Supporting Information

A General Route to Very Small Polymer Particles with Controlled Microstructures

*Vincent Monteil, Peter Wehrmann, and Stefan Mecking**

General considerations. All manipulations (catalyst preparation and polymerizations) were performed using standard Schlenk techniques under an argon atmosphere. NMR spectra of polyalkenamers were recorded with a Varian Inova 400 spectrometer in $CDCl_3$ at 25°C. High temperature NMR spectra (for 1,2-polybutadienes) were recorded with a Bruker Avance DRX 600 in 1,1,2,2-tetrachloroethane-d_2 at 100°C. 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. Surface tension were measured on a Krüss K100 tensiometer with the Wilhelmy plate method.

Materials. Ethylene of 3.5 grade supplied by Gerling Holz + Co and 1,3-butadiene (99.5 % purity) supplied by Messer-Griesheim GmbH were used without further purification. Norbornene (NB) from

Fluka, cyclooctadiene (COD) from Acros, cyclooctene (COE) from Fluka were dried over CaH_2 and distilled under argon. Toluene was dried over Na and distilled under argon. Ethanol, isopropanol and pentanol were degassed by repeated freeze-pump-thaw cycles. Deionized water was degassed by distillation under nitrogen prior to use. Sodium dodecyl sulfate (SDS) and dodecyltrimethylamonium bromide (DTAB) were purchased from Fluka and degassed under argon prior to use. 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil), triphenylphosphine, cobalt(II) 2-ethylhexanoate, sodium borohydride, carbon disulfide, catalyst **3** (Grubbs 1st generation) and **4** (Grubbs 2nd generation) were purchased from Aldrich and degassed under argon prior to use. Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate (antioxidant) was purchased from Aldrich. Bis(1,5-cyclooctadiene)nickel ($[Ni(cod)_2]$)[1], $[(tmeda)NiMe_2]$[2] and salicylaldimine ligand[3] (corresponding to complex **2**) were prepared according to literature procedures.

Synthesis of polyethylene particles.

Catalyst **1** was prepared according to literature:[4] equal molar amounts of 2,3,5,6-tetrachloro-1,4-benzoquinone and PPh_3 were dissolved under argon in a mixture of the given amounts of toluene and alcohol (isopropanol for microemulsions stabilized by DTAB or pentanol for microemulsions stabilized by SDS as a surfactant). After stirring for about 20 min, the solution obtained was transferred to a 1.1-fold molar excess of bis(1,5-cyclooctadiene)nickel.

Polymerization procedure (also cf. Table 1): To the catalyst solution (**1** or **2**) in toluene was added an aqueous solution of surfactant (SDS or DTAB) and optionally ‘cosurfactant’ (pentanol). A transparent catalyst microemulsion formed spontaneously upon gentle stirring with a magnetic stirr bar. The catalyst microemulsion was transferred to a mechanically stirred 250 ml pressure reactor equipped with a heating/cooling jacket controlled by a temperature sensor dipping into the reaction mixture. The reactor was flushed and pressurized with ethylene, while rapidly heating to the specified temperature under stirring (1000 rpm). The pressure was kept constant during the entire polymerization by feeding monomer. After the desired reaction time the reaction was stopped by cooling and releasing the gas pressure.

Synthesis of butadiene particles. CAUTION when working in glass vessels under pressure. A toluene solution (5 ml) of cobalt(II) 2-ethylhexanoate (320 μmol) was introduced under argon to a mechanically stirred 250 ml pressure glass reactor equipped with a heating/cooling jacket controlled by a temperature sensor dipping into the reaction mixture. After evaporating toluene in vacuo, 6.5 g of butadiene were condensed at -5°C. An ethanol solution (3 ml) of sodium borohydride (710 μmol) was added, affording a solution of the precatalyst $[Co(C_8H_{13})(C_4H_6)]$. An aqueous solution of surfactant (9.3 g SDS/ 4 g pentanol and 80 g H_2O) was then transferred to the reactor by means of a pump under stirring (1000 rpm), affording a transparent butadiene/precatalyst microemulsion. A toluene solution of carbon disulfide (320 μmol, $[CS_2] / [Co] = 1$) was pumped into the reactor, which was then rapidly heated to the desired temperature ($T = 40°C$). After 2h the reaction was stopped by cooling and releasing residual gas pressure, affording a light brown transparent latex.

Synthesis of poly(cycloolefin) particles. To a toluene solution of catalyst (**3**, 30 μmol for norbornene polymerization or **4,** 50 μmol for COD or COE polymerization, 3.25 g toluene) was added under argon an aqueous solution of surfactant (4.65 g SDS / 2 g pentanol / 40 g H_2O), affording a purple transparent catalyst microemulsion. The monomer microemulsion was prepared in a 150 ml flask equipped with a condenser by mixing the desired amount of monomer (2.5 g norbornene dissolved in 0.75 g of toluene, 3.25 g COD or COE) and an aqueous solution of surfactant (4.65 g SDS / 2 g pentanol / 40 g H_2O). The monomer microemulsion was then transferred to the catalyst microemulsion, while heating to the specified temperature ($T = 25°C$ for norbornene polymerization and $T = 80°C$ for COE or COD polymerization). Polymerization for 3.5 h (norbornene) or 2.5 h (COD and COE), respectively, afforded light gray latices.

Workup of latices. The latices obtained were filtered through a funnel with glass wool prior to further workup and analysis. Solids contents were determined with a moisture analyzer. For determination of polymer content, the latex was added to an excess of methanol (after adding octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate to latex for preventing crosslinking of unsaturated polymers). The precipitated polymers were isolated by filtration, washed with methanol and dried at 50 °C under vacuum over night.

Additional polymerization data and polymer analysis for poly(cycloolefins).

monomer	pol. cont. (wt%)	coag. polym. (g)	conversion (%)	vol. av. size (nm)[a]	Mw, g/mol (PDI)[b]	Tg (°C)	Tm (°C)	Microstructure (cis/trans)[c]
NB	1.8	0.05	65	23	5000 (3.4)	42	-	20/80
COD	3.2	0.4	100	32	62400 (1.9)	- 88	-	26/74
COE	1.8	-	55	22	220000 (1.7)	n.o.[d]	20	34/62

[a] Volume average particle size determined by DLS. [b] Determined by GPC vs. linear PE standards. [c] Stereochemistry of double bonds determined by ^{1}H or ^{13}C NMR according to literature.[5] [d] n.o.: not observed.

(1) Schunn, R. A.; Ittel, S. D.; Cushing, M. A. *Inorg Synth.* **1990**, *28*, 94.

(2) Kaschube, W.; Poerschke, K. R.; Wilke, G. *J. Organomet. Chem.* **1988**, *355*, 525.

(3) Zuideveld, M. A.; Wehrmann, P.; Röhr, C.; Mecking, S. *Angew. Chem.* **2004**, *116*, 887; *Angew. Chem. Int. Ed.* **2004**, *43*, 869.

(4) Bauers, F. M.; Mecking, S.; Chowdhry, M. M.; Mecking, S. *Macromolecules* **2003**, *36*, 6711.

(5) For ^{13}C NMR analysis of polyalkenamers see: Dounis, P.; Feast, W.J.; Kenwright, A. M. *Polymer* **1995**, *36*, 2787. For ^{1}H NMR analysis of polynorbornene see : Petasis, N. A.; Fu, D-K. *J. Am. Chem. Soc.* **1993**, *115*, 7208.

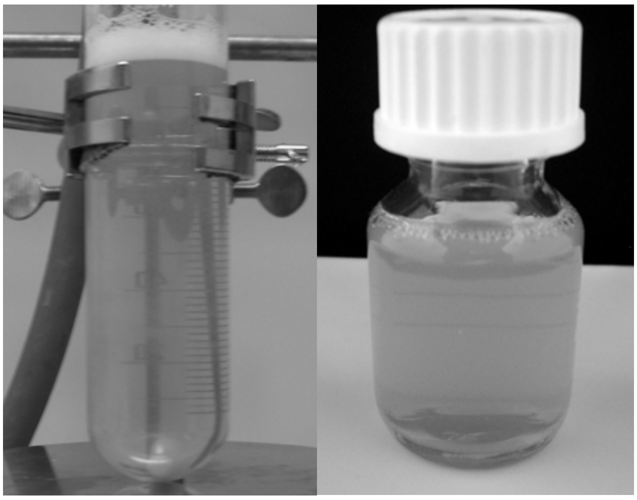
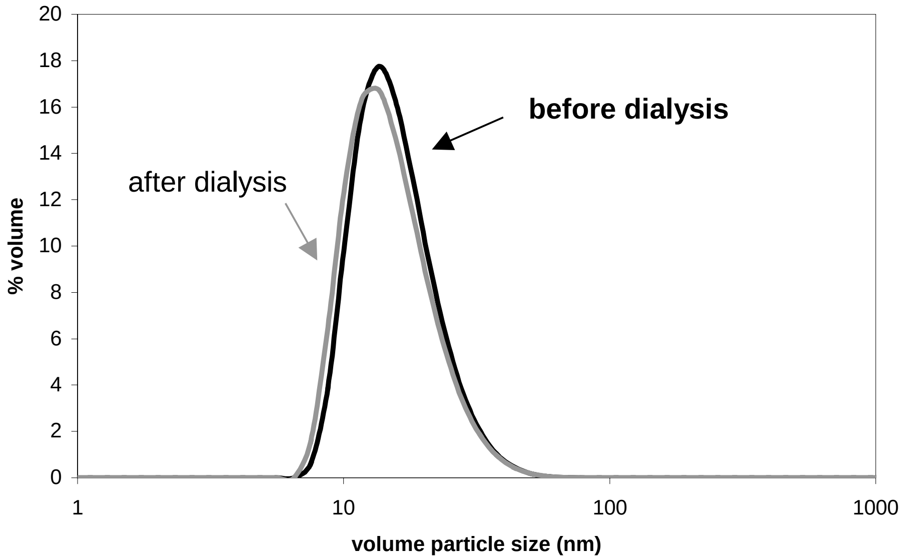


Figure S1. Optical appearance of : a) microemulsion of solution of catalyst **1**; b) polyethylene latex (Table 1, entry 4).



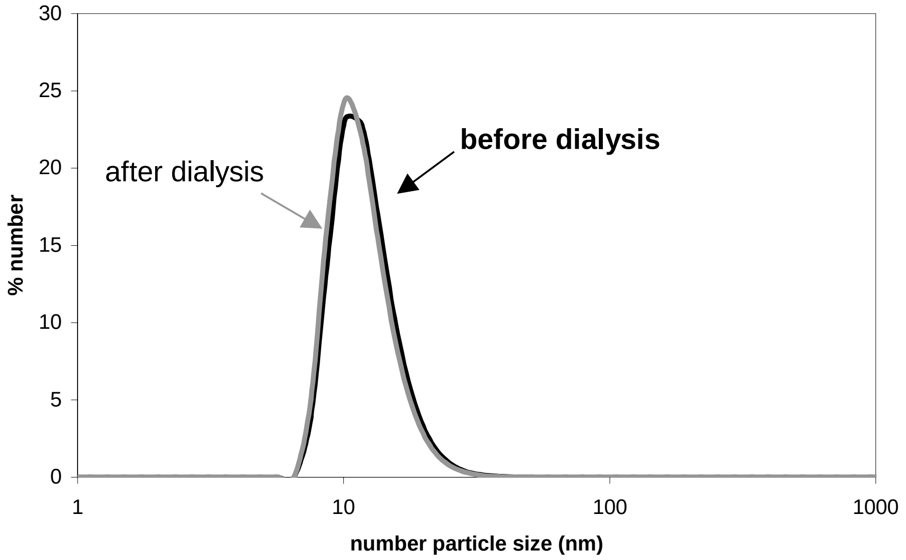


Figure S2. Volume and number particle size distribution of polyethylene latices obtained by DLS (Table 1, entry 4 before and after dialysis).

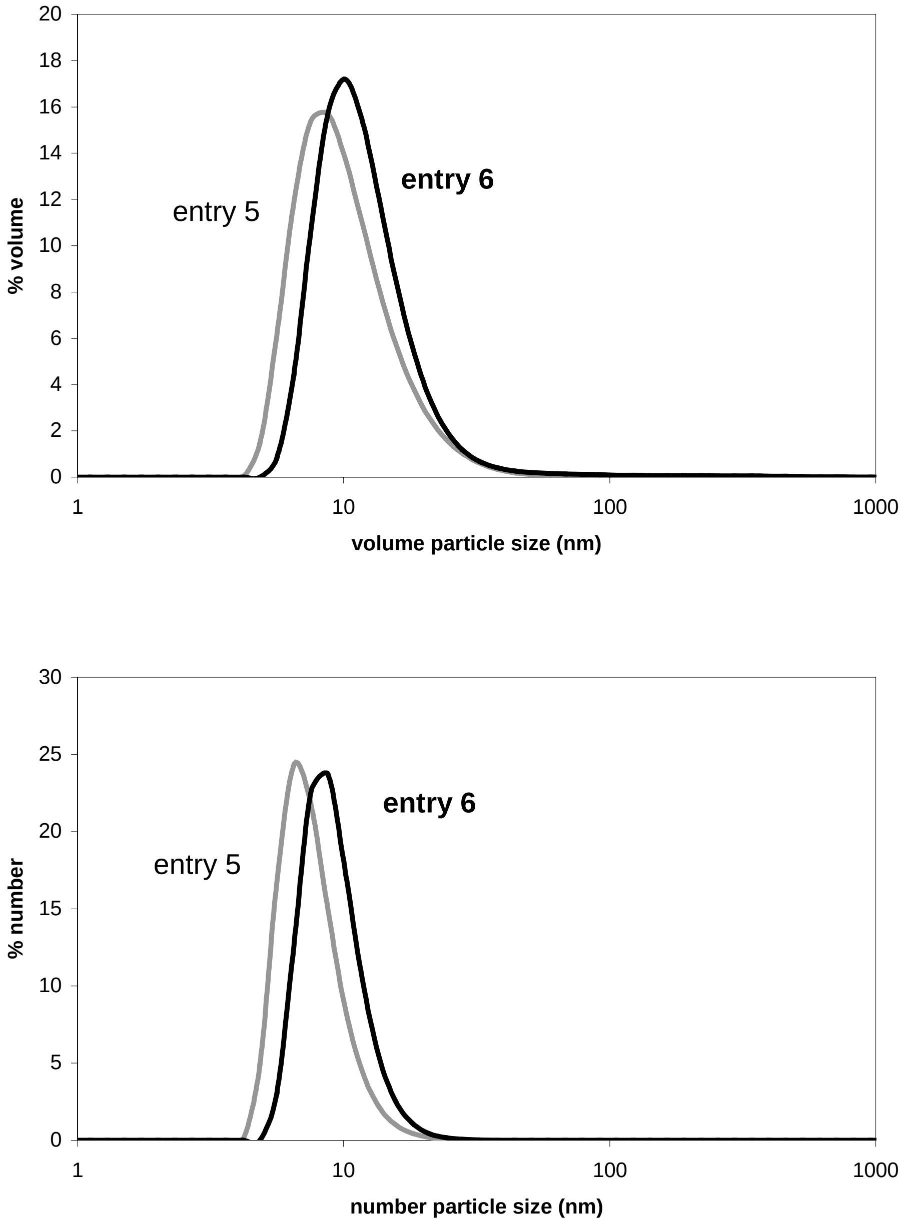
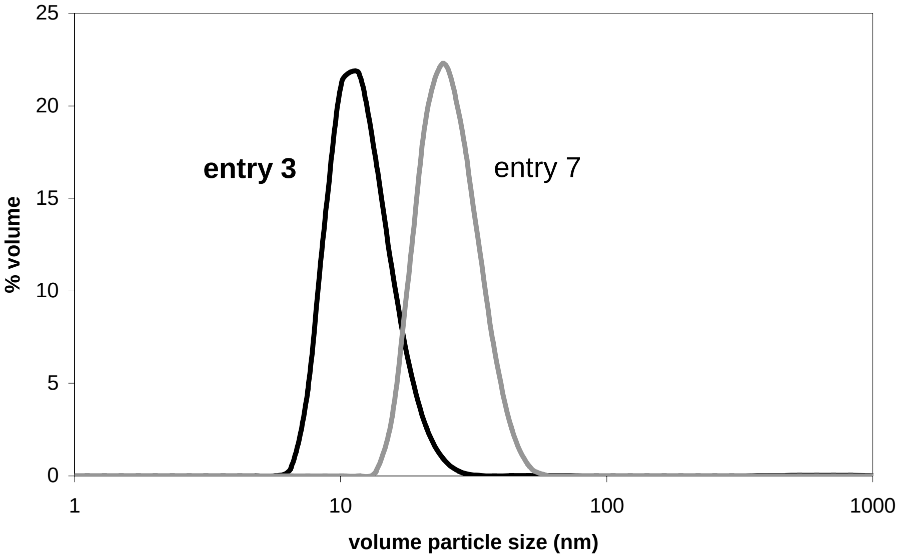


Figure S3. Volume and number particle size distribution of polyethylene latices obtained by DLS (Table 1, entries 5 and 6).



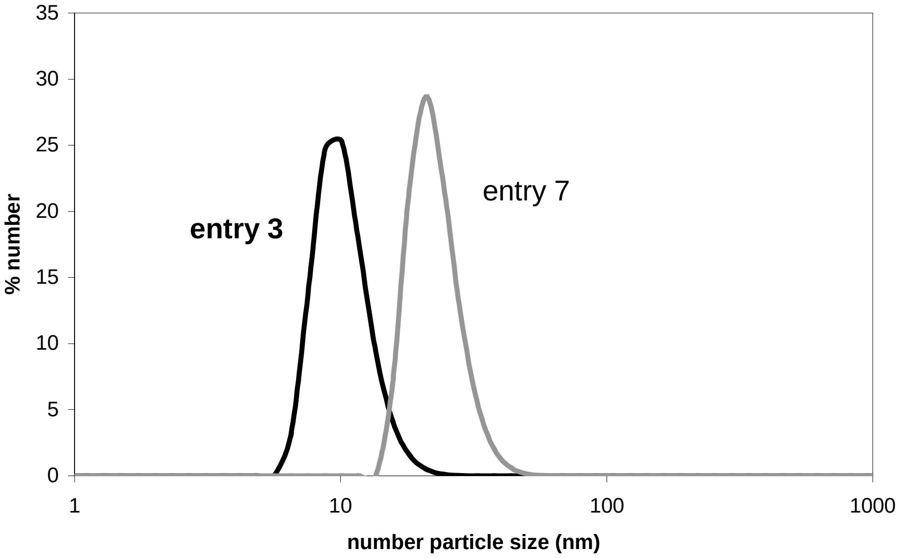
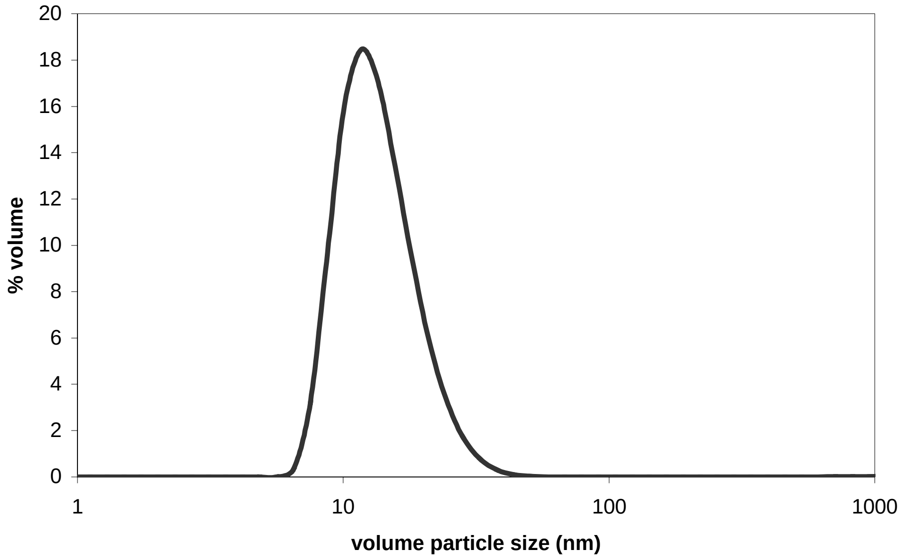


Figure S4. Volume and number particle size distribution of polyethylene latices obtained by DLS (Table 1, entries 3 and 7).



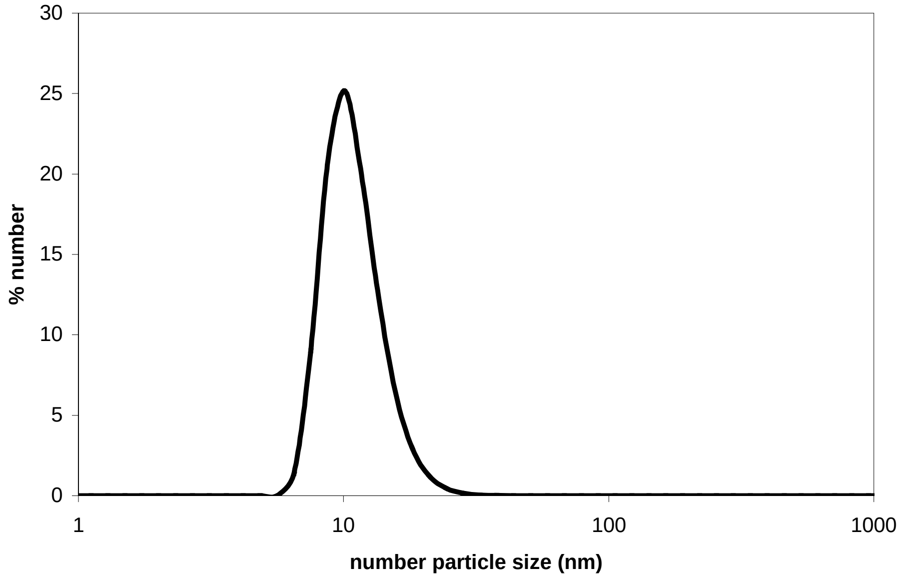


Figure S5. Volume and number particle size distribution of 1,2-polybutadiene latex obtained by DLS.

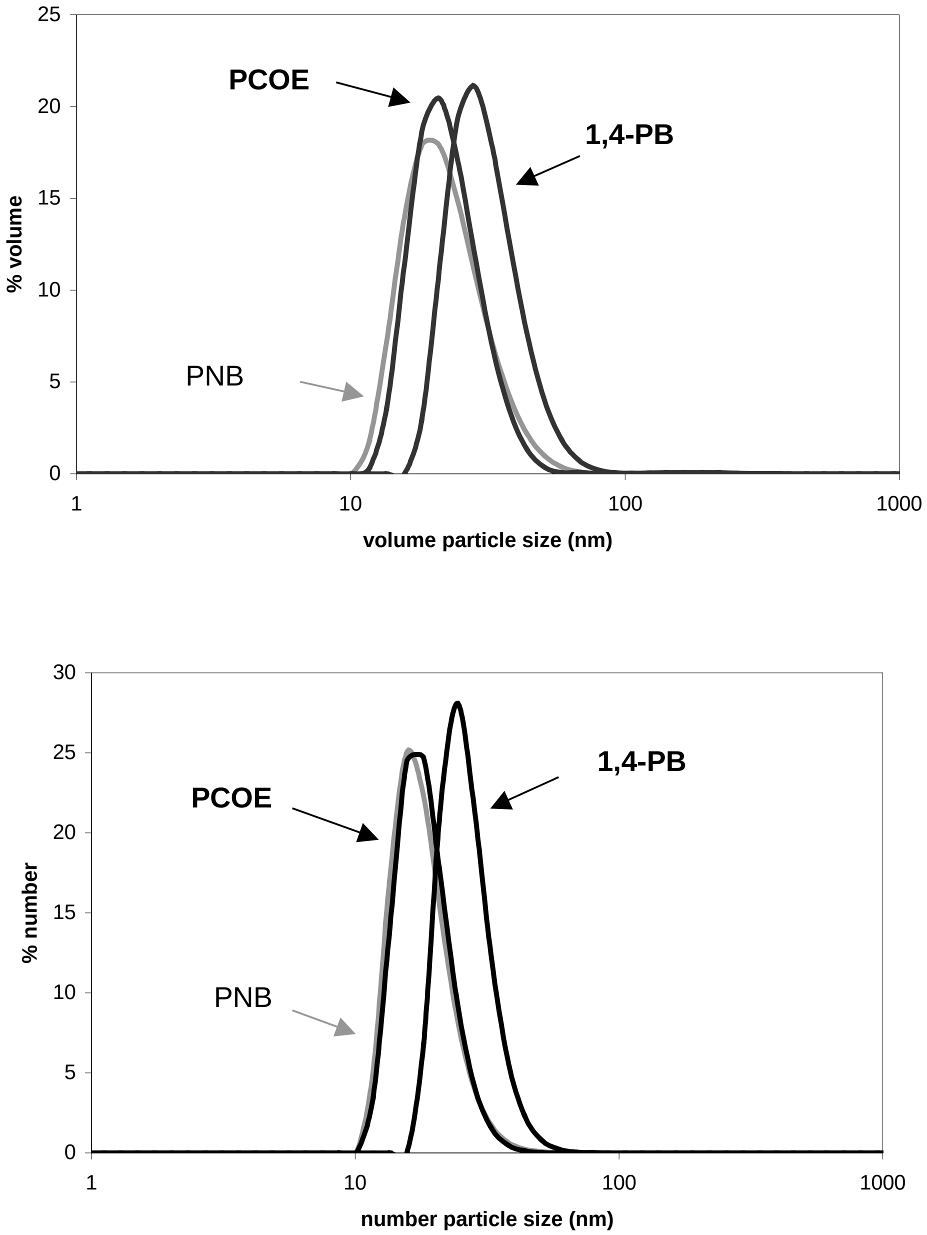


Figure S6. Volume (a) and number (b) particle size distribution of poly(cycloolefins) latices obtained by DLS (PNB: Polynorbornene, PCOE: Poly(cycloctene), 1,4-PB: Poly(cyclooctadiene)).