

A General Route to Very Small Polymer Particles with Controlled Microstructures

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Generation and control of submicron structures is of fundamental interest. In the synthesis of polymer particles, the size range of <30 nm is challenging. Mechanical disintegration is of great practical importance as a general route; however, it is not suited for target particle sizes of <50 nm, and very broad particle size distributions are obtained.¹ A complementary route is the generation of larger structures from small molecules (or atoms, respectively, ions) as a precursor. Free radical emulsion polymerization is applied industrially on a large scale for the synthesis of polymer dispersions. Particles sizes are in the range of 50 nm to 1 μm .²

Generally, some high degree of dispersion of the initial reaction mixture is a prerequisite for generating a large number of small particles. Microemulsions are highly disperse. A microemulsion is a thermodynamically stable mixture of at least two immiscible liquids and a surfactant, which exists in a certain range of compositions.^{3,4} Frequently, an alcohol is added to achieve the microemulsion regime. Microemulsions can possess globular phase structures (oil-in-water, o/w, or water-in oil, w/o), lamellar, or irregular bicontinuous structures.³ Spontaneous formation is an indicator for the existence of a microemulsion.

Free radical polymerization of monomer microemulsions can afford polymer particles as small as 10 nm.^{3,4} Examples are restricted to a limited number of monomers, such as styrene or acrylates (o/w) or acrylamide (w/o). Note that monomer droplets are usually not necessarily polymerized 1:1 to particles, rather rearrangement processes occur. The use of water-soluble radical initiators (classical emulsion polymerization) is not sufficient to generate small particles; also, the monomer must be strongly dispersed (microemulsion). In classical free radical emulsion polymerization, initiator radicals are formed continuously over the duration of the reaction. Therefore, a large part enters already existing particles, only a small portion generates new particles.⁵ This can be different in catalytic polymerization, where chain termination is slower or absent and all active catalyst can be present at the beginning of the reaction.⁶

By contrast to free radical techniques, catalytic polymerization offers a much broader scope of control of polymer microstructure. In terms of the monomers applicable, both techniques are complementary. Catalytic polymerization in aqueous systems affording polymer latices has been reported recently.^{6–10} Average particle sizes are 80–500 nm. The synthesis of smaller 20 nm particles has been reported; however, this requires a water-soluble catalyst and is restricted to the particular case of polymerization of ethylene to low molecular weight linear polyethylene by an undefined catalyst.⁶ We report herein a general route for the catalytic synthesis of previously inaccessible very small polymer particles of 10–30 nm size by means of catalyst microemulsions. Known lipophilic catalysts are employed.

Under typical polymerization conditions (up to 40 bar, 20–60 °C), ethylene does not form a liquid phase. An o/w transparent microemulsion of a solution of a (water-insoluble lipophilic) catalyst

Table 1. Synthesis of Polyethylene Particles^a

entry no.	toluene/H ₂ O/ SDS/pentanol/ DTAB (g)	cat.	time (h)	polymer content (wt %)	particle size (nm) ^b	<i>M_w</i> , g mol ⁻¹ (<i>M_w</i> / <i>M_n</i>) ^c
1	6.5/80/9.3/4/–	1	1	4.5	73	1.8 × 10 ³ (2.8)
2 ^d	6/83/6/5/–	1	2	3.5	157	2.0 × 10 ³ (2.3)
3	2/93/–/–/5	1	2	1.9	12	2.9 × 10 ³ (2.8)
4	2/93/–/–/5	1	2	4.7	16	7.2 × 10 ³ (3.8)
5	2/93/–/–/5	1	4	7.5	11	3.0 × 10 ³ (3.7)
6 ^e	2/93/–/–/5	1	4	16.6	13	1.7 × 10 ³ (2.9)
7	6.5/80/9.3/4/–	2	0.5	3.2	26	2.0 × 10 ⁵ (2.6)

^a Polymerization conditions: *T* = 60 °C (entry 7: 20 °C); ethylene pressure = 20 bar (entries 1–3) or 40 bar (entries 4–7); catalyst **1**: 100 μmol PPh₃, 100 μmol chloranil, 110 μmol Ni(cod)₂ (entry 6: all amounts doubled), 0.9 mL of 2-propanol in entries 3–6; **2**: 40 μmol salicylaldimine + 40 μmol [(tmeda)NiMe₂]. ^b Volume average particle size from DLS. ^c GPC versus linear PE standards. ^d Coagulated polymer: 1 g. ^e Coagulated polymer: 7 g.

precursor in a small amount of toluene formed spontaneously by mixing appropriate amounts (Table 1) of toluene catalyst solution, water, and cationic surfactant (dodecyltrimethylammoniumbromide, DTAB) or anionic surfactant/alcohol mixtures (SDS, sodiumdodecyl sulfate/pentanol).¹¹

Reacting a mixture of triphenylphosphine and chloranil with bis-(1,5-cyclooctadiene)nickel affords an active catalyst (**1**) for polymerization of ethylene in emulsion.^{8c} Presumably, the active species is a nickel(II) phosphinoenolate complex.^{8c} Exposure of microemulsions of **1** to ethylene in a pressure reactor afforded polyethylene latices (Table 1 and Figure S1 in Supporting Information).¹² With the SDS/pentanol system, colloiddally unstable latices with relatively large average particle size are obtained (entries 1 and 2). Probably this is related to an insufficient microemulsion stability in the early stages of polymerization for this particular system with catalyst **1**, and not to insufficient stability of once-formed particles, as SDS is a good stabilizer for polyethylene particles (also cf. results with **2**). With the DTAB-based system, colloiddally stable latices consisting of very small particles of 11–16 nm exclusively are obtained (Table 1, entries 3–6; particle size distributions from DLS cf. Supporting Information). Dispersions with polymer contents up to 17 wt % are formed. The catalyst retains its activity over several hours (Table 1, entries 4 and 5). The particles consist of low molecular weight linear polyethylene (*M_w* < 10⁴ g mol⁻¹; *T_m* = 120–130 °C), as expected for catalyst **1**. These molecular weights are close to the entanglement limit,¹³ which can be considered as the borderline between oligomers and polymers. In terms of material properties, higher molecular weights are desirable. Ni(II) salicylaldimine complexes, such as [{ κ^2 -*N,O*-6-*C*(H)=NAr-2,4-*I*₂C₆H₂O}NiMe (tmeda)] (Ar = 2,6-{3,5-(F₃C)₂C₆H₃}₂C₆H₃) (**2**), are known to polymerize ethylene to high molecular weight polymers.^{8d,14} A microemulsion of a toluene solution of **2** with SDS/pentanol afforded a colloiddally stable latex consisting of 26 nm particles (entry 7; Figure S4 in Supporting

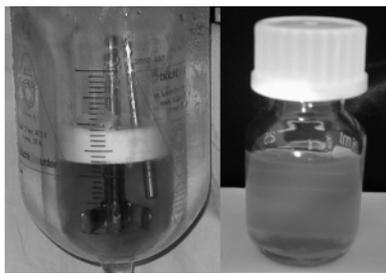


Figure 1. Optical appearance of (a) microemulsion of butadiene and cobalt catalyst precursor, and (b) 1,2-polybutadiene latex.

Information). As anticipated, molecular weight is high. In contrast to **1**, **2** lost activity rapidly during polymerization.

The amount of surfactant is dictated by the composition of the microemulsion regime of the individual system. Albeit surfactant content of the nanoparticle dispersions is moderate (5 wt % DTAB versus up to 17 wt % polymer), in terms of a general route to small particles, a lower surfactant content is desirable. Dialysis allowed for removal of ca. 70% of the surfactant. Stability and particle size are retained (16 nm after dialysis of latex from entry 4; Figure S2 in Supporting Information). Surface tensions increase from 37 to 60 mN/m during dialysis, indicating the absence of free surfactant micelles in the dialyzed latices.

Syndiospecific 1,2-polymerization of butadiene by the catalyst system $[\text{Co}(\text{C}_8\text{H}_{13})(\text{C}_4\text{H}_6)]/\text{CS}_2^{15}$ was studied. Butadiene is liquid under the reaction conditions. A monomer microemulsion containing dissolved cobalt precatalyst was prepared (Figure 1a; composition: 6.5 g of butadiene/9.3 g of SDS/4 g of pentanol/80 g of H_2O). CS_2 was added to start the polymerization. As observed previously,^{9b} the cobalt catalyst is deactivated by DTAB. In contrast, with SDS/pentanol, a 6 wt % colloidal stable latex consisting of 14 nm particles was obtained (Figure 1b and Figure S5 in Supporting Information).

^1H , ^{13}C NMR, and DSC reveal the particles to consist of regio- and stereoregular syndiotactic 1,2-polybutadiene, as anticipated (94% 1,2; 6% 1,4-cis, $T_m = 160$ °C, $M_w = 2 \times 10^5$ g/mol, $M_w/M_n = 2.3$).

Ring opening polymerization of strained and nonstrained cycloolefins with Ru alkylidenes was studied. Due to the high polymerization activity of the catalysts even at room temperature, the procedure of butadiene polymerization (activation of catalyst solution in monomer by CS_2) cannot be used.

A toluene solution of norbornene (mp 40 °C) was added to a stirred microemulsion of a solution of $[(\text{PCy}_3)_2\text{Cl}_2\text{Ru}=\text{CHPh}]$ (**3**) in toluene over 5 min. All attempts afforded only coagulated polymer. Apparently, the catalyst microemulsion is destabilized upon adding the monomer. Polymerization occurs in the large droplets formed, similar to suspension polymerization.

As a different approach, a monomer microemulsion was added to a catalyst microemulsion (compositions cf. Supporting Information). Microemulsion stability is retained, and apparently, the monomer progressively diffuses into the catalyst droplets. With SDS/pentanol, stable lattices of poly(cycloolefins) were prepared. Norbornene polymerization at room temperature with **3** afforded a transparent colloidal stable latex of 23 nm volume average size (polymer content 1.8 wt %; $M_w = 5 \times 10^3$ g/mol; $M_w/M_n = 3.4$; 80% trans double bonds). Less strained cyclooctadiene (COD) and cyclooctene (COE) were polymerized by $[(\text{PCy}_3)(\eta\text{-C-C}_3\text{H}_4\text{N}_2\text{-Mes}_2)\text{Cl}_2\text{Ru}=\text{CHPh}]$ (**4**) at 80 °C to stable lattices. Particles of perfect 1,4-polybutadiene from COD polymerization with a volume average size of 32 nm were obtained (polymer content 3.2 wt %; $M_w = 6.2 \times 10^4$ g/mol; $M_w/M_n = 1.9$; 76% trans). Poly-COE

particles of 22 nm size were prepared (polymer content: 1.8 wt %; $M_w = 2.2 \times 10^5$ g/mol; $M_w/M_n = 1.7$; 62% trans).

In conclusion, we report a simple and general strategy for the preparation of very small polymer particles by catalytic polymerization. The systems described differ with respect to the state of the initial reaction mixture (ethylene as a gaseous monomer versus liquid monomers; catalyst microemulsified with monomer or separately). However, they have in common a very high degree of dispersion, which appears to be the key to obtain a large number of very small particles (note that, just like in free radical microemulsion polymerization, the particle sizes are not simply a reproduction of the structure of the initial microemulsion¹¹). Conventional lipophilic late transition metal complexes can be employed. High molecular weight materials of various structures, including stereo- and regioregular polymers, can be prepared in the form of particles of 10–30 nm size.

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Supporting Information Available: Synthetic procedures and polymer and latex analyses, photo of PE latex. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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