

Surfactant-aided catalytic copolymerization of carbon monoxide with ethene in water as a solvent

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Introduction

The perfectly alternated ethene-carbon monoxide co-polymerisation to poly(1-oxo-trimethylene) was in the last decade an important topic in the field of catalysis [1]. Since we have focalized our research on the influence of solvent on this reaction [2], we are also interested to study the possibility to use green solvents such as water. In fact, water is cheap, readily available, non-toxic, non-flammable, and safe to environment [3]. The use of water may be interesting for many other reasons, in particular for the possibility to obtain very high molecular weight polymers [2]. The catalytic polymerization is efficiently carried out in methanol by using the [Pd(OAc)₂(DPPP)] complex in the presence of an acid (*p*-toluenesulfonic, TsOH) [1]. By replacing methanol with water it is necessary to use the more expensive but solvable [Pd(OAc)₂(DPPP-S)] complex as precursor (DPPP-S is the sulfonated ligand) [4]. As an alternative to the sulfonated ligand we propose to carry out the catalysis in water with the aid of surfactants.

Here we report our preliminary results on the preparation of *alt*- poly(1-oxo-trimethylene) by using the [Pd(OAc)₂(DPPP)] complex in water containing a surfactant above the critical micelle concentration. The performance of various surfactants are highlighted.

Experimental

The polymerization reactions were carried out by using a Hastelloy C autoclave of *ca.* 250 mL provided with a four-blade self-aspirating turbine. The gaseous monomers were supplied to the autoclave in the ratio 1/1 from a gas reservoir. In a typical experiment, 0.650 mg of [Pd(OAc)₂(dppp)] (8.88·10⁻⁴ mmol) was added to 80 mL of solvent. The autoclave was washed with a 1/1 mixture of CO/C₂H₄ (*ca.* 0.5 MPa), at room temperature with stirring. The autoclave was then heated to 90°C and the pressure was then adjusted to the desired value (typically 4.5 MPa total pressure) and, while stirring, maintained constant throughout the experiment (1 h, rate stirring 700 rpm). At the end of the experiment the autoclave was quickly cooled and carefully depressurized. The polymer was completely precipitated by addition of 150 mL of H₂O and the slurry obtained was filtered, washed with water and acetone and dried under vacuum at 70°C. The dried polymer was weighted and the productivity was calculated as (g of polymer)/(gPd·h); the reproducibility was within *ca.* 5%. In the liquid phase, analysed by GC, not soluble oligomers were found. The polymers obtained were fully determined by FT-IR, ¹H and ¹³C NMR spectroscopies.

Results/Discussion

The addition of a surfactant, above the critical micelles concentration, to water permits to dissolve efficiently the hydrophobic [Pd(OAc)₂(dppp)] complex. The catalysis occurs only in the presence of an acid promoter, for instance *p*-toluenesulfonic acid (TsOH). Table 1 shows the influence of different type of surfactants on the productivity to *alt*- poly(1-oxo-trimethylene) at 90°C, 4.5 MPa (CO/ethene = 1/1) and TsOH/Pd (mol/mol) = 865/1.

Table 1. Influence of different surfactants on the *alt*- poly(1-oxo-trimethylene) productivity.

surfactant	Productivity (g/gPd·h)
/	Polymer in traces
Sodium dodecylsulfate (SDS)	4550
Alkyl ethersulfate 26% MW 430-440(AES)	4500
Cetyl Trimethylammonium Bromide (CTAB)	415
Tetrapropylammonium hydroxide (TPAH)	Polymer in traces
Tetrabutylammonium bromide (TBAB)	Polymer in traces
Triton X-100	917

Run conditions: [Pd(OAc)₂dppp] = 0.650 mg ; TsOH/Pd (mol/mol) = 865/1; surfactant = 250 mg; V = 60 mL; 90°C; 50 atm (CO/C₂H₄ = 1/1); 1 h; stirring = 650-700 rpm.

Noteworthy, SDS and AES anionic surfactants lead to the highest productivity *ca.* 4500 g/(gPd·h) whereas with Triton X (non ionic surfactants) only 910 g/(gPd . h) are obtained. Catalytic activity is very poor or not occurs at all when cationic surfactants (CTAB, TPAH, TBAB) are used. It is reported that the ionic surface of micelles forms an *electrical double layer* which contains both counterions and oriented water molecules. It is plausible that anionic surfactants lead to high productivity because the transport of H⁺ ions into or through the layer around the micelles will be facilitated by its negative charge. The acid strongly influences the activity because avoids the Pd(II)-catalyst deactivation to less active or inactive Pd(0) species [1, 2]. According to this, for cationic surfactants, there will be poor or no catalytic activity as a result of unfavorable electrostatic interactions with the surface of micelles.

References.

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