EMULSION POLYMERIZATION OF ETHYLENE IN WATER MEDIUM CATALYSED BY ORGANOTRANSITION METAL COMPLEXES

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SUMMARY : Ethylene was polymerized for the first time in water emulsion or miniemulsion conditions with the aid of an organotransition metal catalyst, at ethylene pressures of 10-30 bar and temperatures of 45-80°C. A maximal productivity of 2520 kg PE/g-atom active metal was achieved, which represents about 60% of the productivity of the same catalyst when used in ethylene suspension polymerization in organic phase at 4 bar reaction pressure. The particle size distribution of the latexes prepared is rather large, with a maximum at 235 nm in the case of emulsion and 640 nm in the case of miniemulsion polymerization respectively.

1. Introduction

The catalytic polymerization of ethylene in water emulsion is of great interest, not only because the process would be environmentally benign, but also because of the possibility for preparation of a variety of new materials. Although the radical initiated emulsion polymerization of ethylene is well known to produce highly branched and often crosslinked polymer, [1-4], the emulsion polymerization of ethylene in water by using an organotransition metal catalysts to give a HDPE latex has not to the best our knowledge been described anywhere. There exist at least two possibilities for application of the catalytic ethylene polymerization in water emulsion :

- High density polyethylene (HDPE) latexes
- composite nanomaterials based on HDPE

Although a large variety of Ziegler-Natta and related catalysts based on early transition metal complexes are widely used in olefin polymerization, their oxophilic nature does not permit their use in polar media. On the other hand, the late transition metal based catalysts are especially attractive in this aspect because of their enhanced resistance with respect to the polar molecules. It was first demonstrated by Klabunde et al. that nickel based olefin polymerization catalysts are quite resistant towards a number of polar species [5]. However they were completely deactivated when water in a 1000-fold excess with respect to the

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catalyst used was added to the catalytic mixture [6]. A rhodium based catalyst able to polymerize ethylene in water was also described elsewhere [7]. The catalyst showed very low productivity and low molecular weight polymer was obtained. Sen and Jiang [8] studied the alternating ethylene-CO suspension polymerization in water using a palladium/bis-phosphine catalyst. Brookhart et al. [9] reported for an observed productivity of 50 kg polymer/mol Pd for a suspension ethylene polymerization reaction using a palladium complex in water. Kurtev and Tomov showed that the binuclear nickel-ylide complexes (BINYC) [10, 11] are more active ethylene polymerization catalysts that the corresponding mononuclear ones, both in polar or nonpolar media. Some of these catalysts showed significant productivities in water-methanol mixtures. However all the reported data consider ethylene polymerization/ co-polymerization reaction which are performed in suspension conditions, and in which no emulsifier was used and no emulsions were formed.

We recently found that some binuclear nickel-ylide catalysts are able to polymerize ethylene with high productivity in water emulsion or miniemulsion conditions to give a HDPE latex. Herein we describe for first time the emulsion polymerization of ethylene in water, catalyzed by an organotransition metal catalyst.

2. Experimental

All experiments were performed in an oxygen-free atmosphere. The bis(cis,cis-1,5-cyclooctadiene)nickel(0) was purchased from Strem. The nickel-ylide complexes were synthesized as in [10] and [12], or using similar procedures. The ^{1}H- and ^{31}P- spectra of the complexes were recorded either at 300 MHz on a Brüker AC 300 spectrometer or at 400 MHz on a Brüker DRX 400 instrument. The ^{13}C-NMR spectra of polyethylene were recorded at 100.6 MHz on a Brüker DRX400 spectrometer. The thermal analyses of the polymers were performed on a DSC 101 calorimeter. The size of polyethylene particles and their distribution was examined by dynamic light scattering on a DDL Lowci Malvern instrument. The morphology of the particles was determined by transmission electron microscopy (Phillips CM12 TEM at 120 kV). Samples were prepared by placing a small drop of diluted polyethylene latex directly onto a copper grid.

2. 1 Emulsion Polymerization of Ethylene

The emulsion or miniemulsion polymerization of ethylene were performed in a 1L or 2.5L stainless steel reactors, supplied with an inlet valve, a mechanical stirrer, a pressure gauge, a thermocouple and a device for maintaining of constant pressure. A general example is given below.

An amount of 45 - 300 mg of the corresponding catalyst and 50 - 300 mg bis(*cis, cis*-1,5-cyclooctadiene)nickel (0) were dissolved in 5 - 40 ml of toluene and stirred for 5 minutes. In the case of miniemulsion polymerization 1-3 ml co-surfactant were added. Thus prepared catalytic mixture was transferred under nitrogen in the reactor in which 1.5 - 12 g of the corresponding surfactant (usually sodium sodium dodecylsulfate, SDS) and 500 - 2000 ml water were charged in advance. The mixture was stirred for 1 min at 1000 rpm, quickly pressurized with ethylene at a pressure with 2 - 5 bar lower than the desired reaction pressure, and the stirring rate was adjusted to 500 rpm. The ethylene valve was closed and the temperature adjusted to the desired level (usually 65 °C). After an initial rise in pressure, it fell back to the set value. The ethylene valve was then reopened, the reaction pressure adjusted and kept constant during polymerization. The reactions were typically run for 1 - 3h and then the ethylene pressure slowly released. The contents of the reactor was transferred in a beaker and the coagulated polymer separated from the latex by filtration.

3. Results and Discussion

The nickel P$\overset{\frown}{}$O chelate complexes are very active ethylene polymerization/co-polymerization catalysts, and show an enhanced resistance with respect to the polar molecules. We recently found that the binuclear nickel-ylides (Figure 1) [10] are precursors which, upon activation give extremely active catalysts in organic media as well as in water emulsion or dispersion conditions. Their turn-over frequencies approach 1600/s, and productivity over 250 kg PE/ g Ni were often observed. The complexes of the type shown on Figure 1 are usually soluble in organic medium. This has predetermined their use in the emulsion polymerization of ethylene by analogy with the oil soluble initiators. In most cases the presence of a phosphine scavenger [6] able to coordinate the labile phosphine ligands is required.

A number of polymerization runs are listed in Table I. As can be seen the use of the binuclear nickel-ylide catalysts in ethylene polymerization in water medium leads to a decreasing of their productivity compared to this obtained in toluene. It is worth mentioning however that water does not have a poisoning effect on the catalyst. The lower productivity seems to be due to the lower solubility of ethylene in water. The scavenger to catalyst molar

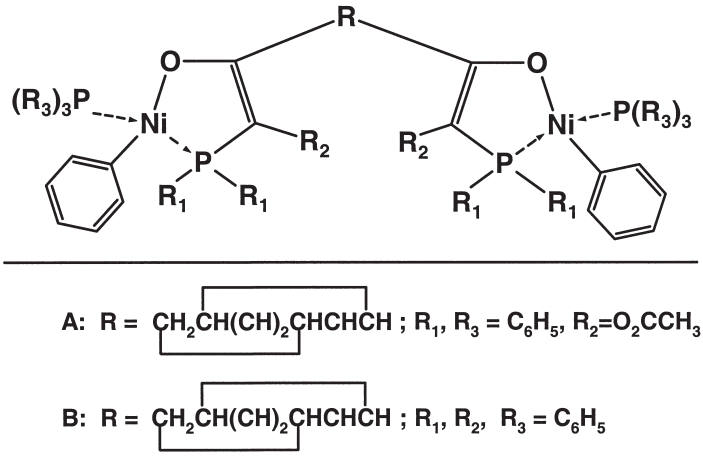

Figure 1. The catalyst precursors used in the emulsion polymerization of ethylene.

ratio has the strongest impact on the catalyst activity. Increasing this ratio leads to higher catalyst activity and productivity. The concentration of surfactant does not have a strong effect on the catalyst activity. However at concentrations over the CMC, it slightly reduces the productivity of the catalyst. The molecular weight of the polymer obtained depends mainly on the catalyst used. When produced in water emulsion or suspension conditions, the polyethylene has a lower molecular weight, which is due to the lower concentration of ethylene in the water phase.

The catalytic emulsion polymerization of ethylene produces an HDPE latex (Figure 2) with average particles sizes in the range of 130 - 280 nm, and very low solid contents (~1%). However it is still not completely clear whether a) only a small part of the polymer chains are formed in the reach of monomer droplets, stabilized by the surfactant, or b) the polymer is formed entirely in the droplets, but the latex coagulates during the pressure release. Often the

Table 1. Polymerization conditions [a], latex and polymer properties

Run n°	Cat.	C_{SDS}	P_{C2H4}	$C_{cat.}$	Ratio [d] cat./scav.	Productivity	Mw	Particle size	PE_{latex}/PE_{total}
		g/l	bar	µmol/l	mol/mol	kg/mol Ni	g/mol	nm	%
1	A	3.0	20	83.8	14	358	102400	240	8
9	A	8.0	24	139.0	4	282	88000	277	8
3	A	12.0	20	51.2	13	363	94200	137	14
4	A	8.0 [c]	22	52.3	10	344	92800	731	100
5	B	1,5	24	19.9	9	766	21900	266	10
6	B	3.0	25	15.4	24	2525	67800	228	9
7	B	6.0	27	33.8	15	1094	18500	230	20
8	B	12.0	22	21.7	7	651	58300	265	12
9	B	12.0 [c]	20	115.0	19	270	8700	620	100
10	B	0.0	26	61.8	14	1056	51200	no latex	0
11 [b]	A	-	4	23.4	7	1100	159700	-	-
12 [b]	B	-	4	28.1	6	4300	103700	-	-

a) reaction temperature - 65 - 68°C
b) reaction carried out in toluene medium
c) in presence of hexadecane as a co-surfactant
d) phosphine scavenger : bis (cis, cis-1,5-cyclooctadiene)nickel(0)

samples withdrawn during the reactions via a shock pressure decrease had a milky appearance. However they coagulated several seconds after sampling. This gives support to the second

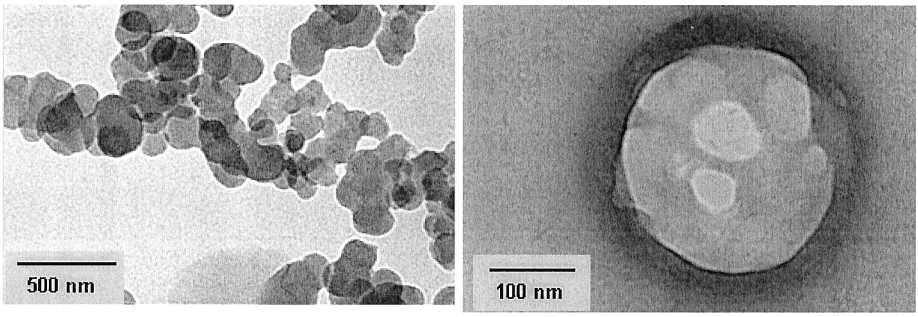

Figure 2. TEM photographs of high density polyethylene nanoparticles, prepared by catalytic emulsion polymerization of ethylene.

hypothesis above. Moreover when the polymerization was carried out in the same manner, but with no surfactant added, no latex was formed at all. All the polymer obtained was completely separated from the water phase.

All the polyethylene obtained during the miniemulsion polymerization of ethylene was in the form of a latex with an average particle size in the range of 620 - 730 nm. The latex slowly coagulated to form a "cream".

The ^{13}C-NMR analysis of the polyethylene obtained via emulsion or miniemulsion polymerization of ethylene showed that it is formed from almost linear chains, terminated by a double bond. The DSC analysis shows a melting temperature of 135 °C, which corresponds to a highly crystalline polyethylene. Figure 2 show TEM photographs of polyethylene nanoparticles prepared by catalytic emulsion or miniemulsion ethylene polymerization. The higher degree of crystallinity of the polymer determine the polyhedral shape of the particles.

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