Supporting Information

Aqueous Dispersions of Polypropylene and Poly(1-butene) with Variable Microstructures formed with Neutral Ni(II)-Complexes

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General considerations. All manipulations (catalyst preparation and polymerizations) were performed using standard Schlenk techniques under an argon atmosphere. NMR spectra were recorded on a Bruker ARX 300 or a Varian AS 400 spectrometer. ^1H and ^{13}C NMR spectra of polymers were obtained in 1,1,2,2-tetrachloroethane- d_2 or CDCl_3 at room temperature. Branching structures were assigned according to [1]. Dynamic light scattering (DLS) on diluted latex samples was performed on a Malvern Nano-ZS ZEN 3600 particle sizer (173° back scattering). The autocorrelation function was analyzed using the Malvern dispersion technology software 3.30 algorithm to obtain volume and number weighted particle size distributions. Differential scanning calorimetry (DSC) was performed on a Netzsch DSC 204 F1 at a heating rate of 10 K/min. DSC data reported are determined from the second heating scan. Molecular weight were determined with a PL GPC-220 instrument equipped with mixed B columns in trichlorobenzene at 160°C vs. polyethylene standards.

Materials. Propylene (99.95% purity) and 1-butene (99.6 % purity) supplied by GHC GmbH were used without further purification. 1-hexene was dried over CaH_2 and distilled under argon. Toluene was dried over Na and distilled under argon. Deionized water was degassed by distillation under nitrogen prior to use. Sodium dodecyl sulfate (SDS) was purchased from Fluka and degassed under argon prior to use. Metal complexes were prepared according to a literature procedure.²

Polymerization in non-aqueous media were carried out in a mechanically stirred (500 rpm) pressure reactor equipped with a heating/cooling jacket supplied by a thermostat controlled by a thermocouple dipping into the polymerization mixture. For experiments with propene a 1 L stainless steel vessel was used and in experiments with 1-butene a 500 mL glass vessel. After evacuation for 30 min at 80°C, the reactor was charged with a solution of the catalyst in toluene. The monomer, which had previously been condensed at -78°C into a steel cylinder hanging from a balance equipped with a dip tube connected to the reactor, was transferred by means of back pressure to the precooled autoclave at 5°C (in the case of 1-hexene, the monomer was added to the toluene solution of the catalyst). The total volume of the reaction mixture amounted to 150 mL in all cases. After a specified reaction time the reactor was rapidly vented, and subsequently heated to 50 °C under reduced pressure to remove any unreacted monomer. The polymerization mixture was poured into a threefold volume of methanol to completely precipitate all dissolved low molecular weight material. The polymer was separated by decanting, washed three times with methanol and dried in vacuo.

Polymerization in aqueous emulsion. The pressure reactor was heated under vacuum at 80°C for 30 min and then flushed with argon. An aqueous (150 mL water) solution of 1.125 g sodium dodecyl sulfate and a solution of catalyst precursor in a mixture of toluene (2 mL), hexadecane (0.1 mL), both prepared separately in Schlenk tubes under argon, were transferred to the reactor by a pump. The monomer, which had previously been condensed at -78°C into a steel cylinder hanging from a balance equipped with a dip tube connected to the reactor, was transferred by means of back pressure to the precooled autoclave at 5°C. The two phase system was homogenized by means of an ultrasound sonotrode mounted in the reactor (operated at 250 W, ten minutes), keeping the temperature below 5 °C. The resulting miniemulsion was stirred at 5°C for the specified reaction time. The reactor was vented and heated to 50 °C under reduced pressure to remove any unreacted monomer. The emulsion

obtained was filtered through glass wool to separate any coagulate and to determine its amount. For determination of yields and for further polymer analysis a specified portion of the latex was precipitated by pouring into excess methanol. The liquid polymer was separated, washed with methanol and dried in vacuo.

(1) a) Randall, J. C. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1989**, C29, 201 – 317. b)

Axelsson, D. E.; Levy, G. C.; Mandelkern, L. *Macromolecules* **1979**, 12, 41. c) Assakura, T.;

Nakayama, N.; Demura, M.; Asano, A. *Macromolecules*, **1992**, 25, 4876.

(2) Zuideveld, M. A.; Wehrmann, P.; Röhr, C.; Mecking, S. *Angew. Chem.* **2004**, 116, 887; *Angew.*

Chem. Int. Ed. **2004**, 43, 869.

Figure S1. ^{13}C NMR spectrum of polypropylene with assignments (polymer prepared with **3**).

Figure S2. ^{13}C NMR spectrum of poly(1-butene) with assignments (polymer prepared with **1**).

Figure S3. ^{13}C NMR spectrum of poly(1-hexene) with assignments (polymer prepared with **1**).

Note the absence of ethyl- and propyl-branches.

Figure S4. ^1H NMR spectrum of polypropylene prepared with **3**; signals of endgroups enlarged.

Figure S5. ^1H NMR spectrum of poly(1-butene) prepared with **1**; signals of endgroups enlarged.

Figure S6. DSC trace of polypropylene prepared with **3** in toluene solution. Heating rate: 10K min⁻¹

Figure S7. DSC trace of poly(1-butene) prepared with **1** in toluene solution. Heating rate: 10K min⁻¹

Figure S8. DSC trace of poly(1-butene) prepared with **1** in miniemulsion. Heating rate: 10K min⁻¹.

Figure S9. DSC trace of poly(1-butene) prepared with **3** in toluene solution. Heating rate: 10K min^{-1} .

Figure S10. DSC trace of poly(1-butene) prepared with **3** in miniemulsion. Heating rate: 10K min^{-1} .

Figure S11. DSC trace of poly(1-hexene) prepared with **1** in toluene solution. Heating rate: 10K min^{-1} .