Catalytic Insertion Polymerization of Norbornene in Miniemulsion

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ABSTRACT: The catalytic insertion polymerization of norbornene (NB) was implemented under miniemulsion conditions. Using sodium dodecyl sulfate (SDS) as surfactant and hexadecane as hydrophobe, the insertion polymerization was initiated by multicomponent catalysts generated in situ by reacting allylpalladium chloride dimer, $[(\eta^3\text{-allyl})Pd(Cl)]_2$, with a desired phosphine ligand and then activating the resulting procatalyst with a salt of noncoordinating anion, typically the lithium salt of tetrakis(pentafluorophenyl)borate ($Li[B(C_6F_5)_4]\cdot 2.5Et_2O$). By choosing either an organo-soluble (tricyclohexylphosphine) or a water-soluble phosphine ligand (tris(3-sulfonatophenyl)phosphine sodium salt), two palladium procatalysts **I** and **II** exhibiting different solubilities in water were generated and then used to polymerize NB in miniemulsion. After activation, both **I** and **II** displayed high activity and led to stable PNB latexes with good particle size control throughout the course of the reaction. Stable polynorbornene latexes with a relatively broad particle size distribution were produced. The number-average particle diameter is often below 100 nm. The nature of the surfactant and the effect of changing the concentrations of activating agent, procatalyst, and hydrophobe on the polymerization kinetics, latex stability, and particle size were investigated.

Introduction

There are two related methods for polymerizing the cyclic olefin norbornene (NB) to high molecular weights products,[1] resulting in two structurally different polynorbornenes. Ring-opening metathesis polymerization (ROMP) produces an unsaturated rubbery polymer used for sound barriers and oil-spill recovery.[2] The second route is much less investigated: catalytic insertion polymerization (CIP), which yields a hard cycloaliphatic polymer,[3] leading to plastic materials with excellent chemical and heat resistance, moisture absorption resistance, optical transparency, and mechanical strength. This unique combination of properties makes insertion polynorbornene (PNB) highly attractive for optoelectronics,[4] microelectronic packaging,[5−7] and microlithography.[8,9] These new applications have become possible because of major advances in catalyst design, with the development of highly active late transition metal complexes.[10] In contrast to early transition metal catalysts that are similar to Ziegler−Natta catalysts, these complexes, based on palladium[11−15] and also on nickel,[4,7,16] can polymerize norbornene-type monomers effectively, including those with functional pendant groups. A vast range of substituents including alkyl, silyl, and ester groups could be incorporated into the polynorbornene backbone to finely control the properties of the resultant polymer. Furthermore, the activity of these complexes is not limited to pure exo isomers, and unlike the first generation of cationic catalysts such as $[Pd(CH_3CN)_4](BF_4)_2$[17,18] and various palladium(II)−alkyl complexes,[19−21] they can polymerize the less reactive endo isomers of norbornene derivatives. As introduced by Sen[22] and Risse et al.,[23] the catalytically active species are formed through the concerted use of a cationic palladium or nickel complex with noncoordinating anions.

The insertion polymerization of norbornene has hitherto been limited to solution and bulk conditions. The present work extends CIP to aqueous environments and polymerization processes in dispersed media, allowing for the first time an effective control of the particle size. Conventional free-radical polymerization in a dispersed medium is currently conducted on a large scale by industry and offers many advantages.[24] This process leads to a stable dispersion of polymer nanoparticles in a liquid medium, usually water. Excessive exotherms and high viscosities that can be encountered with insertion PNB could be minimized by polymerization in a dispersed medium, which involves a latex that is easily stirred and pumped. The nonflammability, low cost, and environmental friendliness of water are obviously advantageous. Given the difficulties of thermoforming norbornene homopolymer or casting in solution, a process in a dispersed medium could also overcome many industrial problems. Finally, many applications could be optimally achieved by confining this polymer in the form of nanoparticles, where its properties may differ from those in bulk.

Four groups have reported results on polymerizing NB in dispersed media. Rinehart[25] was the first to describe the suspension polymerization of NB using a cyclooctadienylpalladium chloride complex. However, only low yields of polymer (22%) were obtained with high catalyst loadings, and similar results were obtained with $PdCl_2$. In 1993, the groups of Perez[26] and Novak[27] used $PdCl_2$ for polymerizing respectively NB and polar substituted norbornadienes in aqueous emulsion conditions using sodium dodecyl sulfate (SDS) as surfactant. The polynorbornene latex prepared by Perez et al. showed very small particles with a diameter of 10−20 nm consisting only of oligomers (M_n = 690). Some examples of aqueous solution polymerizations have also been given, in which some water-soluble glycopolymers[28,29] and polycationic[30] polymers based on polynorbornene were synthesized. A breakthrough occurred when B.F. Goodrich Co. showed that some cationic palladium complexes that were efficient in polymerizing functional norbornene derivatives in organic solution could also retain their activity in the presence of water.

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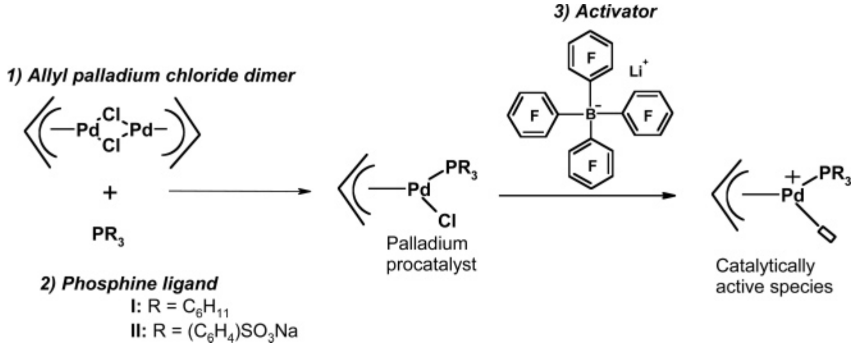
Scheme 1. Multicomponent Catalyst System Used To Initiate the Miniemulsion Insertion Polymerization of Norbornene[a]



[a] 1) Catalyst precursor: $[(\eta^3\text{-allyl})Pd(Cl)]_2$; 2) phosphine ligand: PR_3; 3) activating agent: $Li[B(C_6F_5)_4]\cdot 2.5Et_2O$.

This team subsequently employed η^3-allylpalladium complexes coordinated by various phosphine ligands to initiate the suspension and emulsion-type polymerizations of 5-butylnorbornene.[12] Despite incomplete conversion and uncontrollable particle size, high polymerization activity was achieved, and latexes containing high molecular weight polymer were obtained for the first time.

This suggests that a polymerization performed under miniemulsion conditions[31] might lead to substantial improvements. In miniemulsion, polymerization occurs within thermodynamically metastable monomer droplets in the submicron range in water, ideally with each droplet becoming a particle and in the absence of any other form of particle formation.[32]

We present here the first miniemulsion polymerization of NB and other norbornene derivatives. The present study deals with the kinetic aspects of these reactions and the colloidal properties of such dispersions. For this purpose, a multicomponent catalyst was prepared in situ by reacting allylpalladium chloride dimer, $[(\eta^3\text{-allyl})Pd(Cl)]_2$, with an appropriate phosphine ligand (L) and then activating the resulting procatalyst with a salt of noncoordinating anion, typically the lithium salt of tetrakis(pentafluorophenyl)borate ($Li[B(C_6F_5)_4]\cdot 2.5Et_2O$). By choosing either an organosoluble (PCy_3 = tricyclohexylphosphine) or a water-soluble phosphine ligand (TPPTS = tris(3-sulfonatophenyl)phosphine sodium salt), two palladium procatalysts **I** and **II** (Scheme 1) exhibiting different solubilities in water have been generated and then used to perform the polymerization of NB in miniemulsion. After activation, both **I** and **II** displayed a high activity and led to stable PNB latexes with good particle size control throughout the course of the reaction. Latex particles with desirable dimensions in the nanometer size range could be obtained through this novel miniemulsion process.

Experimental Section

Materials. All steps related to the synthesis of the organometallic procatalyst η^3-allylpalladium tricyclohexylphosphine chloride were carried out under an inert atmosphere. Toluene, norbornene (NB), and 5-acetyl-2-norbornene were dried, stored, and used under an inert atmosphere. *endo*-Dicyclopentadiene (DCPD) was prepared by allowing cyclopentadiene to undergo dimerization by storage at 25 °C for 2 weeks; the product was dried, stored, and used under an inert atmosphere. Hexadecane and 1-hexene were used after a deoxygenation procedure. Ultrapure water (18.2 MΩ cm) was purged with nitrogen for 15 min before use.

Allylpalladium chloride dimer $[(\eta^3\text{-allyl})Pd(Cl)]_2$, tricyclohexylphosphine (PCy_3), tris(3-sulfonatophenyl)phosphine sodium salt (TPPTS), silver hexafluoroantimonate ($AgSbF_6$), sodium dodecyl sulfate (SDS), dodecyl trimethylammonium bromide (DTAB), hexadecane, and all norbornenes were from Aldrich. Lithium tetrakis(pentafluorophenylborate)$2.5Et_2O$ ($Li[B(C_6F_5)_4]\cdot 2.5Et_2O$) was obtained from Boulder Scientific. Teric PE64 (a block copolymer of propylene oxide and ethylene oxide) and Teric 17A25 (an ethoxylated cetyl−oleyl alcohol) surfactants were provided by Ajax Chemicals. Dowfax 2A1 surfactant (often referred to as “sodium dodecyl phenyl ether disulfonate”) was obtained from Dow Chemical Co.

Methods. The *exo* and *endo* isomers of norbornene derivatives were separated and quantified by gas chromatography. Conversions of norbornene and norbornene derivatives to polymer were determined by gravimetry after evaporating the volatile compounds in a vacuum oven at 80 °C. Conversion rates were also confirmed by the use of gas chromatography with toluene as internal standard. Average particle size was determined by photon correlation spectroscopy (PCS-Brookhaven, comprising a BI-200SM Version 2 goniometer with 633 nm 35 mW HeNe laser, BI-APD Avalanche photodiode detector and PC1 B1-9000AT EN correlator), and light scattering (HPPS for backscattering, Malvern PCS for dynamic light scattering). The particle size distribution was also investigated by capillary hydrodynamic fractionation (CHDF1100, C560 cartridge, Matec Applied Sciences). For these three techniques, the samples were purged with nitrogen before analysis to remove residual toluene. TEM pictures were made on a Biofilter transmission electron microscope with a CCD camera and an accelerating voltage of 120 kV. The thermal behavior of polynorbornene polymers was analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The amount of coagulum in a polymerization reaction was evaluated from the amount of polymer left in the reactor after removal of the latex, plus that retained on a quartz-wool filter.

Miniemulsion CIP of Norbornene Initiated by a Water-Insoluble Catalyst. This was implemented by several different means. Recipes are given in Tables 1 and 2.

Batch Mode (Runs a to q Excepting o, Tables 1 and 2). $(\eta^3\text{-allyl})Pd(PCy_3)(Cl)$ procatalyst (**I**) was first formed in situ by mixing $[(\eta^3\text{-allyl})Pd(Cl)]_2$ (4 mg) and PCy_3 (10 mg) in 1 g of toluene. After a dissolution step of 5 min, a yellow solution was obtained that was added to a mixture of NB (1 g) and hexadecane (0.2 g). Gas chromatography showed that the resulting organic mixture remains inactive, confirming that procatalyst species was unable to initiate the polymerization without activating agent. The solution containing both NB and **I** was added to 20 mL of degassed ultrapure water including 0.63 wt % of SDS as surfactant and then emulsified by ultrasonication for 5 min using a Vibra-Cell ultrasonic processor with a standard probe at 30% amplitude. Miniemulsion polymerization was initiated by introducing a charge of $Li[B(C_6F_5)_4]\cdot 2.5Et_2O$ (40 mg) dissolved in 1 mL of water. The

Table 1. Influence of Surfactant Concentration on Particle Size[a]

				d_n(CHDF), nm		$\bar{d}_z$(HPPS), nm		$\bar{d}_z$(PCS), nm		
run	[SDS], g L^{-1}	conversion (NB), %	d_n(TEM), nm	before reaction	after reaction	before reaction	after reaction	before reaction	after reaction	coagulum, wt %
A	6	100	57	30	56	81	90	73	103	0
B	9.5	100	43	27	40	70	75	62	73	0
C	3	100	80	41	78	82	114	81	126	7

[a] Insertion polymerization of norbornene in miniemulsion: 1 g of norbornene, 1 g of toluene, 0.2 g of hexadecane, 0.63 wt % SDS (sodium dodecyl sulfate), 21 mL of water, (η^3-allyl)Pd(PCy_3)(Cl) procatalyst, 40 mg of Li[B(C_6F_5)$_4$]·2.5Et_2O, sonication treatment of 5 min at 30%. The procatalyst is formed in situ from PCy_3 (10 mg) and palladium complex ([(η^3-allyl)Pd(Cl)]$_2$, 4 mg) using a P/Pd molar ratio of 1.6/1. Average particle diameter was determined by photon correlation spectroscopy (PCS), light backscattering (HPPS), and capillary hydrodynamic fractionation (CHDF).

Table 2. Variation of Particle Size as a Function of Various Experimental Parameters[a]

run	monomer	mass monomer, g	mass toluene, g	surfactant	[hexadecane], g L^{-1}	procatalyst $\times 10^{-5}$, mol	activating agent	mass activating agent, mg	conv, %	$\bar{d}_z$ (HPPS), nm	$\bar{d}_z$ (PCS), nm	coagulum, wt %
a	NB	1	1	SDS	9.52	1.1	L	40	100	87	103	0
d	NB	1	1	SDS	4.76	1.1	L	40	100	180	215	15
e	NB	1	1	SDS	0	1.1	L	40	100	>1 μm	>1 μm	>20
f	NB	1	1	Dowfax 2A1	9.52	1.1	L	40	100	160	230	10
g	NB	1	1	DTAB	9.52	1.1	L	40	100	134	180	0
h	NB	1	1	teric PE64	9.52	1.1	L	40	100	191	200	5
i	NB	1	1	teric 17A25	9.52	1.1	L	40	100	150	155	0
j	NB	1	1	SDS	9.52	1.1	L	80	100	87	93	0
k	NB	1	1	SDS	9.52	1.1	S	40	42	89	95	0
l	NB	1	1	SDS	9.52	2.2	L	40	100	102	105	0
m	NB	2	1	SDS	9.52	1.1	L	40	100	110	120	3
n	NB	1	2	SDS	9.52	1.1	L	40	100	91	110	3
o	NB (2nd route)	1	1	SDS	9.52	1.1	L	40	100	180	260	0
p	DCPD	1	1	SDS	9.52	1.1	L	40	98	82		0
q	NB-acetyl	1	1	SDS	9.52		L	40	5	-	-	-

[a] 21 mL of water, 0.63 wt % surfactant, Pd(η^3-allyl)Pd(PCy_3)(Cl) procatalyst, sonication 5 min at 30%. Activating agent: L = LiB(PhF_5)$_4$, S = $AgSbF_6$. Surfactant: SDS (sodium dodecyl sulfate), Dowfax 2A1 surfactant (sodium dodecyl phenyl ether disulfonate), DTAB (dodecyl trimethylammonium bromide), Teric PE64 (a block copolymer of propylene oxide and ethylene oxide) and Teric 17A25 (an ethoxylated cetyl–oleyl alcohol). Average particle diameter was determined by photon correlation spectroscopy (PCS) and light backscattering (HPPS).

Table 3. NB Insertion Polymerization in Miniemulsion Initiated by a Water-Insoluble Catalyst (Run b) and a Water-Soluble Catalyst (Runs A–C)[a]

run	procatalyst	temp, °C	toluene, g	conv, %	$\bar{d}_n$(TEM), nm	$\bar{d}_n$(CHDF), nm	$\bar{d}_z$(HPPS), nm	$\bar{d}_z$(PCS), nm
b	**I** (toluene)	25	1	100	43	40	75	73
A	**II** (H_2O)	25	1	100	47	46	94	101
B	**II** (H_2O/EtOH)	25	1	100	45	40	82	80
C	**II** (H_2O)	60	0	100			74	

[a] [SDS] = 9.5 g L^{-1}, 1 g of NB, 0.2 g of hexadecane. Average particle diameter was determined by photon correlation spectroscopy (PCS), light backscattering (HPPS), and capillary hydrodynamic fractionation (CHDF).

miniemulsion becomes yellow but remains opalescent throughout the reaction.

Semibatch Mode (Run o, Table 2). [(η^3-allyl)Pd(Cl)]$_2$ (4 mg) and PCy_3 (10 mg) were dissolved in 1 g of toluene and 0.2 g of hexadecane to form (η^3-allyl)Pd(PCy_3)(Cl) procatalyst (**I**). The procatalyst solution was then added to Li[B(C_6F_5)$_4$]·2.5Et_2O (40 mg) to generate an active cationic palladium complex in situ. Some emulsified catalyst droplets were produced by mixing the catalyst solution with 21 mL of degassed ultrapure water containing 0.63 wt % SDS. The mixture was then ultrasonicated (5 min at 30% amplitude), yielding a stable miniemulsion of catalyst. NB (1 g) dissolved in 0.5 mL of toluene was slowly added to the above reaction medium, over a period of 1 h. The reaction mixture progressively changed from opalescent to completely turbid as monomer solution was added.

Miniemulsion CIP of Norbornene Initiated by a Water-Soluble Catalyst. This was implemented in two ways, with details given in Table 3.

Solvent-Containing Method (Runs A and B, Table 3). Water-soluble (η^3-allyl)Pd(TPPTS)Cl procatalyst (**II**) was first formed in situ by vigorously mixing [(η^3-allyl)Pd(Cl)]$_2$ (4 mg) and TPPTS (10 mg) in 1 mL of degassed ultrapure water. An organic solution including NB (1 g), hexadecane (0.2 g), and toluene (1 g) was then added to 20 mL of degassed ultrapure water containing 0.63 wt % SDS. The resulting emulsion was then ultrasonicated for 5 min using a Vibra-Cell ultrasonic processor with a standard probe at 30% amplitude. Miniemulsion polymerization was initiated by introducing the procatalyst solution followed by a charge of Li[B(C_6F_5)$_4$]·2.5Et_2O (40 mg) dissolved in 1 mL of water.

Solvent-Free Polymerization (Run C, Table 3). Water-soluble (η^3-allyl)Pd(TPPTS)Cl procatalyst (**II**) was first formed in situ by vigorously mixing [(η^3-allyl)Pd(Cl)]$_2$ (4 mg) and TPPTS (10 mg) in 1 mL of degassed ultrapure water. NB (1 g) and hexadecane (0.2 g) were then added to 20 mL of water containing 0.63 wt % SDS. The mixture was stirred and heated at 60 °C to form a dispersion of liquid NB in water. Sonication (5 min, at 30%) was then used to form a NB miniemulsion. The aqueous procatalyst solution was then introduced, giving a yellow color to the mixture, followed by Li[B(C_6F_5)$_4$]·2.5Et_2O (40 mg) dissolved in 1 g of water. The miniemulsion remained opalescent throughout the reaction. After 4 h, the medium progressively turned black, suggesting the formation of black palladium metal, presumably by reductive elimination of the metal species.

Results and Discussion

To perform the catalytic insertion polymerization (CIP) of norbornene (NB) in a dispersed medium, we used a variant of a miniemulsion procedure originally devised for free-radical polymerization.[33] This is the first study of the use of this technique for polymerizing cyclic olefins via CIP. Whatever the polymerization means used, an ideal miniemulsion polymerization starts from kinetically metastable monomer droplets that will serve subsequently as loci for the reaction. Providing destabilization processes are eliminated, polymerization inside droplets gives birth to polymer particles, with each droplet becoming a particle. Two destabilization processes cause deviation from this ideal behavior: (1) coalescence, which may be overcome through addition of an appropriate surfactant at sufficient concentration, and (2) Ostwald ripening, involving monomer diffusion from the small particles to the larger ones, which eventually causes smaller droplets to disappear. Adding a hydrophobe such as hexadecane limits monomer diffusion by increasing the osmotic pressure inside small particles. A suitable homogenization, usually sonication, is necessary for the droplets to be kinetically stable for a sufficient period of time.

An important difference between free-radical polymerization and CIP is that the latter involves a catalyst that is usually sensitive to water. For this reason, insertion polymerization of NB is traditionally conducted in organic solvents or in bulk. Extending CIP to aqueous processes thus requires some adaptations and leads to many issues pertaining to the water stability of catalyst and activating agent.[34] Miniemulsion is particularly suitable because catalytically active species can be confined from the very beginning in stable monomer droplets having limited contact with the aqueous dispersion medium. This will minimize detrimental effects of water on the reactivity of the metal center through hydrolysis, coordination, or nucleophilic attack.[35]

Two miniemulsion techniques were devised to generate PNB nanoparticles in water. As shown in Figure 1, both involve multicomponent η^3-allylpalladium catalysts generated in situ, differing by their solubilities in water. Both water-soluble and water-insoluble catalysts were used.

Miniemulsion CIP of NB Initiated by a Water-Insoluble Catalyst. NB was first polymerized in miniemulsion using a hydrophobic palladium complex as catalyst. This has similarities to a Ziegler–Natta catalyst and is shown in Scheme 1. It comprises η^3-allylpalladium procatalyst **I** [(η^3-allyl)(PCy$_3$)Pd(Cl)] in combination with an activating agent. **I** is readily generated in situ from a mixture of [(η^3-allyl)Pd(Cl)]$_2$ and PCy$_3$ using a P/Pd molar ratio of 1.6/1 without any attempt at isolating and characterizing the resulting monomeric palladium complex.[36] The activating agent is typically a noncoordinating anion salt such as the lithium salt of tetrakis(pentafluorophenyl)borate: [Li-[B(C$_6$F$_5$)$_4$]·2.5Et$_2$O]. The activating agent is a strong Lewis acid:[3] its presumed effect is to generate a catalytically active cationic complex by abstracting the chlorine atom from the procatalyst **I**. This results in the creation of a free coordination site on the palladium complex that can be selectively displaced by a norbornene molecule, thereby initiating the polymerization (Scheme 2). This in situ catalyst is potentially advantageous for industrial applications due to its simplicity and its low oxophilicity.

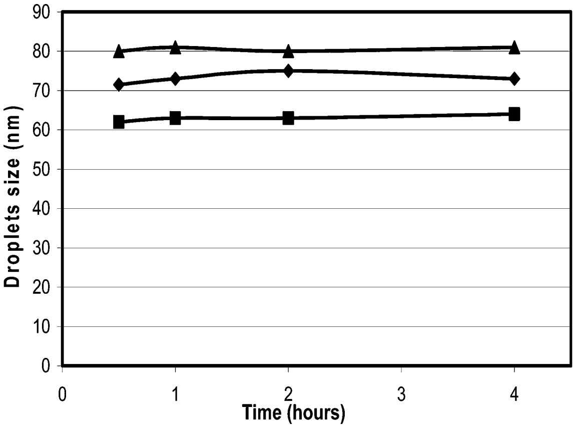
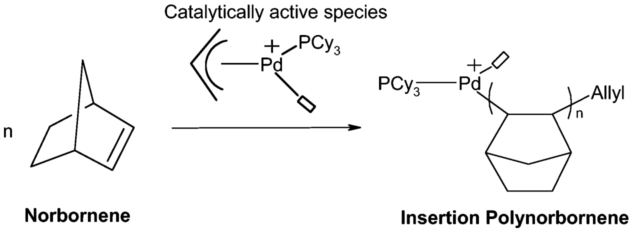


Figure 1. Effect of SDS (sodium dodecyl sulfate) concentration on norbornene miniemulsion average droplet diameter (measured by HPPS backscattering) as a function of time. Surfactant concentration: ▲, 3; ◆, 6; ■, 9.5 g per L water. Norbornene miniemulsion: 1 g of norbornene, 1 g of toluene, 0.2 g of hexadecane, variable amount of SDS, 21 mL of water, (η^3-allyl)Pd(PCy$_3$)(Cl) procatalyst, sonication treatment of 5 min at 30%. The procatalyst is formed from PCy$_3$ (10 mg) and palladium complex [(η^3-allyl)Pd(Cl)]$_2$ (4 mg) using a P/Pd molar ratio of 1.6/1.

Scheme 2. Principle of Catalytic Insertion Polymerization of Norbornene Initiated by the Multicomponent Catalyst: Procatalyst I/ Li[B(C$_6$F$_5$)$_4$]·2.5Et$_2$O



In contrast to free-radical miniemulsion polymerization, the starting miniemulsion in the present CIP procedure comprises not only NB and a hydrophobic agent (hexadecane) but also the lipophilic palladium procatalyst **I** dissolved in a minimal amount of toluene. As **I** is unable to initiate the NB polymerization in the absence of a suitable activating agent, the monomer droplets should ideally remain inactive at this stage. The toluene in the miniemulsion serves both as a reaction medium to generate **I** and as a solvent to dissolve NB, since this cyclic olefin is a solid at room temperature (NB is liquid between 46 and 96 °C). Prior to reaction, the colloidal stability of the miniemulsion was examined. Figure 1 displays the evolution of droplet size, as measured by HPPS, prepared with various amounts of SDS. A long-term stability for these droplets was substantiated for SDS concentration in the range 3–9.5 g L^{-1}. Visual observation and hydrodynamic capillary fractionation (CHDF) measurements also confirmed this result, which can be explained by the high hydrophobicity of the components comprising the droplets: NB in particular has an extremely low solubility in water, 9.9×10^{-5} g L^{-1}. Toluene is slightly more soluble (1.31×10^{-3} g L^{-1}). However, it appears that NB is not capable of playing the role of the hydrophobe, since a rapid phase separation was observed in absence of hexadecane.

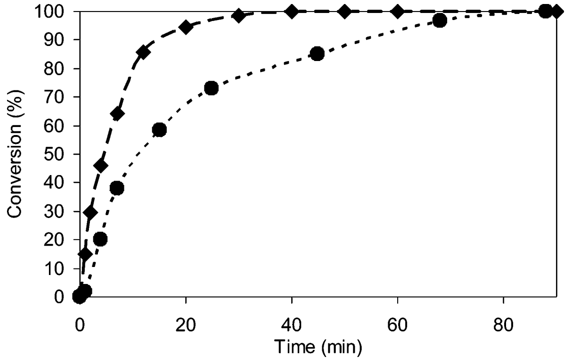


Figure 2. Conversion−time curve for the miniemulsion polymerization of norbornene initiated using a water-insoluble procatalyst (runs a and b, Table 1) at different SDS (sodium dodecyl sulfate) concentrations: ●, 6 g L^{-1}; ■, 9.5 g L^{-1}). Insertion polymerization of norbornene in miniemulsion: 1 g of norbornene, 1 g of toluene, 0.2 g of hexadecane, SDS, 21 mL of water, (η^3-allyl)Pd(PCy_3)(Cl) procatalyst, 40 mg of Li[$B(C_6F_5)_4$]·$2.5Et_2O$, sonication treatment of 5 min at 30%. The procatalyst is formed in situ from PCy_3 (10 mg) and palladium complex ([(η^3-allyl)Pd(Cl)]$_2$, (4 mg) using a P/Pd molar ratio of 1.6/1.

A stable miniemulsion was prepared with 6 g L^{-1} of surfactant and then polymerized (run a, Table 1) after adding the activating agent dissolved in a small amount of water. This activating agent has the significant advantage of being relatively stable in water, thereby allowing the polymerization to be performed under miniemulsion conditions. Its water solubility is also important for preserving the integrity of the monomer droplets. The lithium salt is thought to diffuse through the aqueous phase into the existing droplets to afford an active polymerizing center without causing destabilization.

Polymerization Kinetics and Polymer Characterization. As shown in Figure 2, complete conversion of NB was accomplished in less than 40 min without any apparent loss of colloidal stability, for an SDS concentration of 6 g L^{-1}. This high yield and rate show that the η^3-allylpalladium catalyst does not suffer from severe blocking of coordination sites by water or surfactant molecules. After precipitation in acetone and filtration, the resulting polymer was found to be insoluble in any solvent tested, which is in accordance with the systematic insolubility for Pd(II)-catalyzed polynorbornenes reported in the literature.[37] Given that the solubility of polynorbornene depends not only on molecular weight but also strongly on microstructure,[17] the observed insolubility is not in itself firm evidence that the present process results in high molecular weights. However, TGA showed that the polymer sustains a temperature up to 450 °C in a nitrogen atmosphere with a mass loss of only 5%. This remarkable thermal resistance is most readily ascribed to the formation of high molecular weight chains. The determination of the glass transition temperature (T_g) of polynorbornene would also provide evidence of high molecular weights; however, DSC for polynorbornene is difficult because its T_g is close to the decomposition temperature (see, e.g., ref 18), and indeed DSC analysis of the present system did not reveal any endothermic behavior upon heating the polymer to 500 °C. This indicates that the polynorbornene obtained here is amorphous because the absence of a melting point is consistent with lack of crystallinity.[38] The insolubility precluded further characterization of the polynorbornene microstructure by NMR or size exclusion chromatography. On the whole, the data are consistent with, but do not provide conclusive evidence for, the formation of high molecular weight polymer.

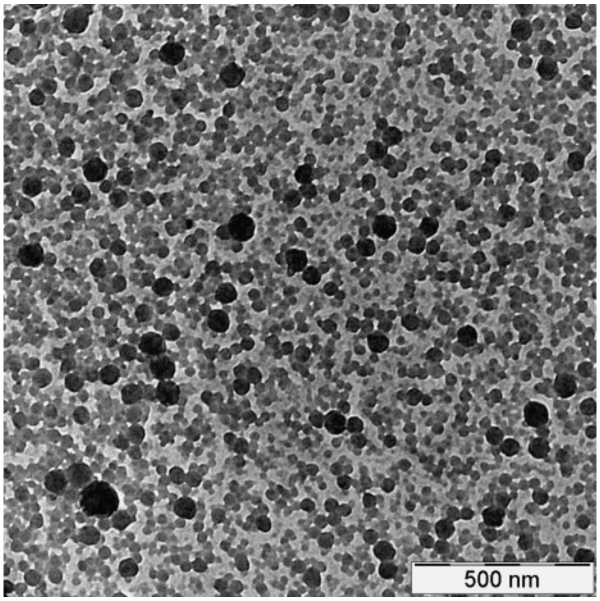


Figure 3. Transmission electron microscopy micrograph of polynorbornene latex particles synthesized by miniemulsion CIP using a water-insoluble catalyst (run a, Table 1). $d_n = 57$ nm (TEM). Insertion polymerization of norbornene in miniemulsion: 1 g of norbornene, 1 g of toluene, 0.2 g of hexadecane, 0.63 wt % SDS (sodium dodecyl sulfate), 21 mL of water, (η^3-allyl)Pd(PCy_3)(Cl) procatalyst, 40 mg of Li[$B(C_6F_5)_4$]·$2.5Et_2O$, sonication treatment of 5 min at 30%. The procatalyst is formed in situ from PCy_3 (10 mg) and palladium complex ([(η^3-allyl)Pd(Cl)]$_2$, (4 mg) using a P/Pd molar ratio of 1.6/1.

Particle Size. The particle size of run a (Table 1) during and at the end of the reaction was measured by light scattering (HPPS, PCS), transmission electron microscopy (TEM), and CHDF measurements. Two main conclusions can be drawn from the size values given in Table 1.

(1) A TEM micrograph of PNB latex from run a obtained after 90 min (Figure 3) shows polydisperse particles, with sizes between 30 and 120 nm. The number-average diameter d_n from counting 2000 particles was 57 nm, compared with $d_n = 55$ nm measured by CHDF. The polydispersity of the sample means that very different results are produced by the light scattering techniques: $d_z = 90$ nm from HPPS and 103 nm from PCS. The value of d_z being considerably greater than that of d_n is expected, since the sample has a wide particle size distribution, and d_z is skewed toward larger particles. The smaller difference between d_z values from different light-scattering techniques is readily explicable in terms of the assumptions made within the instrument software to infer this quantity from different types of light-scattering data.

(2) Estimates of the distributions of sizes of both miniemulsion droplets and the particles subsequently formed by polymerization were made with PCS. The distributions inferred from PCS data are subject to uncertainty because the inversion from correlation function to size distribution is not unique and is sensitive to the numerical parameters adopted for the inversion procedure. Nevertheless, comparison of very similar systems using the same inversion parameters and procedure should be semiquantitatively reliable.

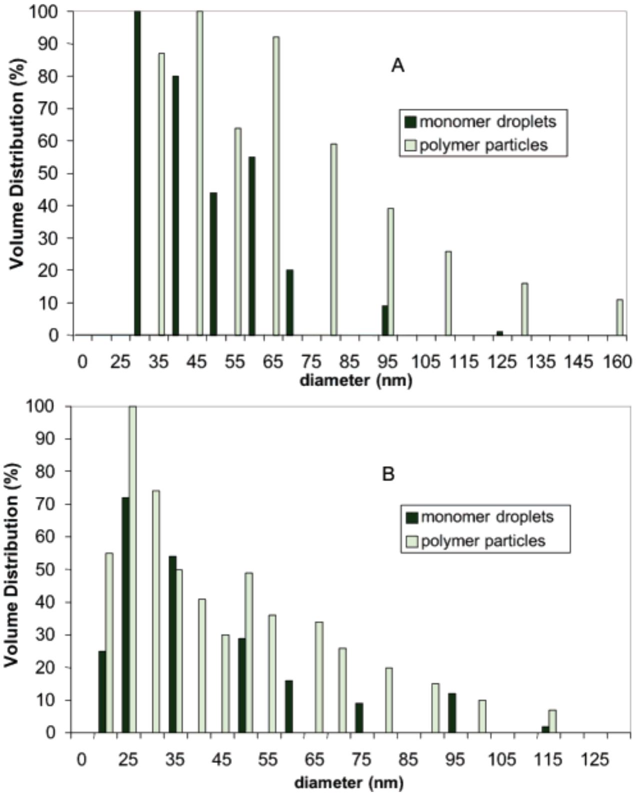


Figure 4. Comparison of particles and droplet size volume distributions at different SDS (sodium dodecyl sulfate) concentrations (per L water), measured by PCS: (A) 6.0 g L^{-1}; (B) 9.5 g L^{-1}. Insertion polymerization of norbornene in miniemulsion: 1 g of norbornene, 1 g of toluene, 0.2 g of hexadecane, SDS, 21 mL of water, (η^3-allyl)Pd(PCy$_3$)(Cl) procatalyst, 40 mg of Li[B(C$_6$F$_5$)$_4$]·2.5Et$_2$O, sonication treatment of 5 min at 30%. The procatalyst is formed in situ from PCy$_3$ (10 mg) and palladium complex [(η^3-allyl)Pd(Cl)]$_2$ (4 mg) using a P/Pd molar ratio of 1.6/1.

Using PCS to measure droplet size distribution measurement requires considerable dilution, but the distributions given here are reproducible and not significantly dependent on the degree of dilution. As can be seen in Figure 4A, for the lower surfactant concentration, there is some similarity between the distributions of droplets and particles, although it cannot be concluded from these data that the reaction occurs under conditions close to those of an ideal miniemulsion, in which all initial droplets are converted into particles. Upon increasing the surfactant concentration, as shown in Figure 4B, discrepancies between droplet and particle size distributions are quite apparent. As the reaction proceeds, toluene initially included in the monomer droplets (50 vol %) is progressively released and must form new pure toluene droplets. This phenomenon certainly affects the miniemulsion size and can also account for the differences between particle and droplet size distributions.

Surface Tension and Latex Coverage. Conductimetry and surface tension measurements are useful to investigate the distribution of surfactant molecules between the different phases of a dispersion. This also permits indirect characterization of the stability of the miniemulsion throughout the reaction. Results are given in Table 4.

Table 4. Conductivity and Surface Tension Measurements Monitored throughout the Miniemulsion Polymerization of Norbornene (Run a, Table 1)[a]

	conductivity (κ), mS cm^{-1}	surface tension (γ), mN m^{-1}
before homogenization	0.85	32
after homogenization	0.62	57
after polymerization	0.7	50

[a] Insertion polymerization of norbornene in miniemulsion: 1 g of norbornene, 1 g of toluene, 0.2 g of hexadecane, 0.63 wt % SDS (sodium dodecyl sulfate), 21 mL of water, (η^3-allyl)Pd(PCy$_3$)(Cl) procatalyst, 40 mg of Li[B(C$_6$F$_5$)$_4$]·2.5Et$_2$O, sonication treatment of 5 min at 30%. The procatalyst is formed in situ from PCy$_3$ (10 mg) and palladium complex [(η^3-allyl)Pd(Cl)]$_2$ (4 mg) using a P/Pd molar ratio of 1.6/1.

Surface tension (γ) increased from 32 to 57 mN m^{-1} after sonication, reflecting the micelles' disappearance from the aqueous phase. In miniemulsion, absence of micelles is crucial for avoiding secondary nucleation (assuming that monomer could migrate to the micelles). Conductivity (κ) was also affected by homogenization: the increase in the number of droplets caused κ to decrease from 0.85 to 0.62 mS cm^{-1}, arising because charged surfactant molecules that had been dissolved in the aqueous phase were then adsorbed onto the surface of the droplets. Both γ and κ remain constant on a time scale of hours prior to addition of initiator, suggesting a high degree of stability for the unpolymerized miniemulsion. After polymerization, the surface tension slightly decreased to 50 mN m^{-1} after 2 h of reaction, whereas the conductivity increased slightly to 0.70 mS cm^{-1}. These results can be attributed to the desorption of SDS throughout the polymerization. In an ideal stable miniemulsion, there should be no change in aqueous phase conductivity. In our case, the slight destabilization may be due to polymer formation and coalescence between droplets and particles.

Comparison between Controlled Radical Polymerization and CIP. Although the mechanism of polymerization is entirely different, the process of chain addition in controlled radical polymerization[39] and CIP have some similarities. In both cases, all the polymeric chains are created at essentially the same time and grow simultaneously, in contrast to conventional free-radical polymerization. Controlled radical polymerization has only recently been successfully implemented in emulsion[40,41] and miniemulsion[42] polymerizations, without the problems of loss of colloidal stability, formation of an oily layer, and use of very large amounts of surfactant that had been previously reported. In the case of the implementation of CIP in miniemulsion polymerization given here, such difficulties were not encountered. The occurrence of Ostwald ripening would be indicated by the disappearance of the smallest droplets. PCS analysis of the unpolymerized miniemulsion clearly showed the presence of very small monomer droplets, and even after several hours, no evolution of the droplet size was observed. This strongly suggests that Ostwald ripening did not occur extensively in our system. This can be ascribed to the high hydrophobicity of norbornene molecules and oligomers that can overcome Ostwald ripening efficiently. The differences between droplet and particle size distributions, although hard to quantify, suggest however that coalescence occurred during polymerization to a greater extent than is desirable.

Effects of Experimental Parameters on NB Miniemulsion Polymerization. *Surfactant Effects.* Data related to the particle size dependence are given in Tables 1 and 2. As expected, particle size decreased with increasing amount of surfactant (Table 1). The concentration in surfactant also affects the kinetics of polymerization. As shown in Figure 2, norbornene consumption was significantly slower when more SDS molecules are present in the water phase. Less than 70% of NB was converted at a SDS concentration of 9.5 g L^{-1} in 20 min, whereas 95% of the same monomer was polymerized after the same period with a lower content of surfactant ([SDS] = 6 g L^{-1}). Another difference is the appearance of a short (1 min) but significant induction period at high SDS concentration. It is plausible that some cationic active sites may be electronically neutralized by SDS molecules, causing a weaker interaction with the double bond of norbornene. However, the decrease in reactivity does not have any significant consequences for the final outcome of the reaction. With a 2-fold decrease in SDS concentration (run c, Table 1), some slight signs of precipitation were detected. Larger polymer particles were generated in this case (d_z(HPPS) = 114 nm, d_z(PCS) = 126 nm), and the distribution becomes also broader. It appears that a relatively high concentration of surfactant was required to sustain the miniemulsion stability. This is not unexpected: owing to the ionic nature of the catalyst and the corresponding ionic strength, electrostatic stabilization is likely to be poor.

Effect of the Hydrophobe. Despite its inherent hydrophobicity, norbornene alone cannot prevent the phenomena that cause destabilization of a miniemulsion. Indeed, a decrease in hexadecane concentration (run d, Table 2) led to a dramatic increase in particle size, indicating that conditions for true miniemulsions were not fulfilled in this case. In the absence of hexadecane (run e, Table 2), phase separation of the monomer emulsion quickly occurred after sonication. Although these experiments are marked by a loss of particle size control, NB conversion was still complete.

Nature of Surfactant. The effects of anionic (SDS and Dowfax 2A1), cationic (DTAB), and polymeric (Teric PE64 and Teric 17A25) surfactants were compared. All of these surfactants resulted in high NB conversion but had differing efficacies for colloidal stability of the particles formed. Dowfax 2A1 was less effective than SDS at the same concentration (run f, Table 2). DTAB led to phase separation of the polymerized miniemulsion (run g, Table 2), presumably because of incompatibility/repulsion between the palladium system and the surfactant, both of which are positively charged. The ethylene oxide/propylene oxide copolymer Teric PE64 (run h, Table 2) yielded large particles (190 nm) and partially coagulated latex, and colloidal stability could only be achieved by using higher loads of surfactant (>10 g L^{-1}). The nonionic surfactant Teric 17A25 (run i, Table 2) resulted in good colloidal stability of the polymer particles, with particles of diameter about 150 nm. More critical than the nature of the surfactant, an appropriate hydrophilic/lipophilic balance appears to be a necessary criterion to ensure colloidal stability.

Effect of Activating Agent. In most experiments described above, the activating agent concentration was typically used in a 2-fold molar excess over palladium (run j, Table 2). Although this concentration was probably insufficient to ensure complete activation of all the palladium active sites (Scheme 1), it was adequate for achieving a satisfactory reaction rate. This was confirmed when a 4-fold molar excess of lithium salt was used. As expected, this also confirmed the poor initiation efficiency. As shown in Figure 5, a higher concentration of activating agent resulted in a higher rate of consumption of NB: 90% after 5 min, compared to 45% with the lower activating agent concentration. This dramatic acceleration did not affect the particle size, consistent with a 1:1 conversion of droplets to particles.

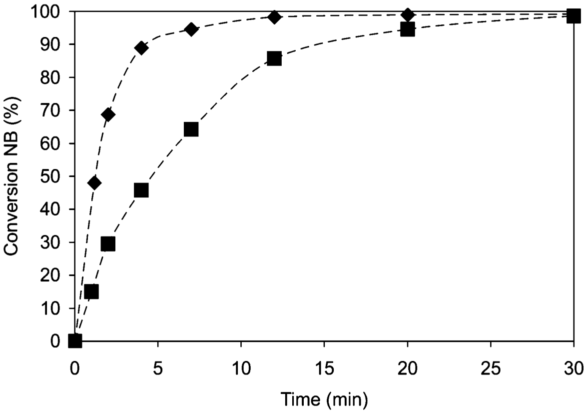


Figure 5. Conversion−time curve for the miniemulsion polymerization of norbornene with different masses of activating Li salt: ■, 40 mg; ◆, 80 mg. Runs a and j, Table 2. Insertion polymerization of norbornene in miniemulsion: 1 g of norbornene, 1 g of toluene, 0.2 g of hexadecane, 0.63 wt % SDS (sodium dodecyl sulfate), 21 mL of water, (η^3-allyl)Pd-(PCy_3)(Cl) procatalyst, $Li[B(C_6F_5)_4]\cdot 2.5Et_2O$, sonication treatment of 5 min at 30%. The procatalyst is formed in situ from PCy_3 (10 mg) and palladium complex $[(\eta^3\text{-allyl})Pd(Cl)]_2$ (4 mg) using a P/Pd molar ratio of 1.6/1.

The nature of the activating agent was also investigated. With silver hexafluoroantimonate ($AgSbF_6$) as activating agent instead of the lithium salt, less than 50% of norbornene was converted (run k, Table 2). A suitable noncoordinating anion thus appears to be an essential part of the multicomponent catalyst system to achieve high activity. In the case of $AgSbF_6$, a lower solubility of the counterion in the organic phase along with an essentially noncoordinating effect toward cationic palladium complexes certainly affect its efficiency. However, higher loads of $AgSbF_6$ (more than 5 molar excess over Pd) allows NB to be converted almost completely. Again, it appears that the type of activating agent does not have a significant impact on the size of the particles formed.

Effect of Procatalyst Concentration. Increasing the concentration of the procatalyst **I** (run l, Table 2) had no major effect on the particle size of the resulting polynorbornene particles. Varying this parameter did not affect the polymerization kinetics significantly. This result confirms that the number of active species is only governed by the amount of activating agent under the chosen conditions.

Effect of Norbornene and Toluene Concentrations. As expected, a higher monomer concentration (run m, Table 2) resulted in larger particles. Also in accord with expectation, at higher solid content (>10%), the colloidal stability of the formed latex becomes poorer, ascribed to poorer surface coverage by surfactant at fixed surfactant concentration. The dependence of the particle size with toluene concentration is more difficult to predict. Although toluene is absent from the final PNB particles, it nevertheless contributes to droplet size. A 2-fold increase in the amount of toluene caused the particles to increase slightly, presumably due to an increased rate of coalescence (run n, Table 2).

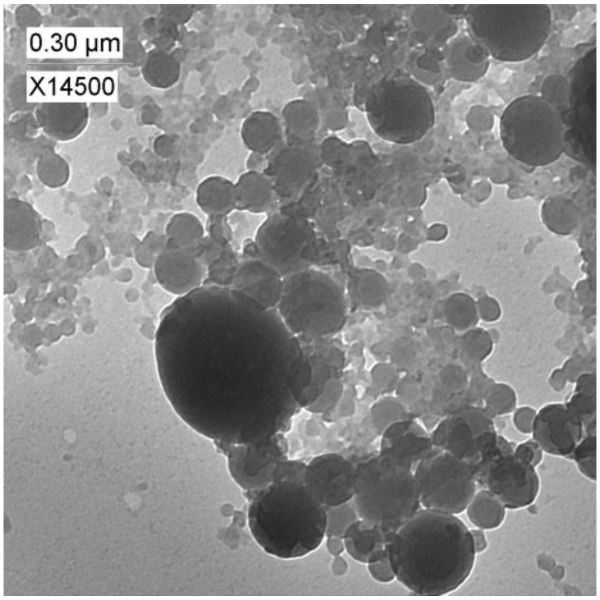


Figure 6. TEM picture showing highly polydisperse polynorbornene particles produced through the semibatch route (run o, Table 2), in which a continuous addition of NB to a catalyst miniemulsion was performed over a period of 1 h.

Semibatch Mode. Here, run o, Table 2, the active cationic palladium complex was dispersed instead of the monomer following the methodology designed by the groups of Claverie[43] for ring-opening metathesis polymerization (ROMP) of norbornene and Mecking and coworkers for ethylene.[44] The resulting catalyst droplets were then put into contact with the monomer through a slow addition of norbornene to the emulsion over 1 h. NB was intended to diffuse through the aqueous phase to the catalyst droplets, where polymerization should occur. Figure 6 shows that the particle size distribution was very different when NB was added continuously in this way: a broad particle size distribution of polynorbornene was produced, ranging from 50 to 700 nm. This dramatic broadening can be attributed to the formation of large norbornene droplets that destabilize the catalyst droplets by coalescence. This clearly shows the importance of incorporating the monomer inside the miniemulsion prior to polymerization: miniemulsion systems are prone to destabilization when mixed with another organic phase.

Miniemulsion Polymerization of Functionalized Norbornenes. Attaching a functional group to the norbornene entity imparts novel and attractive properties to the resultant polymer in terms of solubility, adhesion, and mechanical resistance.[3] Unfortunately, polymerization of functionalized norbornenes is also much more challenging, often resulting in dramatic attenuation of the catalytic activity. This has been ascribed to the *steric* hindrance of the substituent and to its possible *coordination to the metal center* in the particular case of polar functionalities. There is also a strong effect related to the *disposition of the functional group*. Indeed, functionalized norbornenes are synthesized by a Diels–Alder reaction affording *exo* and *endo* isomers. The latter are even more reluctant to polymerize due to an increased steric effect and an enhanced coordinating effect through the formation of a chelate. A preferential uptake of the *exo* isomers has been reported.[45]

The impact of the substituent on the miniemulsion polymerization of two functionalized norbornenes was examined in the present paper: dicyclopentadiene (DCPD) and 5-acetyl-2-NB with *endo*/*exo* ratios of 98/2 and 90/10, respectively. Keeping all the experimental parameters unchanged, DCPD reacted to 98% conversion in 24 h (run p, Table 2), whereas essentially complete conversion of NB was found after only 40 min. This drop in polymerization rate for DCPD compared to norbornene suggests that a hindered substituent may be detrimental to chain propagation during the polymerization reaction. *endo*-DCPD contains two carbon–carbon double bonds that can both coordinate to Pd and thus presumably induce the formation of a chelate. Nevertheless, coordination in this case remains reversible, allowing the polymerization to be quantitative; this shows, unexpectedly, that the η^3-allylpalladium complex is capable of polymerizing an *endo*-substituted norbornene under aqueous conditions. The presence of a polar acetyl function, on the other hand, caused the catalytic activity to be drastically attenuated (run q, Table 2). This clearly indicates that the chelate formation is more effective in this case. Acetone can also act as a ligand because it contains a single functionality for coordination. We found that the time for polymerizing norbornene to essentially complete conversion increased from 40 min (run a, Table 2) to several hours when a small amount of acetone was present in the reaction medium.

Miniemulsion CIP of NB Initiated by a Water-Soluble Catalyst. One major advantage pertaining to the catalytic system stems from being able to vary solubility through the proper choice of phosphine ligand. A water-soluble procatalyst (**II**) can thus be obtained by reacting in water $[(\eta^3\text{-allyl})Pd(Cl)]_2$ with an appropriate water-soluble ligand such as the sodium salt of tris(3-sulfonatophenyl)phosphine (TPPTS) instead of PCy_3 (Scheme 1). Similarly to the previous case, mixing the resulting water-soluble procatalyst (η^3-allyl)(TPPTS)Pd(Cl) (**II**) with the activating agent affords an active cationic catalyst that is soluble in water. The ability of this water-soluble complex to initiate the insertion polymerization of NB in miniemulsion was investigated and its efficiency compared to that of its water-insoluble analogue.

Using a similar protocol to that employed previously, high shear was applied to droplets containing NB, a small amount of solvent (toluene), and a hydrophobic agent (hexadecane). Polymerization was initiated by addition of the water-soluble procatalyst **II** and its activating agent dissolved in the aqueous phase (run A, Table 3). Figure 7 shows that the catalytic activity was sharply attenuated with **II** compared to that of the water-insoluble procatalyst: conversion of NB reaches 10% after 1 h of reaction in this case, in contrast to 100% in the presence of the oil-soluble procatalyst **I**. However, complete consumption of norbornene was achieved after 1 day of polymerization. Such a difference in the rate of reaction can be attributed to the nature of the active catalyst itself, as follows. (1) The water solubility of the catalyst necessitates its entry into the monomer droplet from the aqueous phase to initiate polymerization. Although this event is favored by the very high number of droplets, it also implies a prolonged stay in water that increases the risk of deactivation. (2) Catalyst activity depends on the coordinated phosphine ligand. Compared to PCy_3, TPPTS imparts steric and electronic properties to the catalyst which are less favorable to the insertion of NB molecules. (3) Given the difficulty of dissolving

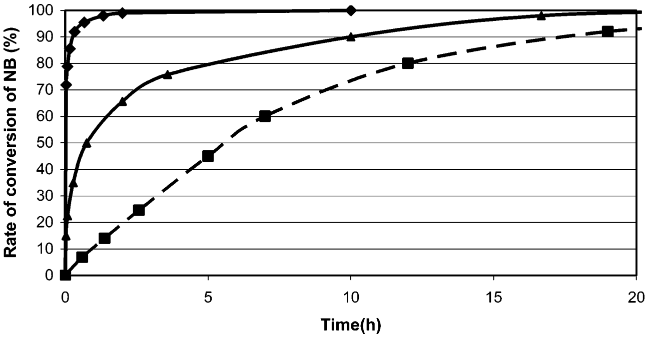


Figure 7. Conversion as a function of time for the miniemulsion insertion polymerization of norbornene initiated using a water-soluble procatalyst **II**: (■, run A, Table 3): **II** formed in water; (▲, run B, Table 3): **II** is formed in a 1:1 weight mixture of water/ethanol; (◆, run C, Table 5): toluene-free polymerization, reaction run at 60 °C.

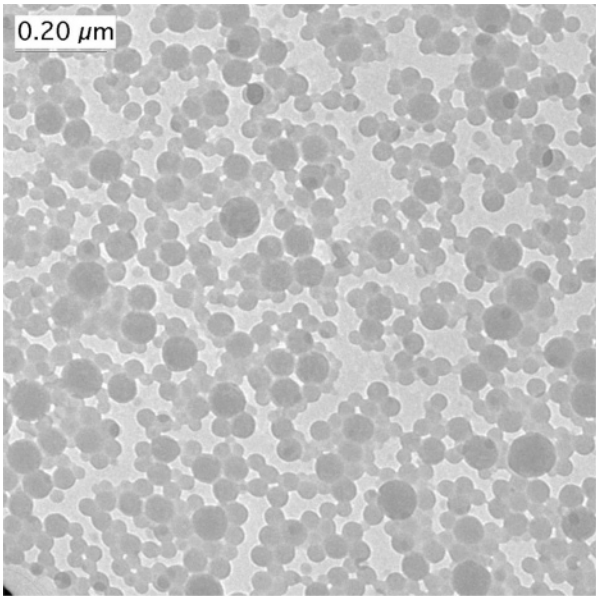


Figure 8. TEM micrograph of a polynorbornene latex prepared by miniemulsion polymerization using a water-soluble catalyst **II** with [SDS] = 9.5 g L^{-1}; d_n(TEM) = 47 nm.

allyl palladium chloride dimer in water, the reaction producing **II** in situ is certainly not quantitative. Fewer active catalyst species are thus generated.

As shown in Table 3, the type of initiator does not significantly affect the particle size. The TEM micrograph displayed in Figure 8 shows a latex exhibiting a wide distribution with an average diameter similar to that obtained with **I** (d_n(TEM) = 47 nm; the d_z size from light scattering is larger due to a higher proportion of large particles). The slower reaction rate is expected to result in more coalescence. No matter what the mode of initiation and its effects on the reaction kinetics, nucleation still occurs inside very stable monomer droplets.

By preparing the procatalyst in a water/ethanol mixture, all the components were readily solubilized in less than 5 min without residual aggregates. The miniemulsion kinetics were found to be accelerated in this case (run B, Table 3), suggesting that more (η^3-allyl)(TPPTS)Pd(Cl) molecules could be produced under these conditions. Attempts to polymerize 5-acetyl-2-norbornene in the presence of this water-soluble catalyst were unsuccessful, while polymerization of DCPD under similar conditions led to a limited conversion (40%).

As the presence of residual organic solvent in the latex can affect its final properties, a toluene-free approach for NB miniemulsion polymerization was devised. Toluene can be avoided providing NB remains in the liquid state. To ensure that norbornene remained liquid, the reaction was carried out above its melting point (46 °C). Very stable monomer droplets containing only NB and hexadecane could be formed by homogenization at 60 °C. The polymerization was then initiated after adding successively the procatalyst **II** and the activating agent (run C, Table 3). Under these conditions, the consumption of NB was dramatically increased: complete conversion was achieved in less than 3 min, whereas more than 15 h of reaction was required to reach 90% at room temperature. The net effect of temperature increase was to increase the productivity of the palladium catalyst by about 10 orders of magnitude.

Conclusions

This study shows that miniemulsion polymerization can be successfully extended to catalytic insertion polymerization of norbornene. Water-soluble and water-insoluble η^3-allylpalladium catalysts proved to be well suited to initiate the quantitative polymerization of NB under miniemulsion conditions using SDS as surfactant. Although a much faster conversion of NB was favored by the water-insoluble catalyst, both strategies yielded stable polynorbornene latexes of similar size with rather broad particle size distributions. Several experimental parameters were varied in order to investigate their influence on the reaction kinetics and the colloidal properties. This study showed that particle size could be efficiently controlled by varying the surfactant concentration and that a number of surfactant types could be used without adversely affecting the conversion of norbornene. Only norbornene derivatives bearing nonpolar functionalities such as dicyclopentadienene could be polymerized effectively. Oxygen-containing groups including acetyl were found to be unsuitable due to their tendency to coordinate the metal center.

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