Catalytic Copolymerization of Ethylene and Polar and Nonpolar α-Olefins in Emulsion

R. Soula, B. Saillard, R. Spitz, and J. Claverie*

LCPP-CPE/CNRS, BP 2077, 43 Bd du 11 Nov 1918, 69616 Villeurbanne Cedex, France

M. F. Llaurro and C. Monnet

Service de RMN de la "Fédération de Recherche des Polymèristes Lyonnais" (FR 2151), CNRS, BP 24, 69390 Vernaison, France

Received July 30, 2001; Revised Manuscript Received October 22, 2001

ABSTRACT: Novel P,O-chelated Ni(II) catalysts for ethylene and α-olefins polymerization have been used for the copolymerization of ethylene with various long-chain α-olefins in emulsion. Nonfunctionalized α-olefins have been copolymerized with ethylene using miniemulsion to disperse the catalyst at the nanometric level. The influence of the comonomer on catalyst performances as well as latex properties has been analyzed. High comonomer incorporation and stable latex of 30% solid content can be achieved by this method. Other comonomers such as α,*ω*-dienes, α-olefins bearing a polar functionality in the *ω*-position, and styrene have also been copolymerized in emulsion. Polymers and latexes have been characterized by an array of techniques including ^{13}C NMR, TEM, DSC, and GPC. It is shown that this emulsion process is specially adapted for copolymerization of ethylene with polar olefins.

Introduction

Emulsion polymerization is a widely spread polymer manufacturing process (roughly 50% of the radical polymers are synthesized by this method),[1] but it is industrially confined to radical chemistry. The generalization of this process to other polymerization mechanisms has stirred a great interest. Indeed, reports about cationic,[2−4] anionic,[5−7] ring-opening metathesis polymerization (ROMP),[8−13] catalytic diene polymerization,[14−17] and catalytic alternating copolymerization of ethylene and carbon monoxide[18−24] have emerged recently. With the development of late transition metal catalysts for olefin polymerization, water can be used as a continuous medium and polar comonomers can be copolymerized.[25−29] We[30,31] and Mecking et al.[32−34] have recently presented catalytic ethylene polymerization in a water dispersed medium. The catalytic systems used in these studies are based on nickel and palladium: Brookhart's cationic Pd(II) α-diimine, Klabunde's neutral Ni(II) with sulfonated P,O-chelate, and Grubbs' neutral Ni(II) salicylaldimine for Mecking[32−34] and neutral Ni(II) with fluorinated P,O-chelate for us.[30,31,35,36] Mecking chiefly tackles the issue of the stability of the nickel and palladium catalysts in aqueous conditions and loss of activity due to diffusion control of the ethylene transport through the aqueous phase. Ethylene homopolymers and copolymers with norbornene are described. We have presented a novel family of very active catalysts[31] and their use in aqueous-borne ethylene homopolymerization.[36] Stable latices of linear PE could only be obtained using a miniemulsion technique. In this system, the catalyst dissolved in a minimum of organic solvent droplets is dispersed by ultrasonication into submicronic droplets stabilized by surfactant/cosurfactant system (Scheme 1). These droplets can be viewed as independent ethylene polymerization nanoreactors. We have also found that the catalyst dispersion could be effected on a very small scale (for example, 10 mL of organic solvent in 50 mL of water) and further diluted with water (up to 1 L) upon starting polymerization: this precludes the use of large-scale sonication equipment, and this also allows to tune the colloidal characteristics of the miniemulsion independently from the reaction scale.

Albeit this system allows the generation of linear PE latices up to 10% solids, several problems were encountered. Colloidal stability was hampered by very high polymer crystallinity (resulting in nonspherical particles) and by the presence of hexadecane (cosurfactant). For example, we observed over a time range of weeks that hexadecane was slowly phase separating from the latex, triggering a creaming process. We also found out that despite the use of miniemulsion, our nucleation process was uncontrolled as the number of polymer particles was greatly different from the number of droplets. In this report, we address these problems and we show that through the use of copolymerization both long-term stability and control over nucleation mechanism can be achieved. Furthermore, solid contents up to 30% can now be reached. These products could potentially compare to industrial PE and PP copolymers that are manufactured by direct emulsification of wax-type polymers under harsh conditions.[37]

The paper is organized as follows: we present results of ethylene copolymerization with α-olefins (synthesis, kinetics, and characterization) and copolymerization with functionalized α-olefin (long-chain α,*ω*-diene and α,*ω*-polar group olefin).

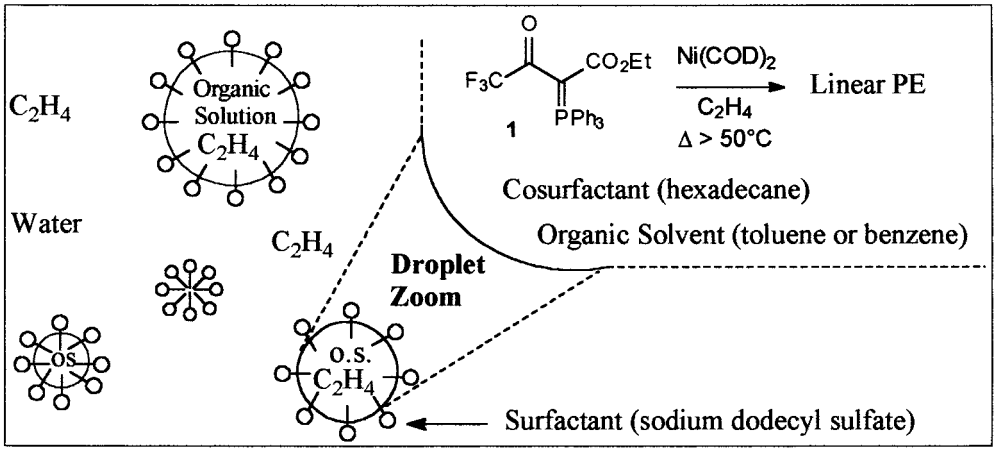
Experimental Part

Ligand **1** was synthesized according to the literature.[38] $Ni(COD)_2$, comonomers, and surfactants were purchased from a commercial supplier. All organic solvents and reagents were dried and degassed according to standard Schlenk techniques. Ultrapure water ($\sigma = 18.2$ MΩ·cm) was obtained from a Purite HP 50 Analyst apparatus. Water was heavily degassed and

* Corresponding author: e-mail claverie@flamel.com; Tel (33)478723434; Fax (33)472783435.

10.1021/ma011366e CCC: $22.00
Published on Web 02/01/2002

Scheme 1



decarbonated with argon, in order for the pH to be between 6.8 and 7.2. High-resolution liquid NMR spectroscopy was carried out with a Bruker DRX 400 spectrometer operating at 400 MHz for ^{1}H and 100.6 MHz for ^{13}C. Spectra were obtained with a 5 mm QNP probe at 363 K. Polymer samples were examined as 25−40% (w/v) solutions. A mixture of tetrachloroethylene (TCE) and perdeuteriobenzene (C_6D_6) (2/1 by volume) was used as solvent. Chemical shift values (δ) were given in ppm in reference to internal tetramethylsilane (TMS); in the absence of TMS the chemical shifts were referenced internally to the major backbone methylene carbon resonance which was taken at $\delta = 30.06$ ppm. Typical accumulations included 70° flip angle, TD = 64 K, and 4.5 s recycle time. Accumulations with gated proton decoupling were about 2500−8000 scans. No significant difference in relative integrals, for the carbons of interest to us (CH_2), was observed between acquisition made under these conditions and those made in absence of the nuclear Overhauser effect (NOE). Methylene carbon resonances chosen for quantitative analysis are sufficiently "internal" to have T_1 lower than 2 s. GPC was determined in 1,3,4-trichlorobenzene at 145 °C using a Waters AlC instrument. Particle size measurements were effected on a LoC Malvern QELS instrument and a 4800S Autosizer from Malvern equipped with a 50 mW laser. Particle size distribution was also followed on a FlowFFF (flow field flow universal fractionation) from FFF Corp., equipped with a static light scattering detector, MiniDawn from Wyatt Technology.

Transmission electron microscopy (TEM) measurements were effected on a Phillips 120-GM_2 ($V = 80$ kV). Negative staining agents (uranyl acetate) were sometimes used to increase the contrast.[39]

Typical Miniemulsion Copolymerization Procedure. In a Schlenk tube, 27.5 mg of $Ni(COD)_2$ is dissolved in 10 mL of toluene. This solution is added to 22.2 mg of ligand **1**. The resulting solution is stirred for 15 min and then added to 300 mL of water containing 20 g/L of surfactant and 20 g/L of cosurfactant copolymerizable (usually hexadecene) in a flask. The biphasic mixture is then emulsified with a 600 W ultrasonic Branson sonifier for 2 min under magnetic stirring (and under argon). Finally, the colloidally dispersed mixture is cannula transferred into a 1 L stainless steel reactor and equipped with a mechanical stirrer (magnetic induction), a thermocouple, a sampling valve, and an external jacket heated at 55 °C. Ethylene is immediately introduced at 20 bar. Ethylene is continuously fed into the reactor at the set pressure from a high-pressure 5.5 L reservoir. The pressure drop in the reservoir is recorded to assess activity and productivity measurements. The reaction medium (300 mL) is collected after having vented the remaining ethylene through a micrometric manifold slowly enough to prevent latex flocculation through creaming. The latex is filtered to determine the floc content, and the liquid residue is analyzed by DLS and gravimetry.

Results and Discussion

A. Copolymerization with Nonfunctionalized α-Olefins (Hexadecene and Octene). 1. Influence of Experimental Parameters over Activity and Productivity. We have previously presented a classical miniemulsion recipe for ethylene homopolymerization which included an organic phase, the catalyst precursors dissolved in an organic solvent, a surfactant, sodium dodecyl sulfate (SDS), and a cosurfactant, hexadecane.[31] The cosurfactant, which is in fact a hydrophobe, is limiting the Ostwald ripening in the initial colloidal dispersion of the organic phase.[40] In the absence of a hydrophobe, rapid coagulation of the organic phase occurs to yield large droplets that upon polymerization give an unstable PE dispersion made of particles of sizes superior to 1 μm (entry 1, Table 1). As we aim at limiting the amount of VOCs, we have decided to use a polymerizable cosurfactant, and therefore hexadecane has been replaced by octene (entry 2, Table 1). Because of its insufficient hydrophobicity, octene has failed to stabilize the initial droplet dispersion by suppression of the Ostwald ripening, leading to large polymer particles (not colloidal in nature, that is to say, larger than 1 μm). Obviously, the stability of the initial dispersion of the catalytic solution is very sensitive to the nature of the hydrophobe,[41,42] and no results in miniemulsion are reported for a cosurfactant smaller than C_{16}.[43] Therefore, hexadecene has been used as hydrophobe equivalent to hexadecane (entries 2−10, Table 1).[44]

First of all, the influence of the comonomer on the catalytic activity is discussed. In early transition metal catalysis (Philipps, Ziegler−Natta, and metallocenes), addition of small amounts of α-olefin to the reaction medium is known to activate the catalytic system (so-called "comonomer effect").[45] Obviously, large amounts of α-olefin result in the inverted effect due to the increased steric congestion at the active center. In late transition metal catalysis, very few data about copolymerization exist. We have checked that with our fluorinated catalyst organic solution copolymerization of ethylene and hexadecene result in lower rates and low incorporations.[46] In emulsion polymerization, only a slight activity decrease that could be insignificant is observed when going from hexadecane/ethylene to hexadecene/ethylene for low concentrations of comonomer (entries 1 and 3, Table 1). However, increasing comonomer concentration to 60 g/L has a more pronounced

Table 1. Representative Results of Emulsion Copolymerization with Hexadecene and Octene[o]

	catalyst					emulsion				
entry	N, μmol	solvent, mL	T, °C	activity,[a] kg/(g_{Ni} h)	prod, kg/g_{Ni}	C_{SDS},[b] g/L	C_{C16ene},[c] g/L	particle size,[d] nm	sc,[e] %	$N_{particles}$/ $N_{droplet}$[f]
1	50	tol 25	70	12.5/10 (40)	7.7	10		1050 ± 1050	9.2[g]	
2	50	ben 25	70	14/2 (75)	10.6	10	10[h]	588 ± 588[i]		
3	50	tol 25	70	8.5/1.8 (50)	5.6	10	10	205 ± 89	7.2	0.72
4	50	ben 25	70	11/2 (60)	8.0	10	10	213 ± 82	8.1	0.81
5	50	ben 40	70	14/3.5 (65)	10.5	20	20	191 ± 69	12.0	0.75
6	100	ben 40	60	6/3.5 (140)	9.8	20	20	195 ± 80	15.4	0.76
7	50	ben 40	60	15.5/6 (175)	24.8	20	20	203 ± 84	18.8	0.94
8	25	ben 40	60	19/15.5 (50)	14.2	20	20	206 ± 74	14.3	0.77
9	50	ben 60	55	15.5/8 (140)	30.5	20	20	210 ± 84	23.7	0.83
10	30	ben 40	55	13/8 (145)	23.5	20	20[k]	186 ± 70[j]	14.3	0.73
11	30	ben 40	55	14/8 (145)	23.9	20	20[l]	188 ± 74[j]	14.9	0.70
12	25	ben 20	55	11/6 (150)	22	20	20	211 ± 73	12.3	1.03
13	25	ben 40	55	17/10 (150)	34	20	20	225 ± 81	17.0	0.97
14	25	ben 60	55	19/14 (150)	42	20	20	238 ± 104	19.0	0.86
15[i]	50	tol 40	55	13/2.5 (170)	20.8	15	15	211 ± 82[j]	23.8[j]	0.74
15[i]	50	tol 30	55	10/2.3 (210)	19.3	10	10	224 ± 81[k]	29.6[k]	nd
16[l]	50	tol 20	55	39/3.8 (150)	29.2	20	20	247 ± 84	20.5	3.85
17[l]	50	tol 40	55	95/2.2 (150)	43.4	20	20	246 ± 98	30.0	2.97
18[l]	50	tol 40	55	24/3 (150)	20.9	20	60	193 ± 74	23.8	0.96

[a] Activity max/activity at the end of the reaction (time indicated in parentheses). [b] Concentrations of SDS related to the volume of water. [c] Concentrations of hexadecene related to the volume of water. [d] Determined by dynamic light scattering at low concentrations. [e] Solid content determined by gravimetry. [f] Ratio of the number of initial miniemulsion droplets to the number of polymer particles. [g] Flocculated after 24 h. [h] Octene was used instead of hexadecene. [i] Complete flocculation at the end of the polymerization. [j] Longer ultrasonication time. [k] Octene was used instead of hexadecene and hexadecane was added in a concentration of 20 g/L. [l] In addition to hexadecene, octene was added in a concentration of 20 g/L. [m] Experiment in two steps: first line, miniemulsion in 200 mL of water (characteristics of this first latex); second line, miniemulsion with 100 mL of water (characteristics of the final latex). [n] Experiment at higher shear rate (300 rpm instead of 100). [o] Reactions were run in 300 mL of water using catalyst **1** at 20 bar of ethylene. Stirring is fixed at 100 rpm.

negative effect on catalyst performances. This issue will be dealt with below.

As we have described previously,[31] the polymerization temperature must be between 50 °C (catalyst formation) and 80 °C (in order to prevent catalyst thermal degradation). In emulsion polymerization, the influence of temperature on activity is low (entries 5 and 7, Table 1), but it is high on productivity because of a longer catalyst lifetime at lower temperature (65 min at 70 °C for entry 5 and 175 min at 60 °C for entry 7, Table 1). The half-life times of the catalyst[47] for these two entries are 45 and 140 min. These results are opposite to what is observed for organic phase polymerizations, where at 55 °C very small activities are obtained (less than 15 kg/(g_{Ni} h)) whereas at 70 °C the activity and the productivity are optimal (activity greater than 1000 kg/(g_{Ni} h)). Several factors contribute to explain the apparent discrepancy between the activation energy for propagation in emulsion (low E_a) and organic phase polymerization (high E_a). The first one is the increased water solubility and decreased ethylene solubility in the organic phase at higher temperatures. This would strongly affect the activity in emulsion polymerization as, according to Mecking,[34] diffusion of ethylene is a limiting factor in such polymerization. Yet, our data do not allow us to completely embrace this conclusion: if ethylene diffusion was a limiting factor, our observed activities should not be greater by 2 orders of magnitude than the ones observed by Mecking. A second explanation can be formulated: in organic phase (especially at 70 °C) polymerization temperature cannot be controlled due to the very high exotherm. Because of the high heat capacity of water, this is not the case in emulsion.

After having described the effect of temperature on our copolymerizations, we embark now on a discussion about the importance of physical (e.g., diffusion) and chemical (e.g., catalyst concentration) factors on activity and productivity. We would like first to point out that a stable latex with solid contents as high as 30% can be obtained (entry 17, Table 1). For this purpose, it is necessary to use our very active catalyst and to stir the reaction medium at medium shear rates (300 rpm, entries 16 and 17, Table 1). Using too high shear rates (above 1000 rpm), we were concerned about the possibility of shear-induced flocculation. At low stir rates (100 rpm), the reaction proceeds smoothly, albeit with a decreased activity. These higher activities at 300 rpm are easily explained by an improved ethylene diffusion from the gas phase to the organic droplets or polymer particles. Indeed, a visual observation of the reactor indicates that a vortex is created at 300 rpm but not at 100 rpm. This result is in agreement with the diffusional limit hypothesis advanced by Mecking.[32] Despite the advantageous catalyst performances at high stir rate, most of the experiments have been conducted at 100 rpm for three reasons: (1) it prevents shear-induced flocculation, (2) it favors comonomer incorporation, and (3) particle growth is slower. Concerning point 2, the comonomer incorporation is favored because the concentration of ethylene in the droplet/particle is less.

For our experiments, the use of benzene as catalyst solvent is favored as the activity and the productivity in benzene are slightly higher than in toluene (entries 3 and 4, Table 1). Benzene is also reported to lead to more stable miniemulsions than toluene.[48] In addition, thanks to its low boiling point, it can be partly removed during the ethylene degassing step when conducted at 80 °C.

Besides the temperature, activity, productivity, and polymer yield are also dependent on catalyst concentration and volume of organic solvent. Indeed, activity increases with the volume of organic phase for a given amount of catalyst (entries 12−14, Table 1) or with decreasing catalyst amount for a given volume of solvent

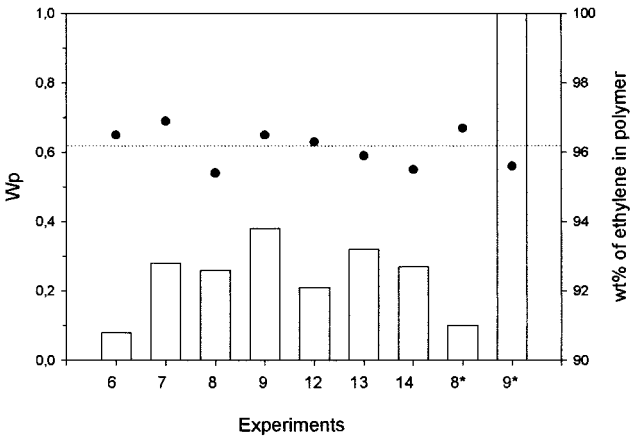


Figure 1. Polymer weight fraction in the polymer particles (plain circles) and comonomer percentage in the polymer (vertical bars) at the end of the reaction. Numbers indicate the corresponding entry of Table 1 for number without * and of Table 2 for the number with *.

(entries 6−8, Table 1). Therefore, in all cases, activity increases when the catalyst concentration in the organic phase (ratio of columns 2 to 3 in Table 1) decreases. Once again, diffusional problems can be invoked to explain this behavior.[34] Productivities (for 150 min reaction time at 55 °C) are proportional to maximum activity, indicating that catalyst deactivation occurs similarly for very active and less active systems. Thus, under our experimental conditions, there is a tradeoff between highly active and productive systems (low catalyst concentration, resulting in low solids) and less active and less productive systems (high catalyst concentration, resulting in still low solids). To reach the highest solids, a compromise must be found between volume of organic phase and catalyst amount. This issue is illustrated in Figure 1, where the weight fraction of the polymer in the polymer particle (polymer and organic solvent) is plotted for each experiment. This weight fraction is found to be constant for a wide range of catalyst amount and solvent volume. This narrow dispersion of ratio for different reaction conditions is highlighting a potential limit of this polymerization process: the amount of polymer synthesized is proportional to the volume of organic phase. Note that the best compromise to obtain the highest solids appears to be when using 50 μmol of catalyst (points above the average), whereas the lowest solids are obtained when using 25 μmol of catalyst.

Our goal being to generate latex particles with the least amount of VOC, we can take advantage of the important comonomer incorporation by using for organic solvent a comonomer of the polymerization. Another possibility is to use an organic solvent which can be polymerized by radical polymerization after catalytic ethylene copolymerization. Further work in this direction is under progress.

Taking into account the previous conclusions, solid contents above 20% can be easily reached either using 50 μmol of catalyst in 60 mL of solvent at a temperature of 55 °C with a stirring rate of 100 rpm (entry 9, Table 1) or using 50 μmol of catalyst in 40 mL of solvent at a temperature of 55 °C with a stirring rate of 300 rpm (entry 16, Table 1). Most of the solvent can be recovered at the end of the reaction by cold trapping the effluents of the reactor in a dry ice trap during the ethylene degassing step.

At 100 rpm stirring rate, latex of higher solid content can be prepared by a two-step procedure, in which a PE latex (entry 15, Table 1) is used as seed for the polymerization. To this latex, a second catalyst dispersion is added (miniemulsion of 50 μmol catalyst in 100 mL of water), and the polymerization is triggered upon contact with ethylene (T = 55 °C). Similar activities and productivities are obtained for both steps, and the resulting latex is 30% solid content. It is interesting to note that particle sizes have not increased upon introduction of the "seed" (vide infra: latex characteristics).

2. Polymer Microstructure and Comonomer Incorporation. Polymer structures were determined by ^{1}H and ^{13}C NMR (Table 2) and GPC. As observed by GPC, each polymer is a low molecular weight material

Table 2. NMR, GPC, and DSC Results of the Polymer Synthesized in Experiments 1−14 of Table 1

	^{1}H and ^{13}C NMR						GPC		DSC
expt[a]	M_n (g/mol)	Me br[b]	internal db[c]	long br[d]	wt % como poly[e]	% remain como[f]	M_w (g/mol)	M_w/M_n	T_m (°C)
1	2800	0.9	1.1	0.5			8470	2.9	123.2
2	1500	1.7	3.4	9.1	6.8	65	3530	1.8	115.1
3	1920	1.4	2.5	5.3	7.8	78	3950	2.1	117.5
4	1950	1.3	2.3	5.7	8.4	67	4460	2.3	116.2
5	2110	1.2	2.2	5.1	7.6	61	4580	2.2	118.8
6	1840	1.4	2.8	7	10.1	3	4510	2.4	112.6
7	2090	1.3	2.4	6.1	8.9	0	4660	2.2	115.3
8	2220	1.2	2.2	5.3	7.8	47	3870	1.8	117.2
9	2370	1.2	2.3	5.2	7.6	0	5450	2.3	116.6
10	2720	1.4	2.0	8.1	6.6	58	4320	2.0	115.8
11	2120	2.1	3.0	11.8	11.7	55[g]	3540	1.7	111.2
12	2000	1.2	2.9	6.5	9.4	50	3660	2.2	115.7
13	2140	1.2	2.6	5.2	7.7	36	4150	2.4	117.1
14	2190	1.1	2.5	4.5	6.7	32	4300	2.4	117.9
16	2120	0.9	1.5	2.9	4.6	65	2400	2.3	118.4
17	2040	0.95	1.3	2.8	4.3	61	2650	2.6	118.9
18	1580	0.9	1.8	4.3	6.4	22	1720	2.4	116.8

[a] These entries correspond to those of Table 1. [b] Me br = methyl branch per 1000 carbons determined by integration of the 2C in α of the methyl branch in ^{13}C NMR. [c] Internal db = all −CH=CH− double bonds (vinylene and all others) determined by integration of the vinyl protons in ^{1}H NMR (5.25−5.50 ppm region). [d] Long br = long branch per 1000 carbons (>C4) determined by integration of the 3C in α of the tertiary carbon in ^{13}C NMR. These branches are characteristic of the incorporation of the comonomer. [e] wt % como incorp = weight percentage of comonomer incorporated in the polymer calculated from the number of long branches. [f] % remain como = percentage of remaining comonomer. [g] 45% out of 12 g of the 1:1 mixture of octene and hexadecene. Octene incorporation was supposed to be equal to the one in entry 10.

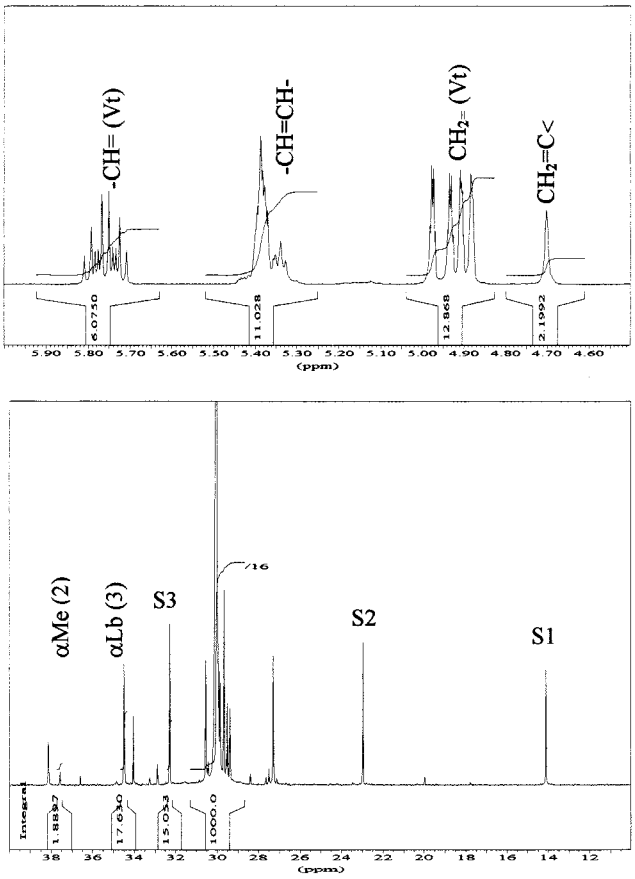


Figure 2. Typical NMR spectra of a ethylene/C16ene copolymer: (top) ^{1}H NMR (400 MHz), low-field resonance region corresponding to olefinic protons, for 4000 protons at higher field; (bottom) ^{13}C NMR (100.6 MHz), high-field resonance region corresponding to CH_3-, $-CH_2-$, and $-CH\langle$ (for complete assignment cf. Schemes 2 and 3).

with polydispersity around 2. The low molecular weight is easily explained on the basis of the lack of steric congestion on the axial faces of the catalyst.[36] ^{1}H and ^{13}C NMR studies gave complementary results. The low-field ^{1}H NMR region (Figure 2, top) gives vinylidene end groups, total internal $-HC{=}CH-$ double bonds, and terminal vinyl (Vt). Concerning the internal double bonds both trans and cis $CH_3-CH{=}CH-$ are observed (by ^{1}H and ^{13}C NMR) and trans and cis symmetrical internal double bond (by ^{13}C only, see Scheme 2) whereas presence of (C2 to C5)$-CH{=}CH-$ is not detected.

The NMR analysis of the copolymer end groups (total double bond content by ^{1}H) indicates a number-average molecular weight that is in good agreement with GPC results (Table 2 for experiments of Table 1). ^{13}C NMR (Figure 2, bottom) allows us to estimate the number of methyl branches per 1000 C and the number of saturated groups per 1000 C. The number of saturated groups corresponds to the number of chains plus all "extra" saturated groups generated by comonomer incorporation, vinylidene end group, and double-bond migration in true internal position. The comonomer incorporation is given either by the number of long branches or by any other specific resonances in ^{13}C or ^{1}H NMR (Scheme 3). But the presence of long branches is the true "fingerprint" of the comonomer incorporation.

Polymers have also been characterized by differential scanning calorimetry (DSC) in order to correlate melting temperature to comonomer incorporation. The copolymers exhibit broad melting transitions, with a peak temperature between 112 and 119 °C (Table 2). The relation between comonomer incorporation rates and melting points is striking, yet we have not been able to vary the melting point by more than 10 °C (number of branches comprised between 6 and 12/1000 C). Except for the absence of short branches (resulting from radical backbiting) the topology and melt characteristics are somewhat similar to radical LDPE. We will see below that this polymer crystallinity is a key parameter to colloidal stability.

In the miniemulsion process, the organic phase droplet can be considered as a suspended microreactor which is confined (diameter around 180 nm), highly concentrated in catalyst (between 0.4 and 2.5 mM) and in

Scheme 2. ^{13}C Chemical Shifts of PE Common Structures (Peaks Used for Quantitative Estimation Are in Bold Character)

1i 2i 3i 4i

$CH_2{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}$ terminal Vinyl (Vt)

114.26 138.99 **34.05** 29.86 29.51⇔29.39

$CH_2{=}C\text{-}[CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{----}]_2$ vinylidene end

109.02 149.88 36.60 28.38

α β γ δ

$CH_3\text{-}CH{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}$ trans vinylene double bond

17.77 124.56 131.92 32.87[b] 30.06[a] 29.56[a] 29.91[a]

(a) same as in internal trans double bond

(b) slightly different from an internal trans double bond

$CH_3\text{-}CH{=}CH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}$ cis vinylene double bond

12.68 123.58 131.06 27.64

$\text{-}CH_2\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH_2\text{-}$ trans symmetrical internal double bond

130.60 130.60 32.90

$\text{-}CH_2\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}CH_2\text{-}$ cis symmetrical internal double bond

130.06 130.06 27.49[a]

(a) overlapping with β carbon of Methyl branch

S1 S2 **S3** S4 "PE"

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}[CH_2]\text{-}CH_2\text{-}$ Saturated end group

14.08 22.95 **32.27** 29.66 30.06

33.25 **37.58** 27.50 30.43

$CH_2\text{-}CH_2\text{-}CH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}$ Methyl branch

CH_3 α β γ

19.94

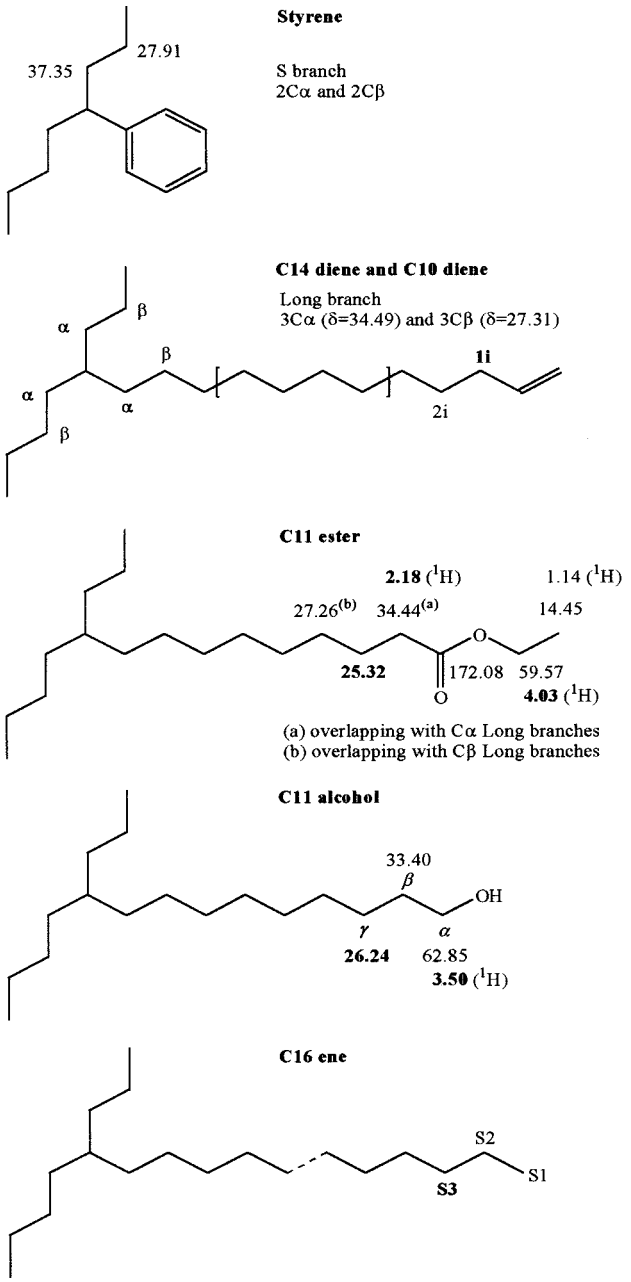
39.69 34.04 27.34 30.46

$CH_2\text{-}CH_2\text{-}CH\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}$ Ethyl branch

26.69 CH_2 α β γ (traces)

11.15 CH_3

Scheme 3. ^{13}C and ^{1}H Specific Chemical Shifts Corresponding to Comonomer Incorporation (Peaks Used for Quantitative Estimation Are in Bold Character)



comonomer (17% weight), and dispersed in water where ethylene solubility is low (2 orders of magnitude lower than in organic solvent, for example 0.1 mol/L at 40 bar). For these reasons, the catalyst in the droplet is subject to ethylene diffusion limitation under certain conditions.[34] This favors comonomer incorporation, as we have shown that the catalyst is able to homopolymerize α-olefins readily.[36] For example, with a concentration of 17 wt % of hexadecene in the initial droplet, the composition of the polymer indicates 8.9 wt % hexadecene incorporated (entry 7, Table 2). All the comonomer is incorporated in this experiment. A polymer of similar composition made by polymerization in solution in toluene (70 °C) requires a comonomer concentration as high as 80% in toluene.[46] In the organic solution process, the comonomer conversion is low (typically between 10 and 20% depending on reaction duration). Obviously, the use of our emulsion process is a method

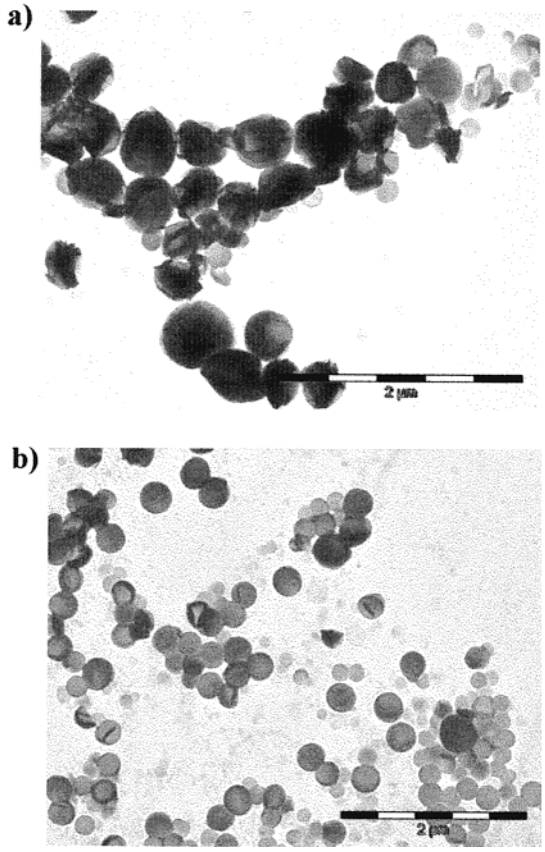


Figure 3. (a) Transmission electron microscopy (TEM) picture of a PE latex.[31] (b) TEM picture of a copolymer ethylene/hexadecene latex (entry 8, Table 1).

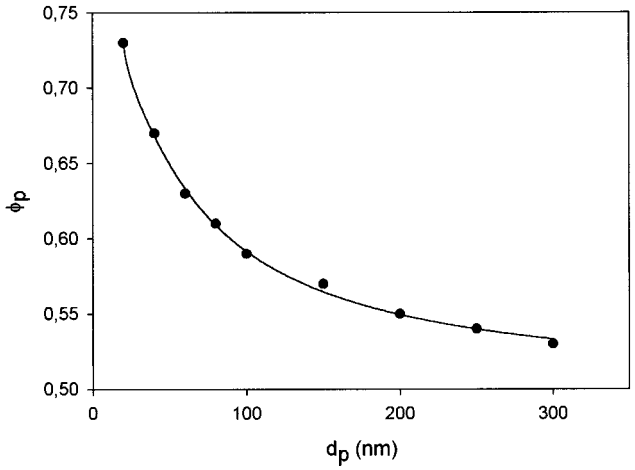


Figure 4. Polymer volume fraction (ϕ_p) calculated for different particle diameter (d_p) with the Morton−Kaizermann−Altier equation.

of choice for the efficient synthesis of copolymers with late transition metals. In this case and in the case of most dispersed processes, as we can infer it, compartmentalization and diffusional limitation of ethylene strongly favor the comonomer incorporation. Of course, this also translates into large compositional drifts, as the concentration of comonomer sharply decreases during the polymerization (as seen by the broad DSC melting exotherms, Figure 5). This "compartmentalization" effect is clearly observed when going from low to high volume of organic solvent (entries 12−14, Table 2), that is to say, from high to low comonomer concentration, and subsequent comonomer incorporation. Simi-

lar conclusions can be drawn from the influence of the catalyst amount (entries 6−8, Table 2). Octene copolymers are nearly twice as branched as hexadecene copolymers because for similar weight amounts, the number of moles of octene is twice as much (entries 10 and 13, Table 2).

3. Latex Characteristics of Ethylene/Hexadecene Copolymers. In a previous study on ethylene homopolymerization in emulsion,[31] we have observed a very large increase in the number of particles (ratio of number of particles to number of droplets between 2 and 100) in the course of the polymerization. This phenomenon has been interpreted as a consequence of the mechanism of particle formation. In homopolymerization, the polymer has been found to be very linear and highly crystalline (above 70% crystallinity), and as the crystallite grows to a significant size, it precipitates out of the organic droplet, generating a crystalline polymer particle and a liquid droplet which still contains catalyst. We expect the polymerization to be much slower in the polymer particle than in the organic droplet, in which a new polymer particle can be formed. This process stops when most of the catalyst has been dispatched into different polymer particles or when most of the organic solvent has been used to swell amorphous regions of the polymer particles. The particle formation mechanism is therefore somewhat related to a precipitation polymerization, as observed for the polymerization of vinyl chloride in an aqueous medium.[49] The polymer particles are characterized by a nonspherical shape resulting from the presence of numerous crystallites in the polymer. In the case of copolymerization, branched, less crystalline material is synthesized (maximum crystallinity:[50] 53% for 5.1 long branches per 1000 C which represents 7.6 wt % comonomer in the polymer, entry 5, Table 1), and polymer particles are nearly spherical (Figure 3b). Because of the low crystallinity, the growing polymer has no reason to precipitate out (in the form of a crystallite) from the organic droplet. This is confirmed by the ratio of the number of polymer particles to the number of droplets: it is consistently between 0.7 and 1.0 for experiments in Table 1.

Moreover, long-term colloidal stability is increased for the copolymer latices as they are now stable for months whereas linear PE latices start coalescing within weeks. Polymer particles are composed of a crystalline phase and an amorphous phase. Only the latter can be swollen by organic solvent, cosurfactant, and eventually surfactant hydrophobic tail. It is clear that the most amorphous particles, that is to say, the ones containing the most branched polymer, will be the most stable in the colloidal sense. This is clearly observed in TEM pictures. Pure PE particles (Figure 3a) are nonspherical and nonhomogeneous, with very rugged shapes. PE−hexadecene particles are nearly spherical and have a smooth contour (Figure 3b).

4. Putative Particle Formation Mechanism. In (mini)emulsion polymerization of ethylene, the final particle size is consistently equal to 200 nm, notwithstanding surfactant and cosurfactant nature and concentration and initial miniemulsion droplet size. For example, when a polybutene oligomer is used as a hydrophobe[42] instead of hexadecene,[51] the miniemulsion droplet size is small (around 100 nm, whereas it is 160 nm for hexadecane miniemulsion under identical conditions), but the resulting polymer particle size is in the same range as for hexadecane experiments. Note that the final latex obtained with polybutene is stable for months, whereas hexadecane latexes have a tendency to slowly coagulate, due to hexadecane phase separation. This slow phase separation is somewhat unexpected to us, as we naively thought that polyethylene and hexadecane would be entirely compatible (same solubility parameter δ), as hexadecane is an oligomer of polyethylene. Thus, latex stability is related neither to particle size nor to miniemulsion droplet size.

In (mini)emulsion copolymerization of ethylene with α-olefins, results that are quite similar in essence are observed: constancy of the final particle size for a wide range of experimental conditions. For example, one can compare a copolymerization of ethylene with hexadecene to a copolymerization of ethylene with octene (in this case, hexadecane is used as hydrophobic surfactant). In both cases, droplet dispersions and final latexes have similar characteristics. Polymer weight fraction in the organic phase are respectively 0.50 and 0.51 for entries 10 and 11.

We have found that both homopolymers and copolymers (isolated under the form of a powder) are not soluble in toluene at 60 °C (copolymers are soluble at 80 °C). These data are in good agreement with the dissolution temperatures of a polyethylene crystal as a function of the fold length of the chain in the crystal: for the smallest fold lengths, it is 75 °C in toluene (11 nm fold length) and 100 °C in hexadecane (14 nm fold length).[52] During the polymerization reaction, the growing polymer particle, swollen with toluene or benzene, is at the temperature of the continuous phase, as heat transfer is very efficient in nanometer scale objects.[53] As reaction exotherms are never higher than 4 °C, we can conclude that we are in conditions under which polymer eventually crystallizes (for the homopolymer) or precipitates (for the low crystallinity copolymer). Polyethylene crystallized from dilute toluene solutions gives rise to lamellae which in their simplest form are lozenge-shaped ({110} growth face) or a truncated lozenge (additional {100} growth face).[54] Lamellae grown from polyethylene melt exhibit an elliptic habit which is bounded by curved growth faces.[55,56] These lamellae are quite similar in aspect to the particles shown in Figure 3a.

On the basis of this set of observations, we can assume that the particles are formed when the growing polymer chains precipitate and/or crystallize in the dispersed organic phase. For polymers with low crystallinity (copolymerization), most of the solvent will be located into the amorphous phase or in organic droplets. As for emulsion polymerization, there is an equilibrium swelling of the polymer particles: the interfacial tension tends to reduce the water/polymer particle interface, but the osmotic swelling by the organic solvent favors particle expansion. The polymer volume fraction ϕ_p at which this equilibrium swelling occurs is given by the Morton−Kaizermann−Altier equation[57]

$$0 = \ln(1 - \varphi_p) + \varphi_p + \chi\varphi_p^2 + \frac{2V^\circ\gamma}{RTr}$$

where χ is the Flory Huggins polymer−solvent interaction parameter, r is the radius of the particle, γ is the interfacial tension PE/water ($\gamma = 52.7$ mN/m), and V° is the molar volume of the solvent ($V^\circ = 0.106$ L/mol).[58] The Flory−Huggins parameter can be suitably estimated from the solubility parameters,[58] and we found for toluene/PE at 70 °C $\chi = 0.751$. Using these values,

Table 3. Representative Results of Emulsion Copolymerization with Functionalized Comonomers[h]

entry	activity,[a] kg/(g_{Ni} h)	prod, kg/g_{Ni}	C_{C16ane},[b] g/L	comonomer[c]	particle size,[d] nm	sc,[e] %	$N_{particles}/N_{droplet}$[f]
1	1.8/1.4	4.5	20	styrene[g]	228 ± 91	12.6	1.40
2	8.6/6.3	18.6	0	C14-diene	270 ± 97	17.9	0.71
3	7.3/6.0	16.7	20	C10-diene	227 ± 90	17.4	0.97
4	6.5/5.5	14.9	0	C11 ester	231 ± 120	16.9	1.10
5	6.0/4.4	12.7	20	C11 ester	217 ± 87	15.6	0.73
6	0.1/0		20	C11 acid	nd	nd	
7	4.6/4.5	11.2	20	C11 alcohol	188 ± 82	14.4	0.63
8	8.2/5.6	17.6	0	C16-ene	230 ± 92	17.2	0.96
9	7.9/6.2	17.7	20		217 ± 87	16.9	2

[a] Activity max/activity at the end of the reaction. [b] Concentrations of hexadecane in the volume of water. [c] Comonomer abbreviations: C14-diene = 1,13-tetradecadiene, C10-diene = 1,9-decadiene, C11 ester = ethyl 10-undecenoate, C11 acid = 10-undecenoic acid, C11 alcohol = 10-undecen-1-ol. [d] Determined by dynamic light scattering at low concentrations. [e] Solid content determined by gravimetry of the filtered latex. [f] Ratio of the droplet number to the number of polymer. [g] Instead of 40 mL of toluene, a 1:1 mixture of styrene and toluene was used. [h] Experiments run at 55 °C under 20 bar of ethylene using 50 μmol of catalyst **1**, dissolved in 40 mL of toluene. 6 g of comonomer is added to the catalytic solution. This organic phase is miniemulsified in 300 mL of water containing SDS (20 g/L of water). Time reaction is 150 min.

Table 4. NMR, GPC, and DSC Results of the Polymer Synthesized in Experiments 1−9 of Table 3

	^{1}H and ^{13}C NMR						GPC		DSC
exp[a]	M_n (g/mol)	Me br[b]	internal db[c]	long br[d]	wt % como poly[e]	% remain como[f]	M_w (g/mol)	M_w/M_n	T_m (°C)
1	1190		1.18		15.1	73	987	3.6	101.1
2	Nd	1.1	4.3	5.6	nd	nd	13640	12.9	118.4
3	Nd	1.4	5.3	8.25	nd	nd	47870	106.8	113.1
4	2110	1.1	2.6	5.6	8.1	41	4290	6.4	115.6
5	2100	1.1	2.5	5.8	7.6	53	4440	8.0	115.6
7	2090	0.9	2.3	5.5	6.2	66	3844	7.2	114.5
8	2160	1.3	2.8	6.7	9.7	16	8189	3.8	115.9
9	3500	0.9	5.4	0.6			9100	2.6	119.8

[a] These entries correspond to those of Table 3. [b] Me br = methyl branch per 1000 carbons determined by integration of the 2C in α of the methyl branch in ^{13}C NMR. [c] Internal db = all −CH=CH− double bonds (vinylene and all others) determined by integration of the vinyl protons in ^{1}H NMR (5.25−5.50 ppm region). [d] Long br = long branch per 1000 carbons (>C4) determined by integration of the 3C in α of the tertiary carbon in ^{13}C NMR, except in the case of C11 ester due to overlapping with the carbon in α of the CO carbon. These branches are characteristic of the incorporation of the comonomer. [e] wt % como poly = weight percentage of comonomer in the polymer chain calculated from the number of long branches. [f] % remain como = percentage of comonomer incorporated in the polymer chain.

the Morton equation has been numerically solved for several particle sizes (Figure 4). It is observed that the limiting degree of swelling (corresponding to the maximum amount of polymer in the particle at thermodynamic equilibrium) is around 55% (in volume) in our size domain. This is in excellent agreement with our observed phenomena (Figure 1), seemingly indicative that the limiting factor in the polymerization is the particle swelling. A further experiment supports this assumption: at the end of a typical experiment (residual activity less than 2 kg/(g_{Ni} h)), fresh toluene has been added. In this case, activity and productivity immediately increase to 8 kg/(g_{Ni} h).

B. Copolymerization with Functionalized α-Olefins. We now embark on a discussion about the copolymerization of ethylene with several functionalized monomers in emulsion. For all the experiments, we have used a standard set of experimental conditions: 50 μmol of catalyst in 40 mL of toluene (instead of benzene). With these experiments, it is hoped to decrease the VOC content in the reaction medium by replacing toluene by a polymerizable solvent such as styrene, second, to increase the polymer molecular weight by using a diene which allows cross-linking, and, finally, to enhance the physical and chemical polymer properties (especially in film-forming experiments) through the use of polar functional groups.

1. Styrene as Catalyst Solvent. We have first considered replacing the organic solvent (toluene) by styrene, so as to reach a higher weight fraction of polymer, w_p, in the particle. With styrene, kinetics are very slow due to (1) chelate formation between the metal center and the α (or β) phenyl group on the active chain or (2) π-donating character of the comonomer, thus blocking the vacant coordination site.[59] Hence, activity and productivity are 5 times lower than for other comonomers (entries 1 and 8, Table 3). High incorporation can be targeted (15.1 wt %, entry 1, Table 4), but the reaction still stops for $w_p = 0.51$. This is in agreement with the mechanism proposed above. Remaining styrene (73%) can be polymerized upon addition of a radical initiator. With styrene, polymer characteristics are highly modified in terms of molecular weight (entry 1, Table 4) and melting point (Figure 5c). Surprisingly, copolymerization with styrene is the only case where the number of particles in the latex is greater than the number of droplets. We are currently further examining this point, but we do not believe that renucleation of particles through a thermal radical mechanism (self-initiation) can be invoked at a temperature of 55 °C.

For the other comonomers (diene and olefin bearing a polar functionality), very different results are observed depending on the position of the functionality relative to the double bond. Klabunde has reported that if the functional group is vinylic (as in butadiene, (meth)-acrylate, or vinyl acetate) or allylic (as in 1,4-pentadiene or allyl acetate), the catalytic activity of neutral P,O-chelated Ni(II) complexes in polymerization is inhibited.[60,61] However, with cationic α-diimine palladium(II) catalysts, Brookhart has reported that ethylene and methyl acrylate can be copolymerized to high molecular

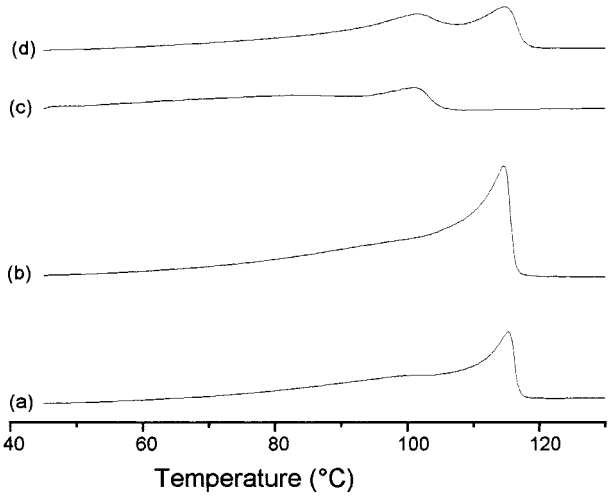


Figure 5. DSC thermograms of ethylene/(a) 1-hexadecene, (b) 1-uncen-1-ol, (c) styrene, or (d) 1,13-tetradecadiene copolymers prepared with catalyst **1** at 55 °C, 20 bar of ethylene, and in miniemulsion.

weight copolymers.[27,62] This copolymerization is possible with α-diimine Pd catalyst since ethylene is able to reversibly substitute the chelating carbonyl group to then insert into the metal−carbon bond. Consequently, the polymer is highly branched, and MA is present only at the end of a branch. The catalyst activity is diminished by addition of this comonomer, but molar comonomer incorporation up to 12% can be achieved.

The coordination of the fourth position by the functionality (olefin or polar group) of the comonomer can be prevented by introducing spacers such as methylene units (at least 3) between the two functionalities. Few details about comonomer incorporation and catalyst activities are provided in the work of Klabunde:[60,61] productivities are only slightly less upon addition of long-chain α,ω-diene as well as α,ω-polar functionality olefins.

α,ω-Diene as Comonomer. The two long-chain α,ω-dienes used are 1,13-tetradecadiene and 1,9-decadiene. First of all, the stability of the organic phase droplets after sonication has been evaluated in the absence of hexadecane. Once again we use a comonomer not only to bring interesting functionality to the polymer but also as hydrophobic cosurfactant. Tetradecadiene is hydrophobic enough to give a stable droplet miniemulsion, but shorter dienes require the addition of hexadecane to generate a stable colloid (entries 2 and 3, Table 3). Stable droplet miniemulsion in hands, activity, and productivity are very similar to the ones obtained with hexadecene (entries 2 and 3 vs 8, Table 3). Latex obtained with hexadecene or α,ω-diene presents identical characteristics (latex stability, ratio of particles number on droplets number, particle size, and solid content).

As α,ω-diene is a bifunctional comonomer, it is able to induce cross-linking to generate a gel above the threshold of percolation and high molecular weight branched polymer below this critical concentration. GPC, NMR, or melt index measurement confirm the synthesis of high molecular weight material (entries 2 and 3, Table 4). By ^{1}H and ^{13}C NMR, long-chain branches can be estimated: they give access to the amount of comonomer inserted either simply or doubly. The incorporation is very similar to what is found for hexadecene (entries 2 and 8, Table 4). The shorter diene presents a higher proportion of long-chain branches since its molar concentration in the feed is higher (entry 3, Table 4). We have not found a precise method to determine the amount of double incorporation (cross-linking). This is due to the fact that the terminal double bonds are isomerized into internal double bonds, thus generating a saturated chain end: it is then very difficult to account for saturated chain ends that come from isomerization or by the hydride reinitiation. DSC thermograms also indicate the specificity of this copolymer (Figure 5d). Two melting transition peaks are present even after the first heating/cooling cycle. It can be postulated that two types of polymer, a cross-linked and a regular one, are present.

α,ω-Functionalized Olefin as Comonomer. Droplet stability has been determined for ethyl 10-undecenoate, 10-undecen-1-ol, and 10-undecenoic acid. Alcohol and acid did not lead to a stable initial miniemulsion, and the use of a hydrophobic cosurfactant is necessary. On the other hand, ester hydrophobicity is sufficient to stabilize the organic phase dispersion. This stems from the higher solubility of 10-undecen-1-ol and 10-undecenoic acid in water compared to ethyl 10-undecenoate. Indeed, it has been reported that only "ultrahydrophobes" (water solubility less than 10^{-7} mL/mL) can be employed as hydrophobes.[41] For the sake of comparison, copolymerization of ethyl undecylenate has also been effected in the presence of cosurfactant. The nature of the functional group strongly influences the level of activity and productivity. No activity is observed in the case of the acid (entry 6, Table 3) whereas the alcohol is slightly inhibiting the polymerization compared to a nonfunctionalized analogue (entries 7 and 8, Table 3). The ester comonomer is almost equivalent to hexadecene (entries 4 and 8, Table 3).

Analyses of these copolymers by GPC, NMR (Table 4), and DSC (Figure 5a,b) highlight characteristics that are quite similar to ethylene/hexadecene copolymers. Molecular weight, comonomer incorporation, proportion of isomerization, melting temperature, and percentage of crystallinity are nearly identical in all cases. As for hexadecene copolymerization, the incorporation of the polar comonomer in emulsion is very high compared to solution incorporation.[46] Once again, we believe that emulsion polymerization is a suitable method for catalytically preparing copolymers of ethylene with functional monomers.

The resulting latex are stable for months without flocculation. Because of the presence of polar groups and low crystallinity, this latex presents interesting film-forming properties, which are currently under scrutiny. Among them should be cited the possibility to form a coating that is compatible with polyolefin. This could eventually lead to the development of an aqueous paint for polypropylene. These products are also currently compared to existing polyolefin latexes that are made by emulsification under harsh conditions of polyethylene and polypropylene.

Conclusion

The miniemulsion process for ethylene polymerization using a neutral Ni(II) catalyst with fluorinated P,O-chelate has been successfully extended to the copolymerization of ethylene with long-chain α-olefins, long-chain α,ω-dienes, styrene, and long-chain α,ω-olefins bearing polar substituents. The need for a highly

hydrophobic compound as miniemulsion stabilizer has been advantageous, as the comonomer could play this role. Therefore, the amount of VOCs in the final product can be reduced using a copolymerizable cosurfactant. 1-Hexadecene was most extensively studied, and we have shown that use of this comonomer allows the control of the polymer particles formation as no additional particles are generated in the course of the polymerization. We believe that this phenomenon is due to the less crystalline nature of the polymeric material. We have also shown that particle swelling is determining the end point of the polymerization. In addition, the copolymer latices present a superior long-term stability (compared to pure PE latex). With improved experimental conditions (catalyst concentration, temperature, etc.) solids content above 30% can be reached without flocculation. Using long-chain α,ω-diene, higher molecular weight material has been synthesized, thanks to the cross-linking of the comonomer. In addition, polar functionalities such as alcohol and ethyl ester have been incorporated to the polymer chain. We have shown that the water dispersed organic medium is a process of choice to improve comonomer incorporation. Using much lower comonomer concentrations in the organic phase compared to classical solution polymerization allows us to reach similar or even higher comonomer incorporation.

References and Notes

(1) Fitch, R. M. *Polymer Colloids, a Comprehensive Introduction*; Academic Press: San Diego, 1997.
(2) Satoh, K.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 3827.
(3) Satoh, K.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2000**, *33*, 5836.
(4) Satoh, K.; Nakashima, J.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2001**, *34*, 396.
(5) de Gunzbourg, A.; Favier, J. C.; Hémery, P. *Polym. Int.* **1994**, *35*, 179.
(6) de Gunzbourg, A.; Maisonnier, S.; Favier, J. C.; Maitre, C.; Masure, M.; Hémery, P. *Macromol. Symp.* **1998**, *132*, 359.
(7) Maitre, C.; Ganachaud, F.; Ferreira, O.; Lutz, J. F.; Paintoux, Y.; Hémery, P. *Macromolecules* **2000**, *33*, 7730.
(8) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542.
(9) Lynn, D. M.; Kanaoka, S.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 784.
(10) Mohr, B.; Lynn, D. M.; Grubbs, R. H. *Organometallics* **1996**, *15*, 4317.
(11) Lynn, D. M.; Mohr, B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 1627.
(12) Lynn, D. M.; Mohr, B.; Grubbs, R. H. *Polym. Prepr.* **1998**, *39*, 278.
(13) Claverie, J.; Viala, S.; Maurel, V.; Novat, C. *Macromolecules* **2001**, *34*, 382.
(14) Rinehart, R. E. *J. Polym. Sci., Part C* **1969**, *27*, 7.
(15) Henderson, J. N.; Donbar, K. W.; Barbout, J. J.; Bell, A. J. (Goodyear) U.S. Patent 4429085, 1984.
(16) Bell, A. J.; Ofstead, E. A. (Goodyear) Eur. Pat. Appl. 0475221A, 1990.
(17) Burroway, G. L.; Magoun, G. F. Gujarathi, R. N. U.S. Patent 5012381, 1991.
(18) Jiang, Z.; Sen, A. *Macromolecules* **1994**, *27*, 7215.
(19) Verspui, G.; Papadogianakis, G.; Sheldon, R. A. *J. Chem. Soc., Chem. Commun.* **1998**, 401.
(20) Bianchini, C.; Lee, H. M.; Meli, A.; Moneti, S.; Patinec, V.; Petrucci, G.; Vizza, F. *Macromolecules* **1999**, *32*, 3859.
(21) Verspui, G.; Feiken, J.; Papadogianakis, G.; Sheldon, R. A. *J. Mol. Catal. A* **1999**, *146*, 299.
(22) Lindner, E.; Schmid, M.; Wald, J.; Queisser, J. A.; Geprägs, M.; Wegner, P.; Nachtigal, C. *J. Organomet. Chem.* **2000**, *602*, 173.
(23) Verspui, G.; Schanssema, F.; Sheldon, R. A. *Appl. Catal., A* **2000**, *198*, 5.
(24) Verspui, G.; Schanssema, F.; Sheldon, R. A. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 804.
(25) Goodall, B. L.; McIntosh, L. H. (BFGoodrich) WO 0001747, 07/1998.
(26) Puech, L.; Perez, E.; Rico-Lattes, I.; Bon, M.; Lattes, A.; Moisand, A. *New J. Chem.* **1997**, *21*, 1229.
(27) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888.
(28) Puech, L.; Perez, E.; Rico-Lattes, I.; Bon, M.; Lattes, A. *Colloids Surf., A* **2000**, *167*, 123.
(29) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460.
(30) Tomov, A.; Broyer, J. P.; Spitz, R. In *Polymers in Dispersed Media I*; Claverie, J., Charreyre, M.-T., Pichot, C., Eds.; Wiley: Weinheim, 2000; Vol. 150, p 53.
(31) Soula, R.; Novat, C.; Tomov, A. P.; Spitz, R.; Claverie, J.; Drujon, X.; Saudemont, T.; Malinge, J. *Macromolecules* **2001**, 2022.
(32) Held, A.; Bauers, F. M.; Mecking, S. *J. Chem. Soc., Chem. Commun.* **2000**, 301.
(33) Held, A.; Mecking, S. *Chem. Eur. J.* **2000**, *6*, 4623.
(34) Bauers, F. M.; Mecking, S. *Macromolecules* **2001**, 1165.
(35) Tomov, A.; Spitz, R.; Saudemont, T.; Drujon, X. (Elf Atochem S. A.) French 98.12476, 11/1998.
(36) Soula, R.; Broyer, J. P.; Tomov, A. P.; Llauro, M. F.; Spitz, R.; Claverie, J.; Drujon, X.; Saudemont, T.; Malinge, J. *Macromolecules* **2001**, 2438.
(37) Keim, H. *Info Chim. Magn.* (in French) **2000**, *421*, 88.
(38) Hamper, B. C. *J. Org. Chem.* **1988**, *53*, 5558.
(39) Ruan, J. J., Ed. *Measuring PSD from Micrograph Images*; American Chemical Society Series: Atlanta, 1992.
(40) Sudol, E. D.; El-Aasser, M. S. In *Emulsion Polymerization and Emulsion Polymers*; Lovell, P. A., El-Aasser, M. S., Eds.; John Wiley & Sons: New York, 1997; p 700.
(41) Landfester, K.; Bechthold, N.; Tiarks, F.; Antonietti, M. *Macromolecules* **1999**, *32*, 5222.
(42) Schork, F. J.; Poelhein, G. W.; Wang, S.; Reimers, J.; Rodrigues, J.; Samer, C. *Colloids Surf., A: Physiochem. Eng. Aspects* **1999**, *153*, 39.
(43) Tang, P. L.; Sudol, E. D.; Adams, H. E.; Silebi, C. A.; El-Aasser, M. S. In *Polymer Latexes: Preparation, Characterization, and Applications*; Daniels, E. S., Sudol, E. D., El-Aasser, M. S., Eds.; American Chemical Society: Washington, DC, 1992; ACS Symposium Series Vol. 492, p 72.
(44) The influence of the cosurfactant on miniemulsion droplet size and its consequence on polymer particle colloidal stability will be discussed in the paragraph "putative latex formation mechanism".
(45) Tait, P. J. T.; Awudza, J. A. M. In *Progress and Development of Catalytic Olefin Polymerization*; Sano, T., Uozumi, T., Nakatani, H., Terano, M., Eds.; Technology and Education Publishers: Tokyo, 2000; p 214.
(46) Claverie, J.; Spitz, R.; Drujon, X.; Touchard, V.; Llauro, M. F.; Soula, R. *Polym. Prepr., Am. Chem. Soc. Div. PMSE* **2001**, *84*, 329.
(47) Half-life time of the catalyst is the time when activity is half the maximal value obtained at the beginning of the reaction.
(48) Brouwer, W. N.; El-Aasser, M. S.; Vanderhoff, J. W. *Colloids Surf.* **1986**, *21*, 69.
(49) Ugelstad, J.; Mork, P. C.; Berge, A. In *Emulsion Polymerization and Emulsion Polymers*; Lovell, P. A., El-Aasser, M. S., Eds.; John Wiley & Sons: New York, 1997; p 589.
(50) The crystallinity has been calculated as the ratio of peak enthalpy of melting to enthalpy of 100% crystalline material. This method is approximative, as one compares a perfectly linear PE (sharp transition) to a branched, derivatized PE (broad transition). T_g has not been measured. See also Figure 3a.
(51) The miniemulsion was formed with 20 g/L of SDS and 10 g/L of polybutene (>90% isobutylene, average M_n = 560 g/mol, Aldrich).
(52) Organ, S. J.; Keller, A. *J. Mater. Sci.* **1985**, *20*, 1602.
(53) Carslaw, H. S.; Jaeger, J. C. *Conduction of Heat in Solids*, 2nd ed.; Oxford University Press: Oxford, 1959. Using the solution of the Fourier equation presented in this book (pp 242−244), the flow of heat in a 100 nm toluene sphere in which a constant heat generation A_0 has been included (A_0 = 0.4 J/(s m^3), a typical value for our polymerizations) can be calculated: the temperature difference between the inside and the outside of the sphere is found to be 10^{-9} K.
(54) Vaughan, A. S.; Bassett, D. C. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon Press: Oxford, 1989; Vol. 2, p 415.

(55) Hoffman, J. D. *Polymer* **1983**, *24*, 3.
(56) Organ, S. J.; Keller, A. *J. Mater. Sci.* **1985**, *20*, 1571.
(57) Lovell, P. A.; El-Aasser, M. S. *Emulsion Polymerization and Emulsion Polymers*; John Wiley & Sons: Chichester, 1997.
(58) van Krevelen, D. W. *Properties of Polymers*, 3rd ed.; Elsevier: Amsterdam, 1990.
(59) Po, R.; Cardi, N. *Prog. Polym. Sci.* **1996**, *21*, 47.
(60) Klabunde, U. (E. I. Du Pont de Nemours) U.S. 4,698,403, 10/1987.
(61) Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* **1987**, *41*, 123.
(62) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267.

MA011366E