

Pd(II)-catalyzed emulsion copolymerization of carbon monoxide with ethene in CH₂Cl₂/water as a solvent

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Introduction

Chemical, physical and mechanical characteristics of *alt* poly(1-oxo-trimethylene) [1] well fit with a wide range of industrial applications and recently several researchers have shown a renovated keen interest for the application of such a polymer in the field of fibers [2]. In order to obtain fibers, however, high molecular weight polymers are required. In some papers we have reported that high molecular weight polymers require high pressure and low temperature but the nature of the solvent must be considered too [2-4]. The choice of the solvent influences both the activity of the catalyst and the average molecular weight of the polymer. Usually the catalysis is efficiently carried out in methanol by using the [Pd(OAc)₂(DPPP)] complex in the presence of an acid (p-toluenesulfonic, TsOH) [5] which leads to polymers with not so high average molecular weight. By replacing methanol with CH₃COOH-water also [PdCl₂(DPPP)] complex efficiently catalyzes the reaction leading also to an increase of the polymer molecular weight [3]. By continuing the research on the influence of the solvent on the molecular weight, here we report our preliminary results on the preparation of *alt*- poly(1-oxo-trimethylene) by emulsion catalytic polymerization. The [PdCl₂(DPPP)] complex has been dissolved in a CH₂Cl₂-H₂O emulsion and the productivity has been optimized.

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. In a typical experiment, 0.650 mg of [PdCl₂(DPPP)] 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 precipitate 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. The viscosity average molecular weight has been measured as LVN (Limit Viscosity Number).

Results/Discussion

The hydrophobic [PdCl₂(DPPP)] is not utilized as catalyst in water. Since such a complex is well soluble in CH₂Cl₂ and water is the activating agent [1-5], we make an emulsion with the aid of SDS (sodium dodecylsulfate). Fig. 1 shows the influence of the CH₂Cl₂-H₂O percent on the productivity when SDS concentration was 4.77 mM. The productivity passes through a maximum of ca. 8000 g/(gPd·h) when the CH₂Cl₂ molar percent in water (O/W emulsion) is 20%.

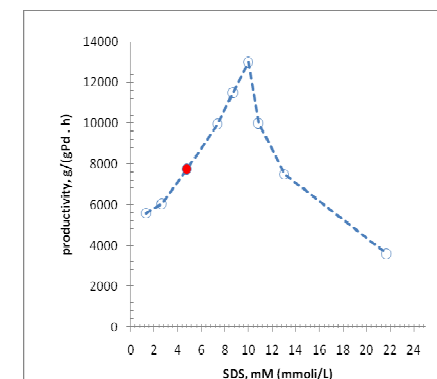
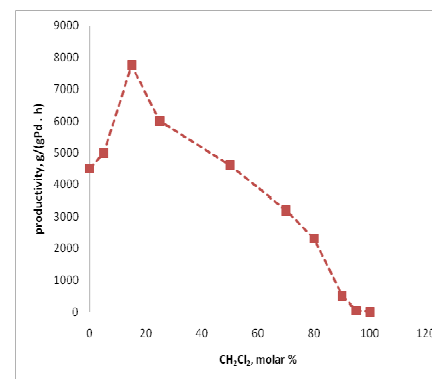


Fig. 1. Influence of CH₂Cl₂ concentration Fig. 2. Influence of SDS concentration
Run conditions: [PdCl₂(DPPP)] = 0.650 mg ; TsOH/Pd (mol/mol) = 865/1; V = 60 mL; 90°C; 5.0 MPa (CO/C₂H₄ = 1/1); 1 h; stirring = 650-700 rpm.

The amount of SDS has been optimized under conditions of Fig. 2 and productivity increases and passes through a maximum of ca. 13000 g/(gPd·h) when the SDS concentration is ca. 10 mM. Emulsion copolymerization is more efficient than the reaction in methanol as a solvent (ca. 8000 g/(gPd·h)). The product is a high molecular weight polymer (LVN is 1.8 dL/g respect to 0.5 dL/g in methanol).

References

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