Polyketone Synthesis

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Morphology Control of Polymer Particles in Ethylene/Carbon Monoxide Copolymerization**

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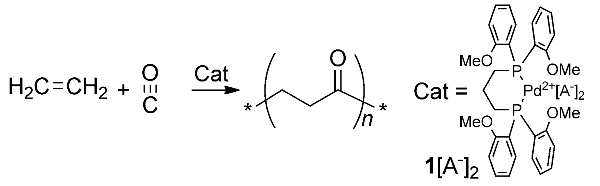
Since the discovery of a highly active catalyst for olefin/carbon monoxide (CO) copolymerization by Shell (Scheme 1),[1] subsequent investigations have been made in both academic and industrial settings.[2] Catalyst **1** exhibits the best activity (exceeding 10 Kg/g-Pd·h) when producing high molecular-weight polymers.[3] Although Shell discontinued research in this area in 2001, Asian industrial development has continued, particularly in areas related to development of fiber applications.[4] The copolymer is insoluble in common organic solvents and precipitates during copolymerization as irregular snow-white particles of low bulk density (ca. 0.10 g mL^{-1}) or as a lump, causing problems in the post-reaction processes. Some of the polymer sticks to the reactor walls and agitator, creating a problem in large-scale synthesis called "reactor fouling".

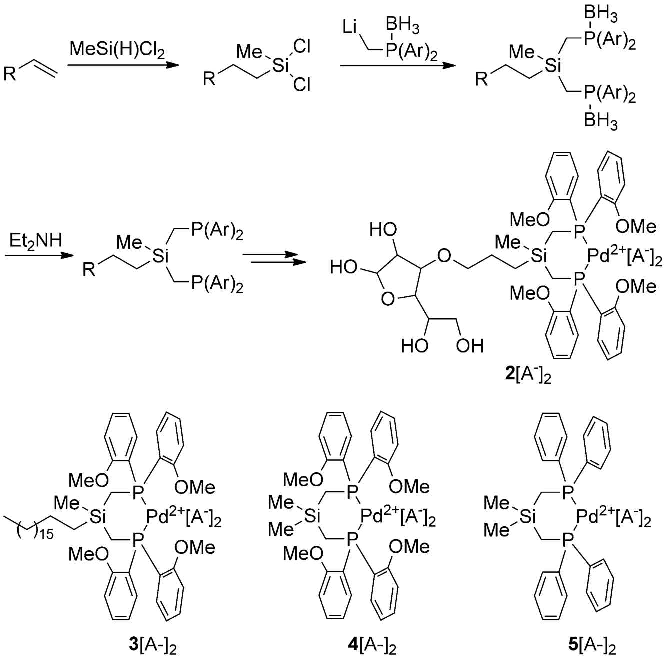


Scheme 1. Ethylene/CO copolymerization.

Morphology control of particles is a hot issue of particular importance in the polymer industry.[5] In radical polymerizations, the traditional suspension polymerization technique produces well-controlled polymer beads of 0.01–1.0 mm, which are easy to handle.[6] In commercial production of polyethylene and polypropylene using slurry and gas processes, morphology control is achieved by immobilizing the catalyst on a solid support such as $MgCl_2$ or silica.[7]

To control the morphology of the polymer particles in the ethylene/CO copolymerization, a strategy is implemented in this work that mimics the traditional suspension polymerization technique: growing polymer particles from catalyst-containing organic droplets dispersed in water or conversely, from catalyst-containing water droplets dispersed in an organic media. Because common catalyst **1**[TsO^- or $CF_3CO_2^-$]$_2$ (TsO^-, *p*-toluenesulfonate anion; Scheme 1) is insoluble in both non-polar organic solvents and water, the strategy cannot be directly applicable using **1**.

To endow some hydrophilicity or lipophilicity, the ligand framework of **1** is modified by replacing the methylene unit (-CH_2-) with a -(RCH_2CH_2)MeSi- unit, where R is a sugar-containing alkyl or a long-chain alkyl (Scheme 2). Treatment of ($LiCH_2$)(2-$MeOC_6H_4$)$_2$P·BH_3 on (RCH_2CH_2)$MeSiCl_2$ gives (RCH_2CH_2)MeSi[CH_2(2-$MeOC_6H_4$)$_2$P·BH_3]$_2$ in high yields (70–85 %), from which BH_3 is quantitatively detached by treatment with diethylamine.[8] Using Me_2SiCl_2 or ($LiCH_2$)(C_6H_5)$_2$P·BH_3 instead of (RCH_2CH_2)$MeSiCl_2$ or ($LiCH_2$)(2-$MeOC_6H_4$)$_2$P·BH_3, bisphosphine ligands for **4** and **5** also are prepared.[9] Reaction of the bisphosphine



Scheme 2. Preparation of functionalized bisphosphine ligands and the catalysts for ethylene/CO copolymerization.

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ligands with $Pd(OAc)_2$ is not clean in some cases,[10] but reaction with $[PdCl_2(NCCH_3)_2]$ affords clean products in all cases. The dichloro complexes **2**–**5**$[Cl^-]_2$ are directly converted into the corresponding palladium **2**–**5**$[A^-]_2$ by treatment with AgA, if AgA is available, or via **2**–**5**$[AcO^-]_2$. Treatment with AgOAc on **2**–**5**$[Cl^-]_2$ affords **2**–**5**$[AcO^-]_2$, which is converted into **2**–**5**$[A^-]_2$ by treatment with two equivalents of strong acid, AH.

Complex **2**$[TfO^-]_2$ (TfO^-, trifluoromethansulfonate anion) is not freely soluble in water but soluble in a mixture of water and methanol (v/v, 1:2).[11] The water/methanol mixture dissolving **2**$[TfO^-]_2$ forms droplets in hexane media. Pressurizing the dispersion with the pressures of ethylene (35 bar) and CO (70 bar) successivley at 85 °C produces the copolymer with good activity (7.3 Kg/g-Pd·h) but the isolated polymer is present in lumps.

Complex **3**$[TfO^-]_2$ is soluble in water-immiscible 1-octanol. When 1-octanol (5 mL) dissolving **3**$[TfO^-]_2$ is dispersed in water (50 mL), droplets are formed. By addition of small amounts of poly[(vinyl alcohol)-*co*-(vinyl acetate)] as a droplet stabilizer, the droplets become stable and are not readily collapsed. However, a negligible amount of copolymers is formed, when ethylene (35 bar) and CO (70 bar) gases are successively pressurized at 85 °C on the droplet dispersion. Complex **3**$[A^-]$ of other anions such as TsO^-, $CF_3CO_2^-$, ClO_4^-, or PF_6^- show no activity.

A high activity is realized when the catalyst is harnessed by additional lipophilicity on the anion; catalyst **3**[dodecylbenzenesulfonate]$_2$ exhibits a high activity (9 Kg/g-Pd·h) in the two-phases of 1-octanol droplets in water, and well-controlled polymer particles are produced without reactor fouling (Figure 1). Dispersion of 1-octanol droplets in water becomes a suspension of the polymer particles in water after polymerization. Almost all of the 1-octanol is absorbed by the polymer particles, which are isolated by filtration. 1-Octanol absorbed in the particles is easily removed through washing with hot methanol. Mean polymer particle size calculated by measuring the weights after fractionation with sieves is 0.58 mm (Table 1, Entry 1). Particle size distribution is narrow; 90% of the particles are in the range of 0.43–0.85 mm. The bulk density of the isolated polymer particles is satisfactorily high (0.22 $g\,mL^{-1}$). An SEM image shows that the polymer particle is not porous (Figure 1); the surface area of the particles determined on BET method is low, 5.2 $m^2\,g^{-1}$. Lipophilicity in a bisphosphine ligand framework is required to obtain good morphology. Complexes not attaching the liphophilic alkyl chain in bisphosphine ligand framework, **4**[dodecylbenzenesulfonate]$_2$ and **1**[dodecylbenzenesulfonate]$_2$, produce irregular polymer particles, resulting in lowered bulk densities of 0.15 and 0.12 $g\,mL^{-1}$, respectively (Table 1, Entries 9,10).

Table 1: Suspension polymerization results.[a]

Entry	Catalyst[b]	Stirring [rpm]	PVA[c] [wt %]	Activity [kg g(Pd)$^{-1}$ h^{-1}]	Particle size[d] [mm]	Bulk density [g mL^{-1}]
1	**3**$[A^-]_2$	800	0.14	9.6	0.58	0.22
2	**3**$[A^-]_2$	700	0.14	9.1	0.69	0.23
3	**3**$[A^-]_2$	600	0.14	8.4	0.88	0.25
4	**3**$[A^-]_2$	500	0.14	6.6	1.01	0.27
5	**3**$[A^-]_2$	600	0	8.8	0.98	0.16
6	**3**$[A^-]_2$	600	0.07	8.6	0.98	0.20
7	**3**$[A^-]_2$	600	0.28	8.2	0.66	0.27
8	**3**$[A^-]_2$	600	0.56	6.8	0.47	0.29
9	**4**$[A^-]_2$	600	0.14	8.3	0.76	0.15
10	**1**$[A^-]_2$	600	0.14	7.5	1.12	0.12

[a] Polymerization conditions: water (50 mL), 1-octanol (5 mL), catalyst (5.0 μmol), ethylene (35 bar) and then CO (70 bar), temperature (85 °C), time (90 min). [b] A^- = dodecylbenzenesulfonate. [c] Poly[(vinyl alcohol)-*co*-(vinyl acetate)] (87–89 % hydrolyzed, w% with respect to water). [d] Mean particle diameter calculated by measuring the weights after fractionation with sieves.

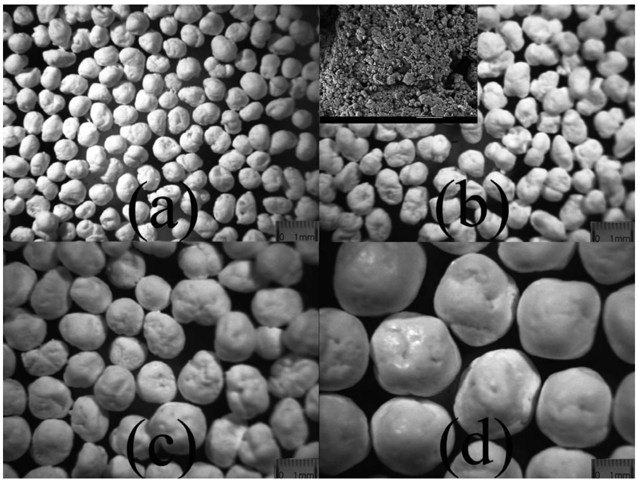

Figure 1. Optical microscopic images of the polymer particles prepared by suspension polymerization (a)–(d) correspond to Entries 1–4, respectively, in Table 1). Insert in (b) is an SEM image (×2000) of the polymer particle, scale bar10 μm.

In a typical suspension polymerization, the particle size can be modulated either by stirring rate or by concentration of the droplet stabilizer.[6a] In agreement with the reported trend, mean particle size increases in the range of 0.58–1.01 mm as the stirring rate decreases in the range of 800–500 rpm (Table 1, Entries 1–4, Figure 1). With the increase of the particle size, the bulk density also increases in the range of 0.22–0.27 $g\,mL^{-1}$. With an increase of droplet stabilizer concentration in the range of 0.07–0.56 w% with respect to water, the particle size decreases in the range of 0.98–0.47 mm, but, in this case, the bulk density increases in the range of 0.20–0.29 $g\,mL^{-1}$ as the particles size decreases (entries 3 and 6–8). In the absence of droplet stabilizer, the particle shape is irregular, resulting in a low bulk density (0.16 $g\,mL^{-1}$, entry 5). In both cases, the activity decreases with an increase of the bulk density. The activities predominantly are in the range of 9.6–8.2 Kg/g-Pd·h, which are satisfactory values compared to those obtained by carrying out copolymerization in the typical single phase of methanol using **1**$[TfO^-]_2$ or **4**$[TfO^-]_2$ (11 Kg/g-Pd·h). Molecular weights of the well-controlled polymer particles are high and their distribution is narrow ($M_n = 213\,000$; $M_w/M_n = 2.8$ for Entry 1). These values are not altered by the stirring rate ($M_n = 200\,000$; $M_w/M_n = 2.7$ for entry 3) and are almost identical to those obtained with **1**[dodecylbenzenesulfonate]$_2$ ($M_n = 267\,000$; $M_w/M_n = 3.3$ for Entry 10).

In a scale-up batch using 350 mL water, 105 mL 1-octanol, and 0.035 mmol catalyst, 199 g of well controlled polymer particles (mean particle size, 0.33 mm) is prepared without reactor fouling by running for 8 h, during which time the rate of polymerization does not decay severely. A high activity of 53 Kg/g-Pd is achieved along with a high bulk density of 0.39 $g\,mL^{-1}$ in this scale-up batch. After polymerization, total volume containing the settled slurry phase becomes 570 mL, which corresponds to productivity per volume of 350 $Kg\,m^{-3}$. In the differential scanning calorimetry (DSC) study of the obtained polymer particles, the peak of melting temperature is observed at 262 °C with $\Delta H_m = 114\ J\,g^{-1}$. The wide-angle X-ray diffraction (WAXD) pattern indicates β-form crystallization.[12] The DSC and WAXD patterns are not changed by the polymerization conditions.

When the copolymerization is carried out in a single phase of methanol, **1**[TfO$^-$]$_2$ produces lumps with a broad molecular weight distribution ($M_n = 249\,000$; $M_w/M_n = 5.0$; Figure 2a). **5**[TfO$^-$]$_2$ produces shapeless snow-white precipitates, of which the bulk density is low (0.10 $g\,mL^{-1}$), with a relatively low molecular weight polymer ($M_n = 112\,000$; $M_w/M_n = 5.1$) due to chain transfer reactions (Figure 2b). Reactor fouling occurs in both cases.

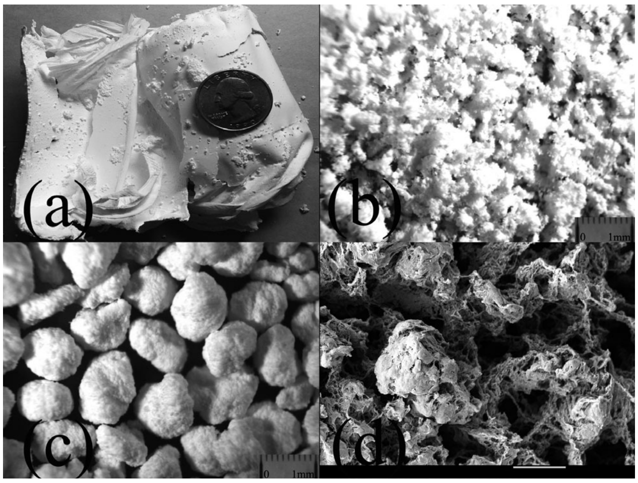

Figure 2. (a)–(c) Images of polymers prepared in methanol with **1**[TfO$^-$]$_2$, **5**[TfO$^-$]$_2$, and **4**[TfO$^-$]$_2$, respectively. (d) SEM image (×2000) of a polymer particle in (c) scale bar 10 μm.

Interestingly, **4**[TfO$^-$]$_2$ produces well-controlled polymer particles even when copolymerization is conducted in a single phase of methanol (Figure 2c). The morphology is not as regular as that obtained in the suspension polymerization and the bulk density is relatively low (0.21 $g\,mL^{-1}$). The polymer particles show some porosity (Figure 2d). The surface area determined using the BET method is 14 $m^2\,g^{-1}$. The particles are disentangled into small pieces by mechanical force. However, reactor fouling occurs, covering the reactor wall and agitator with a thin polymer film. Other complexes bearing a silicon atom, **2**[TfO$^-$]$_2$ and **3**[TfO$^-$]$_2$, also give well-controlled polymer particles with bulk densities of 0.16 and 0.19 $g\,mL^{-1}$, respectively. The anion, TfO$^-$ is crucial. **3**[A$^-$]$_2$ and **4**[A$^-$]$_2$ of other anions such as TsO$^-$, $CF_3CO_2^-$, PF_6^-, NO_3^-, and ClO_4^- produce lumps. Shell realized the morphology control in a single phase of methanol by the usage of seeding polymer powders.[13]

In the bulk production of polymers, morphology control of the polymer particles without reactor fouling is crucial. This goal is achieved by employing the suspension polymerization technique in ethylene/CO copolymerization. Pressurizing with CO and ethylene gases on catalyst-containing 1-octanol droplets dispersed in water produces well-controlled polymer particles with bulk densities in the range of 0.20–0.30 $g\,mL^{-1}$. The catalyst should be harnessed with a lipophilic group on both the bisphosphine ligand framework and anion.

Experimental Section

Suspension ethylene/CO copolymerization: A bomb reactor (125 mL size) was successively charged with poly[(vinyl alcohol)-*co*-(vinyl acetate)] (70 mg, 87–89% hydrolyzed, $M_w = 146\,000$–$186\,000$) dissolved in deairated water (50 mL) and **3**[dodecylbenzenesulfonate]$_2$ (8.0 mg, 5.0 μmol) dissolved in deairated 1-octanol (5.0 mL), while stirring with an anchor-type blade. The reactor was pressurized with the pressures of ethylene (35 bar) and CO (70 bar) successively at room temperature and the solution temperature was increased to 85 °C in 20 min. After running the copolymerization for 90 min at which time the pressure dropped to ca. 40 bar, the reactor was cooled to room temperature, and the remaining gases were vented off. Polymer particles absorbing 1-octanol were isolated by filtration. After the particles were immersed in methanol (40 mL), it was heated under reflux for 30 min. Polymer particles were isolated by filtration and dried under vacuum for 2 h at 90 °C.

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[1] a) E. Drent, P. H. M. Budzelaar, *Chem. Rev.* **1996**, *96*, 663–681; b) E. Drent, J. A. M. Van Broekhoven, M. J. Doyle, *J. Organomet. Chem.* **1991**, *417*, 235–251.
[2] a) T. M. J. Anselment, S. I. Vagin, B. Rieger, *Dalton Trans.* **2008**, 4537–4548; b) T. Kageyama, S. Ito, K. Nozaki, *Chem. Asian J.* **2011**, *6*, 690–697; c) A. Nakamura, K. Munakata, S. Ito, T. Kochi, L. W. Chung, K. Morokuma, K. Nozaki, *J. Am. Chem. Soc.* **2011**, *133*, 6761–6779; d) J. Liu, B. T. Heaton, J. A. Iggo, R. Whyman, *Angew. Chem.* **2004**, *116*, 92–96; *Angew. Chem. Int. Ed.* **2004**, *43*, 90–94.
[3] J. A. M. van Broekhoven, R. L. Wife (Shell), EP 257663, **1992**.
[4] a) A. H. Tullo, *Chem. Eng. News* **2002**, *80*, 13–19; b) T. Morita, R. Taniguchi, J. Kato, *J. Appl. Polym. Sci.* **2004**, *94*, 446–452.
[5] a) W. Feng, L. D. Sun, Y. W. Zhang, C. H. Yan, *Coord. Chem. Rev.* **2010**, *254*, 1038–1053; b) T. L. Kelly, M. O. Wolf, *Chem. Soc. Rev.* **2010**, *39*, 1526–1535.
[6] a) R. Arshady, *Colloid Polym. Sci.* **1992**, *270*, 717–732; b) B. Brooks, *Chem. Eng. Technol.* **2010**, *33*, 1737–1744.
[7] a) L. L. Böhm, *Angew. Chem.* **2003**, *115*, 5162–5183; *Angew. Chem. Int. Ed.* **2003**, *42*, 5010–5030; b) B. Y. Lee, J. S. Oh, *Macromolecules* **2000**, *33*, 3194–3195; c) G. Fink, B. Steinmetz, J. Zechlin, C. Przybyla, B. Tesche, *Chem. Rev.* **2000**, *100*, 1377–1390; d) G. G. Hlatky, *Chem. Rev.* **2000**, *100*, 1347–1376.

[8] a) T. Imamoto, T. Oshiki, T. Onozawa, T. Kusumoto, K. Sato, *J. Am. Chem. Soc.* **1990**, *112*, 5244–5252; b) W. E. McEwen, B. D. Beaver, *Phosphorus Sulfur Relat. Elem.* **1985**, *24*, 259–273.

[9] J. A. van. Doorn, J. J. M. Snel, N. Meijboom, R. L. Wife (Shell), US 4994592, **1991**.

[10] T. J. Mooibroek, E. Bouwman, M. Lutz, A. L. Spek, E. Drent, *Eur. J. Inorg. Chem.* **2010**, 298–310.

[11] a) G. Verspui, F. Schanssema, R. A. Sheldon, *Angew. Chem.* **2000**, *112*, 825–827; *Angew. Chem. Int. Ed.* **2000**, *39*, 804–806; b) W. P. Mul, H. Dirkzwager, A. A. Broekhuis, H. J. Heeres, A. J. Van der Linden, A. G. Orpen, *Inorg. Chim. Acta* **2002**, *327*, 147–159.

[12] O. Ohsawa, K.-H. Lee, B. S. Kim, S. Lee, I.-S. Kim, *Polymer* **2010**, *51*, 2007–2012.

[13] B. Mastenbroek, P. J. M. M. de Smedt (Shell), EP 453011, **1991**.