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Catalytic Copolymerization of Ethylene and Norbornene in Emulsion

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Introduction. The copolymerization of ethylene and norbornene (NBE) has attracted a lot of attention recently.[1] Unlike pure polyethylene, the copolymer is amorphous with a T_g potentially varying from −100 °C to more than 300 °C (corresponding to the T_g of pure PE and PNBE).[2] Clearly, latexes of such polymers would present unique properties, as conventional latexes are usually limited to T_g's up to 125 °C (T_g of PMMA). They would also be highly durable, UV and chemically resistant, and very hydrophobic. Such latexes could be prepared by an emulsion polymerization process which is a widely spread technology in polymer manufacturing.[3] Furthermore, the use of water as a suspending medium is an environmental advantage, and it can be safely used as a continuous phase or a solvent for carrying out very exothermic reactions such as polymerizations because of its very high heat capacity. Heterophase polymerizations (in water or any other medium) also benefit from the fact that even at high solids (up to 60% polymer volume fraction in the liquid) the viscosity remains low or moderate. Finally, the polymer, in the form of a latex, is free-flowing; therefore, it is easily formulated and often does not require any further processing.

We[4] and the group of Mecking[5] have shown that it is possible to prepare latexes of polyethylene by the catalytic polymerization of ethylene. For that purpose, palladium- and nickel-based catalysts were used because of their reduced oxophilicity and their propensity to preferentially coordinate ethylene over water. Such catalysts are usually very hydrophobic, and both groups have shown that it is possible to emulsify the catalytic solution using a miniemulsion process.[6] This miniemulsified catalyst can then be used as "initiator" in a conventional emulsion process.

In this preliminary report, we describe the preparation of latexes of ethylene and NBE, using a palladium-based catalyst.

Experimental Section. Ligand **A**, P(o-OMe-C_6H_4)$_2$(o-SO_3H-C_6H_4), was prepared according to the procedure detailed in ref 7. All manipulations were done under argon using standard Schlenk techniques. Water was ultrapure grade (18.2 Mohm) and degassed by boiling for 120 min, followed by sparging with Ar for several hours. NBE was purified by passing it at 50 °C over a bed of activated basic alumina and activated molecular sieves. Sodium dodecyl sulfate (SDS) was recrystallized five times from methanol. All other chemicals were used without further purification. The molecular weights, relative to polystyrene standards, were determined on a Waters GPC equipped with a RI detector and a set of PolymerLabs Mixed C columns. Particle sizes were measured on a light-scattering Microtrac VSR S3000. Melting points and T_g were measured on a modulated DSC (Q100, TA Instruments). Transmission electron microscopy (TEM) measurements were effected on a Tecnai12 (V = 80 kV, W filament) using uranyl acetate as negative contrast agent.

Table 1. Experimental Conditions for the Copolymerization of Ethylene and NBE

expt	[Pd] (μmol/L)	[NBE] (g/L)	P (psi)	process[a]	TOF max (/h)	conv(NBE) (%)
1	24	0	300	S	52000	
2	24	10	300	S	3000	27
3	23	57	60	S	nd[b]	6
4	24	50	300	S	nd	36
5	24	100	300	S	nd	43
6	25	11	200	S	nd	35
7	25	10	100	S	530	36
8	644	20	300	E	nd	38
9	638	40	300	E	416	51
10	645	100	300	E	nd	42
11	640	50	300	E	326	81
12	644	100	100	E	nd	93
13	1047	50	60	E	nd	32

[a] S stands for solution process, E for emulsion process. [b] nd: not determined (<300/h).

a. Typical Solution Polymerization. In a Schlenk tube, 2.24 mg of ligand **A** (5.57×10^{-3} mmol) and 2.0 mg of $Pd_2(dba)_3$ (2.18×10^{-3} mmol) were suspended in 90 mL of toluene. NBE (10 g) was dissolved in 10 mL of toluene. The catalyst solution and the NBE solutions were then introduced into the 300 mL Parr reactor, immediately pressurized with 100 psi ethylene, and heated at 100 °C. When the temperature was reached, the reactor was continuously fed with ethylene at 300 psi, and the conversion of ethylene was monitored on line. After 90 min, the reaction was stopped, and the polymer collected by precipitation in 4 volumes of methanol.

b. Typical Emulsion Polymerization. In a Schlenk tube, 65.5 mg of ligand **A** (163×10^{-3} mmol) and 59 mg of $Pd_2(dba)_3$ (64×10^{-3} mmol) were dissolved in 20 mL of dichloromethane containing 3.0 g of hexadecane. This solution was introduced in a separate container containing 150 mL of a 20 g/L SDS aqueous solution. The mixture was sonicated using a 600 W Branson sonicator for 4 min and then introduced to the pressure reactor. The reactor was then loaded with NBE and pressurized with ethylene (300 psi). After 1 h (100°C, 1000 rpm), the reaction was stopped, and a free-flowing white latex was collected from the reactor.

Results and Discussion. Drent et al. first reported that the catalytic system we are using can copolymerize ethylene with acrylates[8] and carbon monoxide with ethylene[7] in a nonalternating fashion. The phosphine sulfonate is thought to undergo oxidative addition on the palladium(0) complex (Pd_2.$(dba)_3$) to generate the active species.[9,10] Well-defined neutral alkyl phosphine sulfonate Pd(II) species have recently been described and used for the nonalternating copolymerization of ethylene and CO in the presence of fluorinated boranes.[9] Since this latter species cannot be used in an aqueous environment, we opted for the borane-free catalytic system constituted of a ligand and a source of Pd(0).

In a typical E-NBE run, the catalytic activity, as measured from the uptake of ethylene, increases for the first 20 min and then decreases to virtually zero activity after several hours. In

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Table 2. Characteristics of the Copolymers[a]

run	polym wt (g)	SC[b] (%)	d_p[c] (nm)	M_n (g/mol)	PDI[d]	% NBE[e]	T_g[i] (°C)	T_m[i] (°C)	% cryst[j]
1	1.4	na[f]	na	ncs[g]	ncs	0		127	58
2	2.6	na	na	ncs	ncs	12	15	98	5
3	0.5	na	na	48000	2.0	1.8	113		
4	0.9	na	na	32000	2.1	36	78		
5	0.7	na	na	51000	1.9	43	103		
6	1.5	na	na	26000	1.8	35	17		
7	1.6	na	na	27000	1.8	36	18	110	nd
8	na	5.2	418	9000	2.0	38	−11	90	1.5
9	na	5.7	198	4500	2.2	30	7	98	2.5
10	na	floc[h]	365[h]	1900	3.0	13	0	92	4
11	na	9.3	213	4100	2.8	44	139	88	1
12	na	5.1	765	3900	3.0	44	171	97	2.5
13	na	3.6	226	nd	nd	44	140	88	4.5

[a] For the polymers prepared via a solution process, the weight of polymer is reported, whereas the solid content of the latex is reported for the polymers prepared by emulsion polymerization. [b] Solid content. [c] Particle diameter. [d] Polydispersity index. [e] Molar percentage of NBE in the copolymer. [f] Does not apply. [g] Not completely soluble. [h] Flocculated after several hours. [i] Determined in modulated DSC (heating/cooling rate = 5 °C/min, modulation ±1.5 °C/60 s). Values are reported for the first heating pass. [j] Percentage of crystallinity for the polymer in the native state (first heating), based on the ΔH_f of the orthorhombic PE crystal (290 J/g).

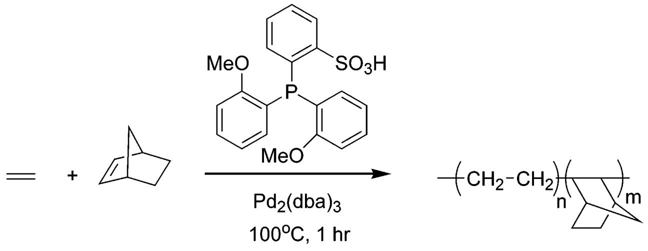

Figure 1. Palladium-catalyzed copolymerization of ethylene and NBE (dba = dibenzylideneacetone).

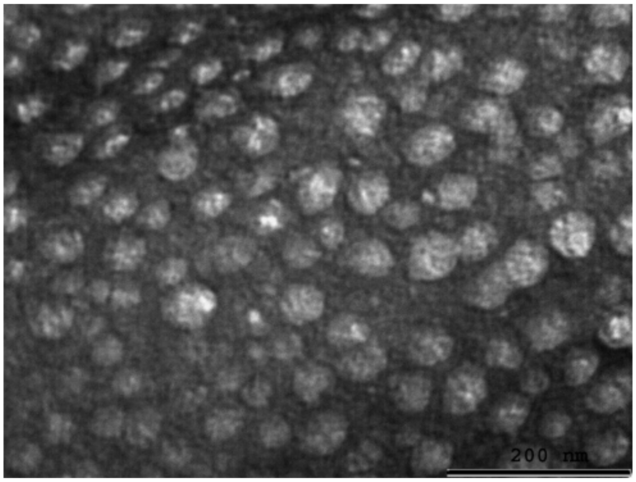

Figure 2. TEM cliché of a PE-*co*-PNBE latex (entry 13, Table 1).

Table 1, we report the maximum turnover frequency (TOF, in h^{-1}). As expected, solution copolymerization of ethylene and NBE in toluene occurs at a slower rate than the homopolymerization of ethylene (entry 1 vs 2 in Table 1). NBE incorporation increases as ethylene pressure decreases and NBE concentration increases, reflecting the expected higher reactivity of ethylene vs NBE.

As a prerequisite to copolymerizing ethylene and NBE in emulsion, it was necessary to assess the solubility of both monomers and of the catalyst in water. Both catalyst components are completely insoluble in water. Our attempts to prepare stable latexes by introducing the catalytic powder in the aqueous dispersion of monomers and surfactant resulted in the formation of polymer microparticles (average diameter ∼ 44 μm) akin to those formed in a suspension polymerization of ethylene in an alkane diluent. Consequently, the catalyst was dissolved in a minimum of organic solvent (either dichloromethane or toluene) containing hexadecane, and the organic solution was then miniemulsified in an aqueous surfactant solution by sonicating. The resulting miniemulsion has a droplet size, as measured by light scattering, of around 150 nm, and it is stable for several hours. The solubility of NBE in water (0.13 g/L at 25 °C)[11] is comparable to the solubility of styrene in water (0.18 g/L). Thus, as in the case of a styrene radical polymerization, it was possible to introduce NBE in the reaction medium where it forms large droplets stabilized by surfactant. These droplets are significantly larger than the miniemulsion droplets containing the catalyst: as with a conventional emulsion polymerization, they serve as monomer reservoirs, and no polymerization occurs in those, as shown by the absence of large particles in the final latex (Table 2 and Figure 2). At 300 psi and 100 °C, the solubility of ethylene in water has been reported to be ∼1 g/L.[12] Because of its small size (large diffusion coefficient) and high water solubility compared to those of most acrylic and styrenic monomers, transport of ethylene through the aqueous phase occurs readily. Therefore, as in a conventional emulsion polymerization, the diffusion of these monomers through the aqueous phase is not expected to control the rate of polymerization. However, the transport of ethylene at the interface gas water can be rate-limiting: in our hands, activity of the emulsion polymerization strongly depends on the design of the reactor, type of stirring blade used during the polymerization, and of course stirring rate.

The polymerization process can be viewed as a hybrid between an emulsion polymerization (monomer and initiator introduced directly to the continuous phase) and a miniemulsion polymerization (monomer and eventually initiator are emulsified in droplets which can be viewed as individual isolated nanoreactors). In our case, the role of the catalytic miniemulsion is unclear: it probably serves as a medium to transport the catalyst. In comparison to a conventional emulsion polymerization, relatively high stir rates (around 1000 rpm) are used, which can promote the fusion and fission of the miniemulsion droplets and therefore diffusion of the catalyst from initial droplets to growing polymer particles.[13]

While keeping in mind that physical limitations occur in this type of emulsion polymerization (at least for ethylene), a few observations can be made on the polymerization kinetics: first, the catalytic activity is significantly lower in an emulsion process compared to solution conditions. DeKock et al. have reported that water hydrolyzes the metal−alkyl bond of cationic palladium diimine and nickel salicylaldiminate polymerization catalysts.[14] We have found that for the catalytic system A + $Pd_2(dba)_3$ water also acts as a strong poison of the catalyst: the rate of homopolymerization of ethylene in THF decreases when small amounts of water are introduced. For example, under otherwise similar conditions, the TOF is 177 000 h^{-1} in dry THF, 117 000 h^{-1} in THF containing 0.1% of water, 7900 h^{-1} in THF containing 1% water, and nonmeasurable in THF containing 10% water. The molecular weights of the E-NBE copolymers are also significantly lower when water is present (Table 2), hinting to the possibility that water may act as a deactivating chain transfer (via hydrolysis of the metal−carbon bond).

It is also interesting to note that NBE conversions are in general higher for emulsion than for solution polymerizations (Table 1). NBE conversions were calculated from the knowledge of the weight of collected polymer and the copolymer composition, as assessed by ^{1}H NMR.[15] For example, for entries 2 and 3 (solution polymerization), the NBE conversions are 27% and 6%, respectively, whereas for entries 11 and 12 (emulsion polymerization), the NBE conversions are 81% and 93% (Table 1). Higher NBE conversions may be attributed to the compartmentalization effect that occurs in emulsion polymerization: the reaction can be viewed as a bulk (solventless) polymerization occurring in a series of nanoreactors dispersed in water. High local concentration of NBE in each nanoreactor, and possibly slow diffusion of ethylene at the interface gas water, globally favors NBE incorporation.

The emulsion copolymers are very heterogeneous in composition. They contain a NBE-rich fraction ($>$20 mol %) which is readily soluble in chloroform at room temperature and another fraction which is rich in ethylene and hardly soluble at room temperature. This compositional heterogeneity translates into a very complex behavior in modulated DSC. At the first heating cycle, the reversible heat capacity curve presents one or several broad T_g transitions and one melting point (on the total heat flow curve), whereas at the second heating a single T_g is usually present. The melting point corresponds to the ethylene-rich fraction which is crystalline, and the high T_g corresponds to the NBE-rich fraction. When the dried latex is analyzed by DSC, both fractions are phase-separated, but when heated past T_g and then cooled, these two fractions become miscible. On the other hand, the copolymer produced in a solvent based is not phase separated when dried. The complex DSC pattern observed for the latex is a signature of the morphological features of the latex nanoparticle which is predominantly developed during the emulsion polymerization process.[16] The exact nature of the morphology of PE-*co*-NBE latex particles is currently under scrutiny.

Using ^{13}C NMR analysis,[17] the polymers were found to contain both *meso* and *racemic* NEN sequences (usually in a ratio m:r = 1:2), as expected in the absence of stereocontrol. No NN diads or NNN triads were observed, which is consistent with the observation that this catalyst does not homopolymerize NBE under these conditions. Polymers having a high NBE content (entries 5 and 12 in Table 1) are nearly perfectly alternated ethylene NBE copolymers, which are similar to those produced by constrained geometry catalysts such as $Me_2Si(Me_4\text{-}Cp)(N^tBu)TiCl_2$.[18] The T_g of these alternated copolymers are ∼140°C (depending on tacticity).[1c]

The resulting latex of this emulsion polymerization is almost devoid of floc and colloidally stable for weeks. Transmission electron microscopy (Figure 2) indicates that the nanoparticles are spherical in shape, with a broad size distribution (typically comprised between 50 and 600 nm). Interestingly, we found that some of these latexes can form continuous films upon drying. We envision this could permit the preparation of very hydrophobic, durable, and UV and chemically resistant aqueous-based coatings.

Conclusion. Using palladium-based catalysts, ethylene and NBE were copolymerized in emulsion. By this route, latexes which are either rich in ethylene or rich in NBE (up to 50%, corresponding to an alternating copolymer) can be obtained, allowing one to vary the T_g over a large range of temperatures.

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