Polymerisation of olefins catalysed by a palladium complex in supercritical carbon dioxide

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A late transition metal catalyst has been used to polymerise hex-1-ene and ethene in supercritical carbon dioxide, yielding high molecular weight polymers; a comparison with polymerisations in CH_2Cl_2 reveal that polymers with identical molecular weight and polydispersity are formed.

Supercritical carbon dioxide ($scCO_2$) has recently emerged as an interesting substitute for organic solvents. CO_2 is environmental friendly compared to organic solvents and has a low critical temperature (31.1 °C) and pressure (73.8 bar). The physical properties of $scCO_2$ range from liquid-like to gas-like and can be manipulated by changing the pressure and the temperature. Physical properties like gas-like viscosities and diffusion rates, coupled with the liquid-like densities, can result in significant advantages in combined reaction, separation and purification processes. A drawback of $scCO_2$ is that only volatile or relatively non-polar compounds are soluble, as CO_2 is non-polar and has a low polarisability and relative permittivity.[1]

Polymerisation reactions using radical initiators and step growth mechanisms have been carried out in $scCO_2$.[2] More recently homogeneous catalysts have successfully been applied in $scCO_2$ for the preparation of small molecules[3] and polymers.[4–6] An interesting extension in the application of CO_2 is the use of CO_2 both as a reactant and as a solvent in a copolymerisation with cyclohexene oxide.[7] The goal of our research is to copolymerise α-olefins in $scCO_2$. Traditional catalysts for poly(olefin) production are based on early-transition-state metals, which are highly oxophilic and therefore not suitable for polymerisations in CO_2. As late-transition-state metal complexes are less oxophilic, they are more likely to be effective polymerisation catalysts in $scCO_2$. Here we describe the polymerisation of ethene and hex-1-ene catalysed by a homogeneous diimine palladium complex as catalyst,[8,9] also known as the Brookhart system, see Fig. 1.

In our polymerisation experiments we were primarily interested to see if high molecular weight polymers could be produced and whether the active catalyst would exhibit complexation behaviour with CO_2. The results of the polymerisations in CO_2 and in CH_2Cl_2 are listed in Table 1. The values of the turnover frequencies (TOFs) show that the activity of the catalyst is similar in both solvents, despite the large difference in phase behaviour of the reaction mixtures. Both the catalyst and the polymers are soluble in CH_2Cl_2. As expected, the polymer does not dissolve in $scCO_2$. Consequently, the polymerisations performed in CO_2 were all precipitation polymerisations as has been observed in the experiments. Although the differences in phase behaviour are rather large, the polymers produced are very similar, both in molecular weight and in molecular weight distribution. This behaviour indicates that there is no diffusion limitation, despite the precipitation in CO_2, suggesting strong swelling of the polymer, either by CO_2 or by the monomers used. More importantly, a similar molecular weight indicates that the active catalyst does not exhibit complexation behaviour with CO_2, since this would have resulted in a lower molecular weight.

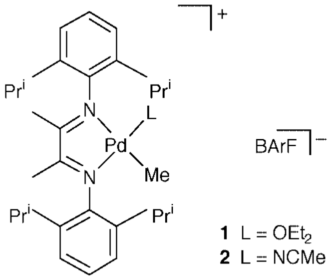

Fig. 1 Catalyst precursors used for polymerizations, BArF ≡ tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

Table 1 Polymerisation of ethene and hex-1-ene in CO_2 and CH_2Cl_2 for 2 h†

Experiment	Catalyst precursor	Catalyst/ 10^{-5} mol l^{-1}	Solvent	Pressure/bar	Monomer[a]/ mol l^{-1}	TOF[b]/h^{-1}	M_n[c]/kg mol^{-1}	M_w/M_n
1	**1**	42	CO_2	239	1.7	450	135	2.1
2	**2**	30	CH_2Cl_2	—	2.7	1010	93	1.5
3	**2**	30	CO_2	194	2.9	560	102	1.5
4	**2**	13	CH_2Cl_2	—	2.3	810	101	1.7
5	**2**	13	CO_2	193	2.1	990	103	2.0
6	**2**	2.6	CO_2	156	0.27	2250	88	2.0

† High pressure polymerisations were conducted in a 75 ml stainless steel high pressure reactor equipped with sapphire windows, a heating jacket and a magnetic stirring bar. The solid catalyst precursor **1** (air and temperature sensitive) was put in the reactor in a glass ampulla, which broke under pressure; catalyst precursor **2** (stable at room temperature in air) was placed directly in the reactor. The air was carefully flushed with CO_2 at low pressure and the reactor was heated. In the case of hex-1-ene as the monomer, the reactor was first filled with CO_2 and then the monomer was added. In the case of ethene, the reactor was flushed and filled with ethene after which CO_2 was added. [a] Experiments 1–5: hex-1-ene, reaction temperature 35 °C; experiment 6: ethene starting pressure 6.9 bar, reaction temperature 40 °C. [b] Turn Over Frequency: mol monomer converted per mol catalyst per hour. [c] GPC (against polystyrene standards).

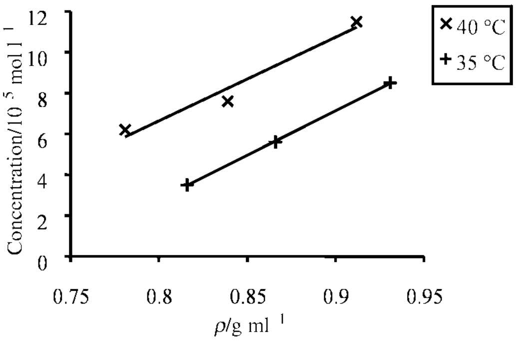

Fig. 2 Solubility of catalyst precursor **2** as a function of $scCO_2$ density.

To study the effect of catalyst concentration on the polymer yield two sets of experiments were conducted, one set with a relatively high catalyst concentration in CH_2Cl_2 and CO_2 (experiments 2 and 3, respectively) and one set with a low catalyst concentration (experiments 4 and 5, respectively). When the experiments were carried out with the high catalyst concentration, the TOF in CO_2 was lower than in the corresponding experiment in CH_2Cl_2. The experiments in the two solvents using the low catalyst concentration showed identical values for TOF, M_n and M_w/M_n, taking into account experimental error. In order to explain the effect of catalyst concentration to the TOF, the solubility of the catalyst precursor was measured in $scCO_2$ with a UV spectrophotometer‡ using a high-pressure view cell with sapphire windows. Although $scCO_2$ is a poor solvent for ionic compounds, the solubility at 35 and 40 °C was found to be in the order of 1×10^{-4} mol l^{-1}, see Fig. 2. However, the rate of solubilisation was low as it typically took 1 h to reach equilibrium. The relatively high solubility can be ascribed to the bulky anion (BArF). Generally, the solubility of an anion in hydrocarbon solvents is known to increase with increasing distribution of charge, *e.g.* the solubility increases in the order BF_4, PF_6, SbF_6, BArF and this is likely to apply for the apolar $scCO_2$ as well. All polymerisations of hex-1-ene in CO_2 were performed above the maximum solubility of the catalyst. Even in experiment 5 with the lowest catalyst concentration, only half of the added amount of catalyst is dissolved in the initial stage of the polymerisation, which follows from Fig. 2 and the density of the reaction mixture. During polymerisation, however, the solubility of the catalyst will be different from pure CO_2, since the catalyst is attached to a growing polymer chain. When the experiments with the low catalyst concentration are compared for the two solvents, no difference in TOF was observed. Obviously, the catalyst solubilisation was not limiting in experiment 5 using CO_2 as the activity was similar to experiment 4 using CH_2Cl_2. Comparing experiment 2 and 3 with the higher catalyst concentration, a difference in TOF was observed, which can be explained by the slow solubilisation and low solubility of the catalyst in CO_2. In experiment 6, ethene was polymerised in $scCO_2$ to high molecular weight polymer. It follows from this experiment that the catalyst is also active in $scCO_2$. In principle, this opens the possibility to copolymerise in $scCO_2$ with monomers such as ethene and propene.

From the foregoing it can be concluded that polymerisation of ethene and α-olefins can effectively be carried out in $scCO_2$. In the case of hex-1-ene, a comparison was made with polymerisation behaviour in an organic solvent, which yielded similar molecular weights and molecular weight distributions. In order to improve the solubility of the catalysts, we are currently modifying ligands to enhance the solubility in $scCO_2$.[10,11] Furthermore, a larger test set-up has been constructed to perform (co)polymerisations of propene, including the use of functional monomers as comonomers. Another extension to our work is the evaluation of other late-transition-state olefin polymerisation catalysts known from the literature.[12,13]

Notes and references

‡ Solubility experiments were conducted in a 1.4 ml high-pressure view cell equipped with sapphire windows and a heating jacket. The cell was filled with about 3 mg (2 μmol) solid catalyst. The air was carefully flushed with CO_2 at low pressure. The cell was then heated, filled with CO_2 at high pressure and placed in a UV spectrophotometer.

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