

# Catalytic Polymerization in Emulsion

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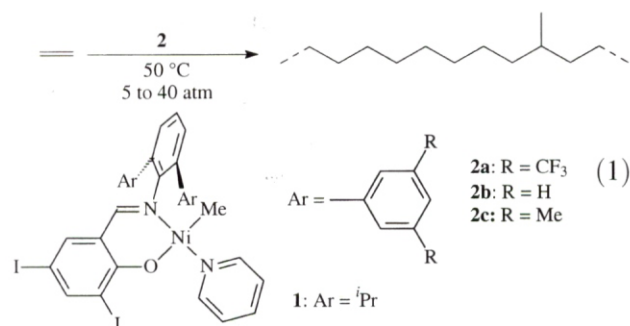
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Emulsion polymerization, affording polymer latexes, is one of the most important polymerization processes. To date, polymer latexes are produced by free radical polymerization exclusively.<sup>[1]</sup> Catalytic polymerizations in aqueous systems are hampered by the fact, that the early transition metal catalysts used commercially for polyolefin production are extremely sensitive to moisture. Such reactions are of interest however, as polymer dispersions and corresponding materials inaccessible by other polymerization types can be obtained. Catalysts based on late transition metals are less sensitive,<sup>[2]</sup> and it has recently been found that polyolefin<sup>[3,4]</sup> and polyketone dispersion<sup>[3e]</sup> can be obtained by catalytic emulsion polymerization.

Issues addressed in this contribution are an increase in catalyst activity in the preparation of high-molecular-weight polyethylene in emulsion; polyethylene latex synthesis with a simple in situ system and also the latex particle structure.

Latexes of high-molecular-weight polyethylene can be obtained with complex **1** as a catalyst precursor.<sup>[3d]</sup> Higher catalyst efficiencies are desirable, however. Upon introduction of steric bulk by means of phenyl groups with electron-withdrawing trifluoromethyl substituents in 3,5-position (**2a**) instead of the typical isopropyl-groups (**1**), catalytic activities exceeding

$4 \times 10^4$  TO h<sup>-1</sup> are observed in toluene as a reaction medium [Eq. (1)], corresponding to five times the activity of **1** under otherwise identical conditions.<sup>[3c]</sup>



Interestingly, polymer properties are strongly dependant on the nature of the remote 3,5-substituents (Table 1). Whereas a semicrystalline polymer with a small amount of methyl branches is obtained for R = CF<sub>3</sub> (**2a**), branching increases for R = H (**2b**), and an entirely amorphous polymer with ca. 76 methyl branches is obtained for R = Me (**2c**). At the same time polymer molecular weight decreases by an order of magnitude. The solid state molecular structures and NMR properties of the catalyst precursors indicate that this effect is due to the electronic properties of R, rather than a steric effect. In preliminary experiments in

Table 1. Ethylene polymerization in toluene and in aqueous emulsion with catalyst precursors **2a–c**.

entry	catalyst precursor	average activity / (mol(ethylene) × mol(Ni) <sup>-1</sup> · h <sup>-1</sup> )	$\bar{M}_n$ g × mol <sup>-1</sup>	$\bar{M}_w/\bar{M}_n$	T <sub>m</sub>	branches per 1000 C
1	<b>2a</b>	> 4.2 × 10 <sup>4a)</sup>	1.9 × 10 <sup>4</sup>	5.1	123 °C	10
2	<b>2b</b>	1.6 × 10 <sup>4b)</sup>	2.9 × 10 <sup>3</sup>	2.3	(80 °C)	52
3	<b>2c</b>	> 4.3 × 10 <sup>4a)</sup>	1.1 × 10 <sup>3</sup>	2.1	–	76
4	<b>2a</b>	5.6 × 10 <sup>3</sup>	1.8 × 10 <sup>4</sup>	3.1	122 °C	14

Temperature: 50 °C. Ethylene pressure: 40 atm. Reaction medium: 100 mL toluene (entries 1 to 3) resp. 98 mL water, **2** miniemulsified in 2 mL toluene/hexadecane (entry 4). 40 μmol **2**. Reaction time: 30 min.

a) mass transfer limited.

b) apparently higher initial activity, but rapid deactivation.

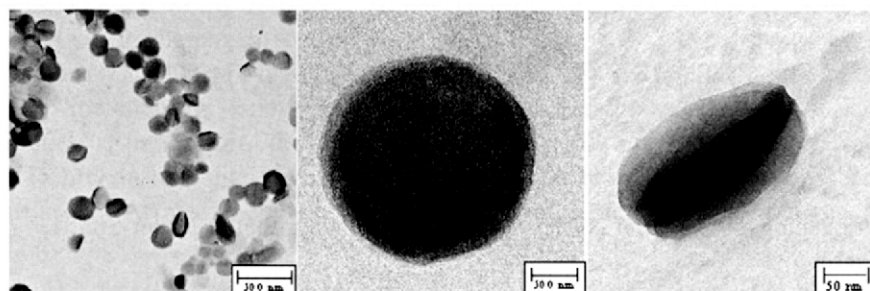


Figure 1. Polyethylene latex particles. Overview (left image, scale bar 500 nm) and single particle (middle, scale bar 50 nm), same particle tilted by 60° (right).

aqueous emulsion with **2a**, a latex was obtained with a five-fold higher catalyst efficiency by comparison to **1**.<sup>[3d]</sup>

For commercial applications and fundamental studies alike, a simple catalyst system which does not require the preparation of metal complexes or specific ligands is desirable. With an *in situ* catalyst prepared from entirely commercially available compounds, namely tetrachloroquinone, triphenylphosphine and *bis*(cyclooctadiene)nickel, polyethylene dispersions can be prepared conveniently. With catalyst activities of  $2 \times 10^3 \text{ TO h}^{-1}$ , dispersion of up to 30% solids content are accessible. Linear low-molecular-weight polyethylene is formed, however molecular weights of

$\bar{M}_n 2 \times 10^3 \text{ TO h}^{-1}$  ( $\bar{M}_w/\bar{M}_n$  2 to 5) clearly exceed the entanglement limit.

Typical latex particles obtained with the latter system are shown in Figure 1. The particles are not spherical, but possess a lentic-like shape. This can be rationalized by the preference of polyethylene to crystallize in lamellae, which results in a higher rate of particle growth in two dimensions. Microtom cuts of latex particles prepared at 70 °C polymerization temperature reveal a lamella spacing of 11 nm. Quantification of particle sizes and thickness by AFM shows a broad distribution, with an average aspect ratio of ca. 10. A significant portion of particles appears to consist of a single lamella.

[1] *Wäßrige Polymerdispersionen* (D. Distler, ed.), Wiley-VCH, Weinheim 1999.

[2a] S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169–204. b) S. Mecking, *Angew. Chem.* **2001**, *113*, 550–57.

[3a] A. Held, F. M. Bauers, S. Mecking, *Chem. Commun.* **2000**, 301–2.

[3b] A. Held, S. Mecking, *Chemistry – Eur. J.* **2000**, *6*, 4623–9.

[3c] F. M. Bauers, S. Mecking, *Macromolecules* **2001**, *34*, 1165–71.

[3d] F. M. Bauers, S. Mecking, *Angew. Chem.* **2001**, *113*, 3112–5.

[3e] A. Held, L. Kolb, M. A. Zuidveeld, R. Thomann, S. Mecking, M. Schmid, R. Pietruschka, E. Lindner, M. Sunjuk, M. Khanfar, *Macromolecules* **2002**, *35*, 3342–7. Reviews:

[3f] S. Mecking, A. Held, F. M. Bauers, *Angew. Chem.* **2002**, *114*, 564–82. g) S. Mecking, J. Claverie in 'Late Transition Metal Polymerization Catalysis' (L. S. Boffa, S. Kacker, B. Rieger, S. Striegler, eds.), Wiley-VCH, Weinheim, 2003, p. 231–78.

[4a] A. Tomov, J.-P. Broyer, R. Spitz, *Macromol. Symp.* **2000**, *150*, 53–8. b) R. Soula, C. Novat, A. Tomov, R. Spitz, J. Claverie, X. Drujon, J. Malinge, T. Saudemont, *Macromolecules* **2001**, *34*, 2022–6. c) R. Soula, B. Saillard, R. Spitz, J. Claverie, M. F. Llaurro, C. Monnet, *Macromolecules* **2002**, *35*, 1513–23.