å. There appears to be little or no intramolecular hydrogen bonding of significance. Thus the shortest H…O contact involving the phosphonium hydrogen is 2.78 Å $[O(8)\cdots H(1)]$. The water oxygens (O9-15) show hydrogen bonded (or artificial) contacts between themselves < 3.1 Å as follows: O(9)..O(11)' 1.83 Å*, O10)···O(13)' 2.86 Å, O(11)···O(15) 2.47 Å*, O(12)···O(15) 2.39 Å*, O(13)···O(14) 2.706 Å, O(14)...O(14). 2.08 Å*, O(15)...O(15) 2.89 Å*. (The *-marked contacts are more likely to be artefacts rather than real contacts given the disorder problems.)

The unique full occupancy SO_3 ...water contact O(1)...O(9) 2.52 Å may be tentatively assigned as that involving the unique proton on the sulfonato groups. There are no short O...O contacts between zwitterions. Thus the zwitterions are heavily solvated by water in the solid state, presumably mimicking the solution behaviour of bdompp-S[H₄]. As may be seen in Fig. 3 the water dominated regions of the structure are arranged in channels around the fourfold axes of the crystal structure, while the hydrophobic parts of bdompp-S[H₄] are located in the intervening regions.

3.3. Catalyst performance

In comparison with Carilon Polymer, Carilite Oligomer is characterised by a much higher propene content. Whereas commercial grades of Carilon Polymer typically contain about 6 mol% of propene on total olefin content, Carilite Oligomer contains 50–100 mol% of propene depending on its application. The target of

the current study was the manufacture of PK-PE-30 with $M_{\rm p} = 2400$, one of the main Carilite Oligomer grades containing 30 mol% of ethene and 70 mol% of propene.1 Synthesis of this material instead of Carilon Polymer is achieved by adjusting the propene-ethene ratio in the reaction mixture and the reaction temperature. As the rate of termination/propagation is concurrently changed, much lower molecular weights are obtained at higher propene content and similar reaction temperature. No fundamental study was undertaken to map the effect of temperature on the rate, the molecular weight and the content of propene. Increasing the reaction temperature while maintaining the COethene-propene partial pressure ratio, generally leads to the manufacture of lower molecular weight materials at a higher reaction rate.

In the present study the catalysts were first tested at 91 °C under standard catalyst screening conditions. The reaction conditions were later optimised to obtain the desired product composition. The CO-ethenepropene polymerisation experiments were carried out using an 'equilibrium' mixture of MeOH-H2O-HOAc-MeOAc (45.5:29.5:5.3:19.6 v/v) as the solvent. This particular solvent mixture was selected for two reasons. Addition of acetic acid in methanol has been found to stabilise the catalyst, while addition of water improves the degree of product-solvent separation, thus facilitating product work-up and catalyst recycling. Polymerisation was started by injecting a solution of the catalyst into the reactor at process conditions and continued for 3 h. The pressure was kept constant with a constant supply of an 80:20 CO-ethene mixture. Propene was only supplied before the catalyst was injected. After the reaction was stopped, the solvent was removed under vacuum and the product analysed (GPC, ¹³C NMR, viscosity).

3.3.1. Preparation of the catalysts

The bdompp-based catalyst was prepared by dissolving $Pd(OAc)_2$ and bdompp (1.05 equiv.) in acetone (Eq. (1)), followed by the exchange of acetate anions for weakly coordinating anions by addition of a fourfold excess of trifluoroacetic acid (Eq. (2)).

 $bdompp + Pd(OAc)_2 \rightarrow Pd(bdompp)(OAc)_2$ (1)

Pd(bdompp)(OAc)₂ + 2 HTFA \rightarrow

$$Pd(bdompp)(TFA)_2 + 2 HOAc$$
 (2)

The bdompp-S[Na]₄-based catalyst was prepared in a similar way (Eqs. (3) and (4)), using a water-acetone mixture as the solvent.

bdompp-S[Na]₄ + Pd(OAc)₂
$$\rightarrow$$

Pd(bdompp-S[Na]₄)(OAc)₂ (3)

 $Pd(bdompp-S[Na]_4)(OAc)_2 + 2 HTFA \rightarrow$

 $Pd(bdompp-S[Na]_4(TFA)_2 + 2 HOAc$ (4)

It should be noted that $Pd(bdompp-S[Na]_4)(TFA)_2$ may also be viewed as $Pd(bdompp-S[Na]_2)\cdot 2NaTFA$, as the coordination behaviour of the TFA-anions is dependent on the solvent. In the applied polar reaction solvent, counterions like TFA⁻, and RSO₃⁻ are essentially non-coordinating as they exhibit virtually no influence on the performance of the catalyst.

Application of the ligand in protonated (zwitterionic) form, bdompp-S[H]₄·nH₂O, required a modified catalyst preparation procedure. Upon mixing Pd(OAc)₂ and bdompp-S[H]₄, ligand complexation and acetate anion exchange take place simultaneously (Eq. (5)), affording Pd(bdompp-S[H]₂), a formally bis-zwitterionic species. The counter cations (H⁺) were exchanged by the addition of sodium hydroxide (Eq. (6)).

bdompp-S[H]₄ + Pd(OAc)₂
$$\rightarrow$$

 $Pd(bdompp-S[H]_2) + 2 HOAc$ (5)

 $Pd(bdompp-S[H]_2) + 2 NaOH \rightarrow$

 $Pd(bdompp-S[Na]_2) + 2 H_2O$ (6)

3.3.2. Performance of the catalysts

Table 3 illustrates the higher catalytic activity obtained with the bdompp-S[Na]₄-based catalyst in comparison with the non-sulfonated catalyst, Pd(bdompp)-(TFA)₂. The average activity for Pd(bdompp)(TFA)₂ and Pd(bdompp-S[Na]₄(TFA)₂ over a period of 3 h amounted to 4.2 and 9.9 kg PK (g Pd)⁻¹ h⁻¹, respectively. The bdompp-S[Na]₄-based catalyst is not only more active than Pd(bdompp)(TFA)₂, but it also produces Carilite terpolymer with an approximately 15% higher molecular weight, and a somewhat higher propene content. Both the molecular weight and the propene content of the terpolymer were controlled by the reaction temperature. So, PK-PE-30 with $M_n =$ 2400 can be produced at a somewhat higher reaction temperature employing Pd(bdomppS[Na]₄(TFA)₂ as the catalyst in comparison with Pd(bdompp)(TFA)₂. As the reaction rate increases with temperature, the effective rate improvement by using Pd(bdompp-S[Na]₄(TFA)₂ instead of Pd(bdompp)(TFA)₂ will be even larger than the factor of about 2.5 found at 91 °C (Table 3).

The rate of polymerisation was not constant during the course of the reaction, e.g. it dropped by about 20% over 3 h when applying Pd(bdompp-S[Na]₄(TFA)₂ as the catalyst. This is most likely caused by physical factors. First, the properties of the solvent changed considerably as at the end of the run, the solvent contains 20–50 wt% of the product. Secondly, the composition of the gas cap changed during the run as gas consumption (CO–propene–ethene in a molar ratio of 50:35:15) and gas supply (CO–ethene in a molar

Table 3				
Manufacture c	of Carilite	Oligomer-	-catalyst	performance a

Property	bdompp	bdompp-S(Na) ₄	bdompp-S(H) ₄
Initial rate (kg PK (g Pd) ^{-1} h ^{-1}) ^b	6.1	14.3	
End of run rate (kg PK (g Pd) ^{-1} h ^{-1}) ^b	4.2	11.5	
Yield (g)	29.7	70.0	43.0
Average rate (kg PK (g Pd) ^{-1} h ^{-1}) ^c	4.2	9.9	6.1
$M_{\rm p}$ (Da)	2870	3280	3590
Mol% ethene built in	37	33	43
1,3-propyl (% of total propyl groups) ^d			
	24	32	29

^a Polymerization conditions: catalyst: Pd(OAc)₂-diphosphine ligand-trifluoroacetic acid (in a ratio of 1:1.05:4); solvent: MeOH-H₂O-HOAc-MeOAc (45.4:29.5:5.3:19.6, v/v); [Pd] = 18 ppm; T = 91 °C; t = 3 h; initial partial pressures: $P_{(H_2)} = 7$ bar, $P_{(ethene)} = 5$ bar, $P_{(propene)} = 30$ bar, $P_{(CO)} = 21$ bar; $P_{total} = 70$ bar (at 91 °C), kept constant by feeding CO-ethene (80:20).

^b Based on gas uptake.

^c Based on polymer yield.

^d Based on total olefin content.

ratio of 80:20) were not identical. During the run the gas cap became less rich in olefins, while the reaction rate is about first-order in olefin and more rich in CO, while the rate is practically zero-order in CO at higher $P_{\rm CO}$ (>15 bar).

Analysis of oligomers by ¹³C NMR revealed the backbone of the Carilite Oligomer to consist of a random combination of mainly -CH2CH2C(O)- and -CH₂CH(CH₃)C(O)-units. Further, a substantial fraction of propene was build in the terpolymer in the 1,3-mode (see Fig. 4), typically in about 25-35%.¹³ A variety of end-groups were detected, n-propyl, iso-propyl, n-propenyl and iso-propenyl being the dominating ones. Only small amounts of ester end-groups were observed. This indicates β -H elimination to be the major termination process and initiation to take place predominantly via the Pd-hydride cycle [3d]. The positive influence of hydrogen on the polymerisation rate is thought to emerge from the conversion of the relatively slowly initiating L₂Pd²⁺-species, present at the start of the polymerisation and formed after termination via protonolysis (Eq. (7)) into a directly propagating L_2PdH^+ -species according to Eq. (8) [13].¹⁴

$$[L_2Pd(CH_2CH_2C(O)R]^+ + H^+ \rightarrow L_2Pd^{2+} + CH_3CH_2C(O)R$$
(7)

$$L_2Pd^{2+} + H_2 \rightleftharpoons L_2PdH^+ + H^+ \tag{8}$$

The bdompp-S[H]₄-based catalyst, Pd(bdompp-S[H]₂), prepared according to Eq. (5), exhibits a considerably lower activity than its sodium counterpart, prepared from bdompp-S[Na]₄. The molecular weight

of the products was far above the target (Table 3). For that reason the majority of further experiments with Pd(bdompp-S[H]₂) were carried out at a higher temperature (100 °C; Table 4). Under further identical polymerisation conditions, 'virgin' Pd(bdompp-S[H]₂) catalyst (no NaOH was added) exhibited an activity of 6.7 kg PK (g Pd)⁻¹ h⁻¹, while the molecular weight of the product dropped from $M_{\rm n} = 3600$ to about 2900. As the average catalytic activity for Pd(bdompp-S[H]₂) was lower than that experienced with Pd(bdompp-S[Na]₄)(TFA)₂, a series of experiments was carried out in which the two remaining sulfonic acid groups of Pd(bdompp-S[H]₂) were neutralised by the addition of (an excess) sodium hydroxide (Eq. (6)). In one case some sodium sulfate was also added (a major constituent of the first batches of bdompp-S[Na]₄ isolated). The results of these experiments are listed in Table 4. A clear trend is observed between the amount of sodium hydroxide added and the catalyst activity. The average catalytic activity over 3 h increased to a value of 10.1 kg PK (g Pd) $^{-1}$ h $^{-1}$ by addition of 8 mol of sodium hydroxide per mole of Pd(bdompp-S[H]₂) and even further to 11.2 kg PK (g Pd)⁻¹ h⁻¹ by an extra addition of sodium sulfate. It should be noted that excess of NaOH (>2 mol per mole Pd(bdompp-S[H]₂)₄ is converted into NaOAc in the acetic acid containing reaction solvent mixture (or into NaTFA, as trifluoroacetic acid was generally a constituent of the catalyst mixture). Besides an increase in activity, a decrease in the



1,2-mode1,3-modeFig. 4. Incorporation modes of propene.

¹³ Incorporation of propene in the 1,3-mode during perfectly alternating CO-propene or CO-propene-ethene copolymerization is a well-known phenomenon. See, e.g. Ref. [3b].

¹⁴ Protonolysis occurs via the intermediacy of a palladium enolate complex. See Ref. [13].

Table 4 Influence of sodium salts on catalyst performance ^a

Entry	NaOH (mol/mol ligand)	Yield (g)	Average rate (kg PK (g Pd) ⁻¹ h ⁻¹)	$M_{\rm n}$	$M_{ m w}/M_{ m n}$	ethene = built in (mol% on total olefin content)
1	None	47	6.7	2910	1.93	38
2	4.02	54	7.7	2460	1.88	36
3	6.12	63	8.9	2300	1.85	31
4	8.00	71	10.1	2260	1.88	31
5	6.12+17.3 Na ₂ SO ₄	79	11.2	2230	1.89	30

^a Polymerization conditions: catalyst: Pd(OAc)₂-bdompp-S(H)₄-trifluoroacetic acid (in a ratio of 1:1.05:4); solvent: MeOH-H₂O-HOAc-MeOAc (45.4:29.5:5.3:19.6, v/v); [Pd] = 18 ppm; T = 100 °C; t = 3 h; initial partial pressures: $P_{(H_2)} = 4$ bar, $P_{(ethene)} = 5$ bar, $P_{(propene)} = 30$ bar, $P_{(CO)} = 21$ bar; $P_{total} = 69$ bar (at 100 °C), kept constant by feeding CO-ethene (80:20).

molecular weight of the product and a decrease of the amount of ethene built in into the oligomer backbone is also observed on increasing the amount of sodium salt. This salt effect was found to be a general phenomenon. Addition of a variety of other salts (including, e.g. NaOAc, NaOTf, Na₃PO₄, LiOTf, CaSO₄, NiSO₄ and FeSO₄) induces a similar effect on rate, M_n and ethene incorporation [1c].

It was a pleasant surprise to note that the bdompp-Sbased palladium catalyst not only exhibits a firmly improved recyclability (vide infra), but also a more than doubled activity for the manufacture of Carilite Oligomer in comparison with the initially tested catalyst, Pd(bdompp)(TFA)₂. The second noteworthy aspect is the positive influence exerted by salts on the performance of the catalyst. An activity increase of up to 70% was observed, while the amount of ethene built in the oligomer backbone decreased substantially (by up to 30%). Also the molecular weight dropped, to below $M_{\rm n} = 2400$. The salt effect might both be chemical or physical in origin. It is not simply related to the conversion of the -SO₃H-units of the bdompp-S ligand into $-SO_3Na$ (Eq. (6)), otherwise addition of more than 2 mol of NaOH per mole Pd(bdompp-S[H]₂ would not have exerted a further positive effect. In fact, the upper limit of the salt effect might not even have been reached in the limited series of experiments described here (Table 4). The fact that salts also containing non-basic, non-coordinating anions (e.g. NaOTf, LiOTf), exert a positive influence, might point to the occurrence of a cation-effect.

Alkali and alkaline-earth metals have been reported to enhance the rate and the position of equilibrium in the migratory insertion of CO in metal–alkyl bonds [14], one of the steps in the catalytic propagation cycle leading to perfectly alternating polyketones [3d]. However, CO-insertion is not expected to be the rate-determining step in perfectly alternating CO–olefin copolymerizations. It is imaginable that cations assist the opening of five- and/or six-membered palladacycles, crucial intermediates in the propagation cycle [15]. On the other hand, the salt effect might emerge from breaking up self-association of the sulfonated, water soluble ligands applied [16], or, if the manufacture of the oligomers occurs under two-phase conditions [17],¹⁵ from increasing the polarity difference between the solvent-rich and product-rich phases leading to residence of a larger part of the running polar catalyst species, [Pd(bdompp-S)R] (R represents the growing polyketone chain), in the solvent-phase. Clearly, further study is required to elucidate the underlying chemical and/or physical aspects of this intriguing salt effect.

3.3.3. Recyclability of the catalysts

Two series of recycling experiments were conducted (Table 5). After the polymerisation run was stopped, the reaction mixture was allowed to separate at room temperature in a product-rich bottom layer and a solvent-rich, product-poor, top layer. After the layers were separated and the bottom layer was washed with a new aliquot of solvent, the combined top layers were used in a next polymerisation experiment.¹⁶ In series A, no additional supply of fresh catalyst solution was applied in the recycles. The product yield declined by about 34% after two recycles. In series B, about 34% of extra catalyst was added at the start of each next cycle in order to compensate for the loss of active catalyst loss via the bottom phase. In this series, the product yield in the first and second recycle was about the same as in the initial run, illustrating that the amount of fresh catalyst added was sufficient to compensate for the loss of catalytic activity.

¹⁵ Recently, experimental evidence has been provided from polymer end-groups analysis for the occurrence of running palladium-based polyketone catalyst species, $[Pd(bdompp)R]^+$, in two different states under slurry process conditions. Depending on the length of the copolymer chain, R, the catalyst is either *dissolved* during CO–ethene copolymerization (at the shorter chains, up to 13–20 [CH₂CH₂C(O)]units) or *polyketone-supported* (at the longer chains, above 13–20 [CH₂CH₂C(O)]-units). See Ref. [17].

¹⁶ The composition of the solvent of the combined top layers was roughly the same as that of the initially applied solvent mixture; the water content was slightly higher and the MeOAc content slightly lower.

Property	Experiment A ^b			Experime	Experiment B ^c		
	Initial	1st recycle	2nd recycle	Initial	1st recycle	2nd recycle	
Initial rate (kg PK (g Pd) ^{-1} h ^{-1}) ^d	10.4	6.9	4.8	11.0	9.9	9.0	
End of run rate (kg PK (g Pd) ^{-1} h ^{-1}) ^d	8.5	5.3	3.4	8.8	7.1	6.4	
Average rate (kg PK (g Pd) ^{-1} h ^{-1}) ^e	7.5	6.7	4.8	7.9	8.0	8.2	
Yield (g)	56.4	50.3	35.8	58.0	58.9	59.9	

^a Polymerization conditions: catalyst: Pd(OAc)₂-bdompp-S(Na)₄-trifluoroacetic acid (in a ratio of 1:1.05:4); solvent: MeOH-H₂O-HOAc-MeOAc (45.4:29.5:5.3:19.6, v/v), [Pd] = 18 ppm (initially); T = 91 °C; t = 3 h; initial partial pressures: $P_{(H_2)} = 4$ bar, $P_{(ethene)} = 5$ bar, $P_{(propene)} = 30$ bar, $P_{(CO)} = 21$ bar; $P_{total} = 65-67$ bar (at 91 °C), kept constant by feeding CO-ethene (80:20).

^b No fresh catalyst was added.
 ^c In each recycle 34 wt% of fresh catalyst was added.

In each recycle 34 wt% of fresh

^d Based on gas uptake.

^e Based on polymer yield of bottom layer.

Table 6				
Partitioning	coefficients	for	L ₂ Pd(TFA) ₂ ^a	

Entry	L ₂	Catalyst (mg)	Weight mixture (g)	Bottom layer (g)	Top layer (g)	[Pd] _{bottom} (ppm)	[Pd] _{top} (ppm)	K [Pd] _{top} /[Pd] _{bottom} (ppm/ppm)	Pd mass balance (%)
1	bdompp	45	11.11	9.22	1.65	513	467	0.9	99
2	bdompp-S	51	8.43	7.09	1.27	24	2541	106	81
3	bdompp-S	78	13.05	10.87	2.11	20	2563	128	86

^a Over a two-phase Carilite-solvent mixture; Carilite PK-PE-30; $M_n = 2560$; solvent: MeOH-H₂O-HOAc-MeOAc (ratio 45.4:29.5:5.3:19.6, v/v).

On bases of the Pd-content analyses of the various phases, the partitioning coefficient for bdompp-S[Na]₄-based catalyst in series B (K value, defined as [Pd]_{top-layer}/[Pd]_{bottom-layer} (ppm/ppm)) was calculated to be 4.7 (initial cycle), 3.8 (1st cycle) and 4.7 (2nd cycle), respectively. Although these values are significantly higher than those found for the non-sulfonated Pd-(bdompp)(TFA)₂, for which K values of about 0.3 were found in separate recycling experiments, the values were lower than expected.

Therefore the actual partitioning coefficients of Pd-(bdompp)(TFA)₂ and Pd(bdompp-S[Na]₄)(TFA)₂ over a two-phase Carilite-solvent mixture were determined in separate series of experiments (Table 6). Using the 'equilibrium' mixture employed in the polymerization experiments described above, the partitioning coefficient K for Pd(bdompp)(TFA)₂ was found to be 0.9, while the partitioning coefficient for Pd(bdompp- $S[Na]_4)(TFA)_2$ was found to be > 100. The lower recycling efficiency observed under actual polymerisation conditions (series A and B) is attributed to the occurrence of part of the catalyst species in non-terminated form, [Pd(bdompp-S)R] (R = terpolymer chain), during recycling. Depending on the length of the terpolymer chain attached to the catalytic palladium centre, these species will be 'attached' to the more apolar Carilitephase via their polymeric tail, and hence diminish catalyst recycling efficiency. It is expected that this efficiency can be improved by introducing a dedicated post-treatment procedure, inducing termination of those catalyst species still containing a polymer chain.

4. Concluding remarks

A new, highly active homogeneous palladium-based catalyst has been developed for the manufacture of low molecular weight CO–ethene–propene-based polyke-tone (Carilite Oligomer). By virtue of the development of a simple, highly efficient and environmentally friendly recipe for the production of the sulfonated diphosphine constituent in the catalyst recipe, bdompp- $S[H]_4$, this new catalyst has become the preferred candidate for the manufacture of Carilite Oligomer.

In comparison with its non-sulfonated counterpart this catalyst not only exhibits a much more favourable partitioning coefficient in liquid–liquid separation of product and solvent, but it also exhibits an approximately 2.5 times higher catalytic activity. An economic evaluation showed that application of this new catalyst reduces the contribution of the catalyst costs to the total manufacturing costs of Carilite Oligomer by a factor of about 7.5 when compared with the non-sulfonated catalyst applied first.

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