First publ. in: Polymeric Materials: Science & Engineering 90 (2004), pp. 740-741

Catalytic Ethylene Polymerization in Aqueous Emulsion: Catalyst Tailoring and Synthesis of Very Small Latex Particles

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INTRODUCTION

Emulsion polymerization yielding polymer latexes, is carried out on a vast scale. The use of water as a dispersion medium offers a unique combination of features, such as effective heat transfer, effective stabilization of polymer particles by surfactants, and environmental friendliness.[1] By contrast to polymerization in solution or in the bulk, in emulsion polymerization a large portion of polymer can be generated in a given volume of reaction mixture without a strong increase in viscosity. The nontoxicity and nonflammability of water are also advantageous.

To date, emulsion polymerization is industrially carried out by free radical processes exclusively. This limits the range of accessible polymer microstructures, and correspondingly the attainable materials properties. Therefore, the preparation of polymer latexes by catalytic polymerization of simple olefinic monomers is receiving increasing interest.[2] The synthesis of dispersions from olefins directly obtained from cracking of hydrocarbon feedstocks, without the need for further energy and raw material consuming conversion to other monomers is desirable.

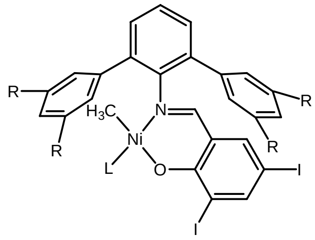
To obtain polymer latexes in catalytic emulsion polymerization, water-soluble complexes can be used, in analogy to traditional free-radical polymerization or as an alternative concept aqueous miniemulsions of a solution of a lipophilic catalyst precursor in a small amount of hydrocarbon can be utilized. The latter approach enables the use of the generally more common lipophilic catalysts and in addition somewhat water-sensitive catalysts can also be employed.

Attractive and challenging issues are catalysts enabling high polymerization activities, a design of simple and industrially applicable catalytic systems and the control of latex particle size and structure.

RESULTS AND DISCUSSION

Synthesis of High-Molecular-Weight Polyethylene Latexes. The use of neutral Ni(II) κ^2-*N-O* salicylaldiminato complexes for the polymerization of ethylene in solution has been reported previously.[3] Their single-site behaviour prompted us to use them as catalysts for the synthesis of stable latexes of high-molecular-weight polyethylene, which are not accessible by other routes to date.[4a] A new family of salicylaldiminato complexes [(N-O)Ni(Me)(py)] with *N*-terphenyl-substituted ligands displays high catalytic activities (Figure 1).[4b] Unexpectedly, the nature of the remote substituents R has a dramatic effect on polymer molecular weight as well as branching and thus crystallinity. While a semicrystalline high molecular weight polyethylene is obtained for R = CF_3, with electron-donating groups, like R = Me, low molecular weight, highly branched completely amorphous material are obtained.

The lability of ligands L is essential for the polymerization activity of a given catalyst precursor.[3d] Depending on the liphophilicity of L, in aqueous emulsion its coordination behaviour can be even more decisive by comparision to traditional non-aqueous polymerization. Lipophilic, water-insoluble catalyst precursors such as **1** are added to the reaction mixture as a miniemulsion of a solution of **1** in a small volume of a hydrocarbon. During the polymerization, the concentration of the catalyst and also of the ligand L in the organic phase (polymer formed + organic solvent) will be much higher by comparison to traditional polymerization.



1a R = CF_3; L = py

1b *in-situ* mixture of salicylaldimine and [(tmeda)$NiMe_2$] R = CF_3; L = tmeda

Figure 1. Catalyst precursors employed.

A relatively weakly-ligated catalyst system can be obtained by mixing [(tmeda)$NiMe_2$][5] (tmeda = *N*,*N*,*N'*,*N'* tetramethylethylenediamine) with an equivalent of salicylaldimine ligand *in-situ*. Presumably, complex **1b** with tmeda occupying the fourth coordination site is formed.

By contrast to polymerization with the pyridine complex (50°C), with the *in-situ* system a much higher activity is observed at lower polymerization temperature (20°C). The *in-situ* system is stable up to 30°C. With the pyridine complex as a catalyst precursor the system is stable for hours at ca. 70°C, as evidenced from monitoring the ethylene uptake with a mass-flow meter, indicating a stabilization by the coordinating ligand. Polymers obtained with both catalytic systems under the same conditions (50°C; 40 bar) are identical within experimental error (M_w: 6×10^4 g mol^{-1}; branching: 8 per 1000C; crystallinity: 51%). This confirms that identical active species are formed from both precursors, as expected.

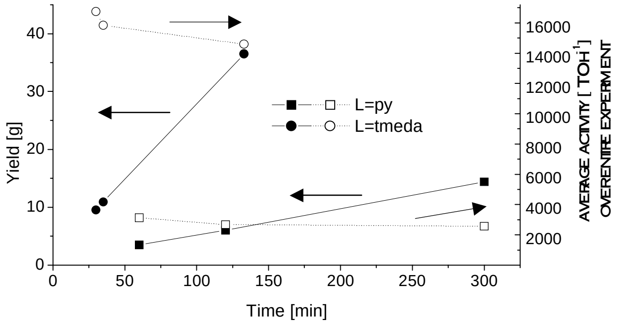


Figure 2. Comparative yield and activity of pyridine complex **1a** and the *in-situ* catalyst **1b** in the polymerization of ethylene in aqueous emulsion. Temperature: 20°C (**1b**); 50°C (**1a**); ethylene pressure: 40 bar.

Water-Soluble Catalyst for the Synthesis of Small Polyethylene Particles. We have recently reported on the synthesis of low-molecular-weight linear crystalline polyethylene by a simple *in-situ* catalytic system composed of tetrachlorobenzoquinone (TCBQ), PPh_3 and [Ni(cod)$_2$] as a source of nickel(0).[6] Polyethylene latex particles with an unusual morphology are obtained.[7] The lipophilic catalytic system is employed by the aforementioned miniemulsion procedure. By comparison, water-soluble catalysts would enable polymerization in the absence of added potencially harmful water-immiscible hydrocarbon solvent, and allow for an improved particle size control. Reaction of TCBQ with appropriate water-soluble phosphines in a small amount of water-miscible alcohol solvent and subsequent reaction with [Ni(cod)$_2$] affords a hydrophilic catalyst which can be employed for catalytic emulsion polymerization without any additional (water-immiscible) liquid organic phase (Figure 3).

Stable polyethylene (M_w ca. 10^4 g mol^{-1}) latexes with up to 13% solids content were obtained to date without optimisation. Monitoring the ethylene consumption over time in polymerization at different temperatures by means of a mass-flow meter, reveals the catalyst to be stable for hours at up to 70°C. At higher temperatures catalyst decomposition occurs (Table 1).

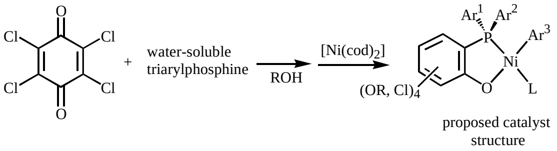


Figure 3. Synthesis of the water-soluble *in-situ* catalyst.

By comparison to the latexes obtained with the previously described lipophilic catalyst system,[7] the latexes obtained with the hydrophilic catalyst system are transparent or only slightly hazy, indicating a very small particle size. This is indeed confirmed by transmission electron microscopy (TEM) (Figure 4). In free-radical polymerization, the synthesis of such small particles (of different types of polymers) requires special techniques like microemulsion polymerization.

Table 1. Polymerization with Water-Soluble Catalysts In Ethylene Polymerization in Aqueous Emulsion[a]

Entry	ncat [µmol]	T [°C]	T [h]	Solid content [%]	Average TOF[b]
1	100	25	2	0.4	71
2	100	50	2	3.3	891
3	100	60	2	9.4	1675
4	100	70	2	13.3	2370
5	100	80	2	6.8	1212
6	66	60	2	4.4	1188
7	66	60	5	11.1	1200

[a] Reaction conditions: 90 mL H_2O, 10 mL ROH; 40 bar ethylene pressure; surfactant: SDS. [b]TOF:[mol (ethylene consumed) x mol $(Ni)^{-1}$ x h^{-1}].

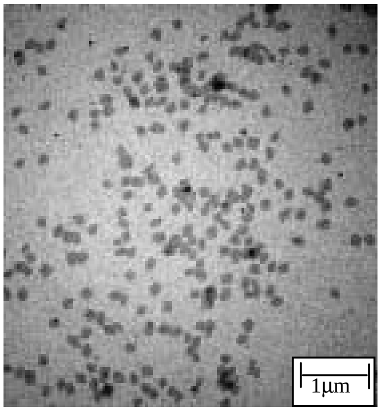


Figure 4. TEM image of polymer particles, overview.

REFERENCES

1. (a) *Wäßrige Polymerdispersionen*; Distler, D., Ed.; VCH: Weinheim, 1999; (b) *Polymer Dispersions and Their Industrial Applications;* Urban, D.; Takamura, K.; Eds.; Wiley-VCH: Weinheim, 2002; (c) *Emulsion Polymerization and Emulsion Polymers*; Lovell, P.A., El-Aasser, M.S. Eds.; Wiley: Chichester, 1997.
2. (a) Mecking, S.; Held, A.; Bauers, F.M. *Angew. Chem. Int. Ed.* **2002**, *41*, 544; (b) Claverie, J.P.; Soula, R. *Prog. Polym. Sci.* **2003**, *28*, 619; (c) Mecking, S.; Claverie, J. in *Late Transition Metal Polymerization Catalysis*; Rieger, B. Baugh, L.S.; Kacker, S.; Striegler, S., Eds.; Wiley-VCH: Weinheim, 2003, pp. 231.
3. (a) Johnson, L.K.; Bennett, A.M.A.; Ittel, S.D.; Wang, L.; Parthasarathy, A.; Hauptman, E.; Simpson, R.D.; Feldman, J.; Coughlin, E.B. (DuPont) WO**98**/30609, **1998**; (b) Wang, C.; Friedrich, S.; Younkin, T.R.; Li, R.T.; Grubbs, R. H.; Bansleben, D.A.; Day, M.W. *Organometallics* **1998**, *17*, 3149; (c) Younkin, T.R.; Connor, E.F.; Henderson, J.I.; Friedrich, S.K.; Grubbs, R.H.; Bansleben, D.A. *Science*, **2000**, *287*, 460; (d) Connor, E.F.; Younkin, T.R.; Henderson, J.I.; Waltman, A.W.; Grubbs, R.H. *Chem. Commun.* **2003**, 2272.
4. (a) Bauers, F.M.; Mecking, S. *Angew. Chem. Int. Ed*. **2001**, *40*, 3020; (b) Zuideveld, M.A.; Wehrmann, P.; Röhr, C.; Mecking, S. *Angew. Chem. Int. Ed.* **2003**, *in press.*
5. Kaschube, W.; Porschke, K.R.; Wilke, G. *J. Organomet. Chem.* **1988**, *355*, 525.
6. Bauers, F.M.; Chowdhry, M.M.; Mecking, S. *Macromolecules* **2003**, *36*, 6711.
7. Bauers, F.M; Thomann, R.; Mecking, S. *J. Am. Chem. Soc.* **2003**, *125*, 8838.