Ring-Opening Metathesis Polymerization in Emulsion

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Received September 11, 2000; Revised Manuscript Received November 21, 2000

ABSTRACT: Ring-opening metathesis polymerization (ROMP) of norbornene (NBE), catalyzed by water-soluble ruthenium alkylidenes **1,** $RuCl_2(PCy_2(C_5H_{10}NMe_2Cl))_2({=}CHPh)$, or **2,** $RuCl_2(TPPTS)_2({=}CHCO_2Et)$ (TPPTS = tris(3-sulfonatophenyl)phosphine, sodium salt), has been carried out in emulsion. Polynorbornene latexes (PNBE) can be obtained in high yields, in the absence of floc, and with high solids, if Dowfax is used as surfactant. The nucleation mechanism of the polymerization has been found to be a continuous homogeneous nucleation. The resulting polymer particles are formed of aggregates of small primary particles, stabilized by the highly ionized chain ends. Typical particle sizes are ranging from 50 to 100 nm, even at higher solids. Less strained olefins, such as cyclooctene, COE, and 1,5-cyclooctadiene, COD, cannot be efficiently polymerized by catalysts **1** or **2**. Nevertheless, these monomers are polymerized by a hydrophobic catalyst, **3**, $RuCl_2(PCy_3)_2({=}CHPh)$. To form colloidal objects, the catalyst is dispersed into water through the use of a miniemulsion technique. The miniemulsion is then fed with monomer, and after polymerization, a latex is obtained. Monomer conversion is moderate, but a latex is generated in the absence of floc.

Introduction

Ring-opening metathesis polymerization (ROMP) has been instrumental in the development of a variety of synthetic polymers, including PNBE, polycyclooctenes, polyacetylenes, and their derivatives. Industrially, ROMP is used for the production of cheap highly unsaturated polymers (Norsorex, Vestenamer).[1] Much work devoted to ROMP has been carried out in organic solution or in bulk, due to the high sensitivity to oxygen and polar compounds of the early transition metal catalysts.[2] These catalysts contain a Schrock carbene, a highly polarized and nucleophilic species that is usually very reactive toward water. There also exist several late transition metal catalysts (based on Ru, Ir, and Os) that exhibit a remarkable tolerance to polar compounds and even water. Before the advent of the so-called Grubbs catalysts, these late transition metal catalysts were ill-defined species that did not contain an alkylidene. It was thought that the alkylidene active species was formed in situ during the polymerization, as evidenced by numerous studies.[3] Despite their low level of control, these compounds offer the extraordinary advantage to be tolerant to numerous functionalities and to be active in aqueous solvents. Early work by Rinehart[4,5] and Michelotti[6] have demonstrated that hydrates of Ru, Ir, and Os chlorides are catalysts for the ROMP of NBE and NBE derivatives in an emulsion process. Using $(NH_4)_2IrCl_6$, Rhinehart has demonstrated the feasibility of NBE emulsion polymerization, using Pluronic F-68, a nonionic surfactant, to stabilize the product. The polymerization rate is extremely low, since in 1 h reaction, 1 g of catalyst polymerizes only 5.4 g of NBE.[4] More recently, dispersion-related processes, usually referred as aqueous ROMP, have been described in which a water-soluble monomer is polymerized to yield a water insoluble polymer.[7,8] Often, derivatives of 7-oxanorbornene are polymerized in water or water/ethanol mixture.[9,10] For example, Grubbs et al. have shown that this class of monomer is very efficiently polymerized in water with $Ru(II)(H_2O)_6(tos)_2$ for catalyst.[11−14] With sugar-modified oxanorbornenes, Kiessling et al. have elegantly designed polymers with protein binding activity.[15−18] Booth et al. have extensively studied the dispersion polymerization of *exo,exo*-2,3-bis(methoxymethyl)-7-oxanorbornene and found that it is possible to generate a small particle size latex (<100 nm) that can be stable for weeks.[19−21] Finally, Heroguez et al.[22] have demonstrated that it is possible to synthesize a latex in organic medium by copolymerizing poly(ethylene oxide) functionalized NBE macromonomers with NBE or COD in a mixture of dichloromethane and methanol.

With the advent of well-defined ruthenium alkylidenes,[23−25] much work has been devoted to controlled polymerization in water. Mechanistic studies have revealed that the carbene is susceptible to be activated, through assisted phosphine dissociation by protonation.[26−28]

We present here our efforts to polymerize in an emulsion process, that is to say, an aqueous process whereby an hydrophobic monomer is polymerized by a water-soluble initiator, in the presence of a surfactant, to produce a latex.[29,30] Latex particles are submicronic polymer particles which are protected against coagulation by a layer of adsorbed surfactant. Clearly, the emulsion process presents numerous advantages: (1) VOCs are greatly reduced as no organic solvent is used. (2) During the reaction, the viscosity remains very low, as long as the polymer is dispersed. (3) Reaction rates are (usually) very high since they are proportional to the number of particles, usually comprised between 10^{13} and 10^{18} part/L. Moreover, the polymerization site is the polymer particle, which is swollen by monomer: therefore, the reaction rate is as fast as bulk polymerization. (4) The heat of reaction is easily absorbed, because of the high heat capacity of water.

On the other hand, (5) the process suffers from a high lack of reproducibility, especially during its nucleation period. (6) The product is very fragile. Although stabilized by surfactant, it is prone to flocculation, especially after freezing, or when it is exposed to high ionic strength conditions. (7) The process is generally restricted to radical polymerization.

10.1021/ma001570m CCC: $20.00

In this paper, the emulsion polymerization of NBE is first described. For this purpose, water-soluble Grubbs type catalysts **1** or **2** are used.[31] A PNBE latex can be very easily synthesized, without generating any floc. Our effort to polymerize less strained monomers, such as 1,5-cyclooctadiene (COD) and cyclooctene (COE) with these catalysts results in extremely low yield reaction, generating low solid latex. More active catalysts are needed, and for this purpose, we use commercial Grubbs type catalyst, **3**. Since this catalyst is very hydrophobic, it is unable to cross the aqueous barrier and to diffuse to the locus of the polymerization (the particles). Therefore, we have used a specific emulsification technique, conventionally called miniemulsion, to generate stable nanometric droplets of catalyst dissolved into a small amount of toluene. In the presence of monomer, polymerization occurs, to yield a latex without floc.

Experimental Section

All commercial products were purified according to standard procedures. Dowfax 3B2 surfactant is a kind gift from Dr. B. Emelie, from Dow. Catalyst **1**[31] and $RuCl_2(TPPTS)_2$[32] were prepared according to the literature procedure. Emulsion polymerizations were carried out in a 250 mL glass jacketed reactor fitted with a condenser, an argon inlet, and a mechanical stirrer set at 300 rpm and a sampling valve. Ultrapure water (18.1 MΩ·cm) was degassed by repeated freeze−pump−thaw cycles. Conversion was followed by gravimetry, and particle sizes were measured using a Malven Autosizer 4800 light scattering instrument equipped with a 50 mW laser. The light scattering measurement could be hampered by the presence of residual NBE, which is solid at room temperature. In this case, a few drops of toluene were added to the scintillation tube containing the diluted latex to analyze. The organic solution (top layer) was then separated from the latex. Particle size distribution was also followed on a flow FFF from FFF Corp., equipped with a static light scattering detector, MiniDawn from Wyatt Technology.

Floc amount was obtained as the percent amount of polymer left in the reactor after drainage of the latex, plus the percent amount of polymer that could not pass through a quartz-wool filter.

TEM pictures were made on a Philips CM 120 instrument and CryoSEM pictures on a Philips XL 30 FEG instrument equipped with a Cryotransfer CT 1500 from Oxford instruments. GPC were carried out on a Waters instrument equipped with two linear Shodex columns and a RI. NMR measurements were carried out on a Bruker AMX 400 spectrometer.

Typical Emulsion Polymerization. *Warning: ethyl diazoacetate, a moderately stable compound, reacts extremely rapidly when in contact with the ruthenium complex, thus generating a large amount of gaseous nitrogen. In addition, NBE polymerization is very exothermic. Although the authors have never encountered any difficulty while performing this experiment, we advise not to carry this experiment on too a large scale.*

153.43 g of degassed ultrapure water and 2.32 g of a 50% solution of Dowfax 3B2 and degassed NBE (68.43 g) are introduced under argon into a polymerization reactor. The mixture is mechanically stirred and heated at 80 °C, to form a dispersion of liquid NBE in water. 936 mg of $RuCl_2(TPPTS)_2$ is then introduced, giving a brown color to the mixture, followed by 84 μL of ethyl diazoacetate. Samples are withdrawn at regular time interval in order to evaluate particle size and monomer conversion. Particle number is calculated from these two values. After 30 min polymerization, the conversion is 89%. The resulting latex is light gray.

Typical Miniemulsion Polymerization. 361 mg of $RuCl_2(PCy_3)_2(=CHPh)$ (1 equiv, 2.88×10^{-4} mol) are dissolved in 5 mL of toluene and 1.5 g of hexadecane. This purple solution is added under argon into 150 mL of water containing 1.5 g of sodium dodecyl sulfate (SDS) as surfactant. The mixture is sonicated for 2 min, yielding a stable toluene emulsion ($d = 157 \pm 86$ nm). This emulsion is then transferred under argon into a polymerization reactor, which is then heated at 80 °C. 15 mL of degassed COE is then cannula transferred into the reactor over a range of 5 min. The reaction medium becomes light gray, and a latex formation occurs.

Scheme 1. NBE Polymerization by Catalyst 1

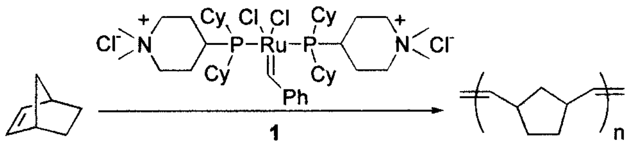


Table 1. Influence of the Ratio $[N_2CHCO_2Et]/[Ru]$ in Emulsion Polymerization of NBE at 80 °C[a]

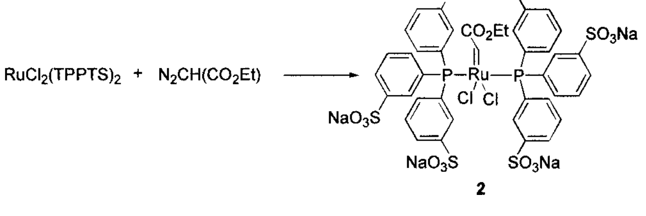
$[N_2CHCO_2Et]$/ [Ru]	[NBE]/ [Ru]	yield (%)	solids (%)	dp[b] (nm)	σ[c] (nm)	Np[e] (/L) × 10^{18}
1.02	800	97.5	13.6	63	27	1.04
1.66	800	86	12.0	64	21	0.87
2.68	800	96	13.4	77	27	0.55
2.98	800	91	12.7	65	21	0.88
10.2	800	35	5.3	49	32	0.86
33	800	10	2.0	*d*	*d*	*d*
1.1	2300	23	3.7	54	25	0.45
3.6	2400	62	8.9	63	31	0.68

[a] For each experiment, 150 g of water, 1.27 g of SDS, and 23 g of NBE are used. Stirring rate is 400 rpm. [b] Particle diameter. [c] Half-width of the particle size distribution. [d] Particle diameter could not be measured because too much NBE is present. [e] Particle number per unit volume.

Preparation of $RuCl_2(PPh_3)_2(=CHCO_2Et)$. 32.8 mg of freshly prepared $(PPh_3)_3RuCl_2$ are dissolved into 600 μL of a 3:2 mixture of deuterated methylene chloride and deuterated THF in an NMR tube equipped with a Teflon inlet. The tube is cooled at −10 °C in an ethanol bath. 4 μL of ethyl diazoacetate is then added, giving a rapid color change from brown to green; the tube is left for 3 h at −10 °C and then quickly analyzed by NMR (cooled at 0 °C). ^{1}H NMR (calibrated by the $CHDCl_2$ resonance, 0 °C): δ 17.2 (b, 1H, $\mathbf{C}\mathbf{H}CO_2Et$), 7.9−6.9 (m, 15 H, aromatic), 3.2 (q, 2H, $C\mathbf{H}_2CH_3$), and 0.9 (t, 3 H $CH_2C\mathbf{H}_3$). ^{13}C NMR (calibrated by the CD_2Cl_2 resonance, 0 °C): δ 278.3 ($\mathbf{C}HCO_2Et$), 170.1 ($\mathbf{C}O_2$), 136.1−128.4 (aromatic), 61.0 ($\mathbf{C}H_2CH_3$), 13.5 ($CH_2\mathbf{C}H_3$).

Results and Discussion

Water-Soluble Catalysts for NBE Emulsion Polymerization. NBE polymerizations can be conveniently performed in emulsion. Two water-soluble catalysts have been studied for this purpose. Catalyst **1**[31] gives very fast polymerization rates, and quantitative yields, even at monomer to catalyst molar ratios as high as 3000 (Scheme 1 and Table 2). As the synthesis of the phosphine ligand of catalyst **1** is cumbersome,[31] we have used another catalyst, **2**, that is generated in situ by reaction of ethyl diazoacetate with bis(TPPTS) ruthenium dichloride (TPPTS = tris(3-sulfonatophenyl)phosphine, sodium salt).



2

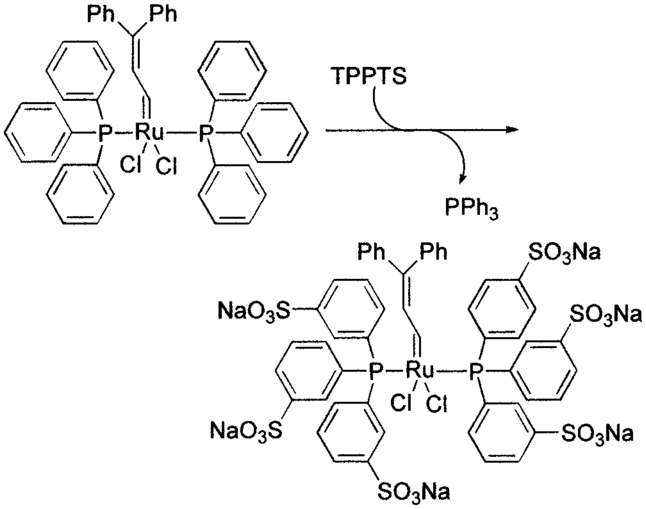
All our attempts to isolate catalyst **2** have been unsuccessful. Nevertheless, we have indirect evidence for the formation of **2**. First, reaction of diazo species

Table 2. Emulsion Polymerization with Catalysts 1 and 2[a]

cat.	T (°C)	mon (g/L)	[mon]/[cat.]	react time (min)	yield (%)	dp[c] (nm)	σ[d] (nm)	Np[e] (/L) × 10^{18}
1	80	356	2600	15	91	148	35	0.19
1	80	196	800	25	94	72	38	0.94
1	50	171	400	15	55	357	199	3.9[f]
2	50	166	450	120	24	199	120	9.6[f]
2	80	149	500	60	73	94	50	0.25
2	80	136	800	15	96	77	27	0.55
2	80	152	2900	15	53	72	27	0.41
2	80	148	3000	25	67	58	29	0.97
2[b]	80	418	2300	30	89	95	36	0.83
2[b]	80	469	800	35	91	116	42	0.52

[a] For each experiment, 150 g of water and 1.27 g of SDS were used (concentration 9.3 g/L). Stirring rate was 400 rpm and $[N_2CHCO_2Et]/[Ru] = 2.5$ [b] Dowfax 2A1 is used as surfactant for this polymerization (7.5 g/L). [c] Particle diameter. [d] Half-width of the particle size distribution. [e] Number of particles per unit volume. [f] × 10^{15} part/L.

Scheme 2. Phosphine Exchange To Form a Water-Soluble Catalyst[33]



with ruthenium complexes has been proved to be a versatile route to generate carbene complexes.[23,24] In addition, it has been disclosed that hydrophobic ruthenium carbenes can be made water-soluble through phosphine exchange (Scheme 2),[33] but the resulting catalysts have not been isolated.[33] To our knowledge, no ROMP catalyst bearing TPPTS ligand has been crystallized in the past. Finally, reaction of ethyl diazoacetate in deuterated dichloromethane/THF mixture with $(PPh_3)_3RuCl_2$, the organosoluble analogue to $(TPPTS)_2RuCl_2$, leads to the formation of an alkylidene: NMR monitoring of the reaction indicates the characteristic presence of the carbene ^1H resonance at 17.2 ppm.

$$RuCl_2(PPh_3)_2 + N_2CH(CO_2Et) \rightarrow RuCl_2(PPh_3)_2({=}CHCO_2Et) \quad (2)$$

This complex rapidly decomposes, as the carbene resonance disappears after 3 h at 10 °C. When ethyl diazoacetate in deuterated water is reacted with $(TPPTS)_2RuCl_2$, no carbene corresponding to the formation of **2** is observed.[33]

Under emulsion polymerization conditions, we have found that $RuCl_2(TPPTS)_2$ alone[34] is not a polymerization catalyst, whereas it triggers immediate polymerization when activated by 1−3 equiv of diazo compound (Table 1). A small excess of ethyl diazoacetate is necessary as it is easily hydrolyzed in the presence of water. Too a large excess is detrimental to the formation of the catalyst. For example, a $[N_2CHCO_2Et]$:[Ru] ratio of 2.2:1 results in a fast polymerization with 96% yield, whereas when this ratio is 30:1, the yield is only 8%.

Emulsion Polymerization of NBE. The typical scheme of an emulsion polymerization consists of the polymerization of a mostly water-insoluble monomer by a water-soluble initiator. At the beginning of the polymerization, the surfactant is dissolved in water, up to critical micellar concentration, and the excess is forming micelles that are monomer swollen. If all the monomer is contained into the micelles, then a microemulsion scheme is prevailing.[35] This usually necessitates as much surfactant as monomer, as a typical micelle (for example, a 4 nm diameter SDS micelle) is constituted by the spherical assembly of around 50 surfactant units, and can accommodate around 50 monomer units. During the course of this work, Grubbs et al.[36] have described the microemulsion of 65 mg of NBE stabilized by 550 mg of a cationic surfactant, using a water-soluble catalyst. Little details are given on the colloidal nature of this process. Under usual conditions for emulsion polymerization, a much smaller amount of surfactant is used, so that most of the monomer ends up in large droplets that are generated by mechanical stirring. These droplets play the role of monomer reservoir and are not the locus of polymerization. For NBE emulsion polymerization, a further difficulty arises, as the monomer is in the liquid state only between 46 and 96 °C. NBE needs to be liquid (or eventually gaseous) in order to diffuse through the aqueous barrier from droplets to particles. We have observed that it is most favorable to effect the polymerization at 80 °C. Indeed, at 50 °C, the emulsion polymerization catalyzed by **2** of 25 g of NBE in 150 mL of water containing 1.27 g of SDS yields a latex and large amounts of floc with 24% conversion in 3 h (particle size 199 ± 120 nm). At 80 °C, under similar conditions, quantitative polymerization is observed, and the latex is prepared without any measurable floc. Higher temperature than 80 °C results in large monomer loss through sublimation.

At 80 °C, polymerization rates have been found to be very high, notwithstanding the amount of catalyst used (Table 2). In general, small particles are generated (less than 150 nm), and particle size distributions are quite narrow, as measured by QELS and flow FFF (see below).

The polymerization rate profiles are unexpected for an emulsion polymerization.[37,38] Usually, a nucleation period is observed at the beginning of the reaction, during which polymer particles are formed. Since the polymerization rate is directly proportional to the number of polymerization microreactors (polymer particles), one expects to see a slow rate increase at the beginning of the reaction. Usually, nucleation quickly stops, as the whole surfactant is utilized to generate and stabilize polymer particles. Unlike a conventional radical emulsion polymerizations, we do not expect to see the nucleation period to be followed by a steady-state regime and an eventual acceleration (Trommsdorff effect), as these effects are entirely related to the radical nature of the process. In our polymerizations, the particle number regularly increases with conversion, as shown in Figure 1, indicating a continuous nucleation

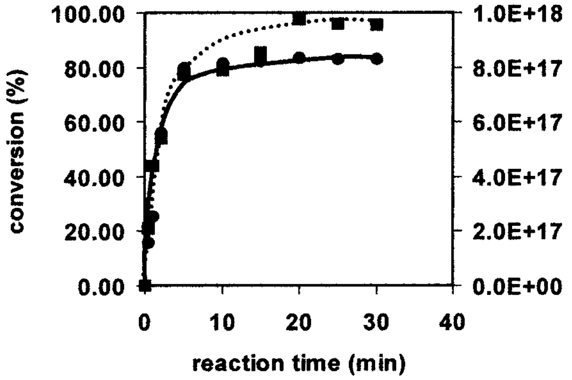


Figure 1. A typical conversion vs time curve for NBE emulsion polymerization. Left axis: conversion in percent (plain line, circles); right axis (dotted line, squares): particle number per unit volume. Experimental points obtained when polymerizing 23.08 g of NBE in 160.15 g of water + 1.27 g of SDS in the presence of 373 mg of $RuCl_2(TPPTS)_2$ and 100 μL of ethyl diazoacetate.

Table 3. NBE Emulsion Polymerization with Catalyst 2: Influence of Surfactant Concentration[a]

surf (g/L)	stirring rate (rpm)	yield (%)	dp[c] (nm)	σ[d] (nm)	Np[e] (/L) × 10^{18}
8.35	400	83	63	23	1.0
5.95	400	76	53	17	1.5
4.02	400	84	57	19	1.3
1.54[b]	400	81	80	28	0.5
8.35	1000	83	62	18	1.0
8.35	200	80	59	23	1.2
1.50[b]	200	75	78	21	0.6

[a] Experimental conditions: 150 g of water, $[N_2CHCO_2Et]/[Ru] = 2.5$, $T = 80$ °C, [NBE] = 23 g/L, [NBE]/[Ru] = 800, reaction time is 1 h. [b] Flocculation occurred early for this polymerization, due to the low amount of surfactant used. [c] Particle diameter. [d] Half-width of the particle size distribution. [e] Number of particles per unit volume.

during the entire course of the polymerization. Yet, it should be pointed that this analysis is prone to error because a small deviation in particle size measurement translates into large errors in particle number (N_p is proportional to d_p^{-3}) and that 80% conversion is reached within 5 min, which obliges to very fast sampling at early conversion.

We have also observed that the *final* particle number is nearly constant and very high (close to 10^{18} part/L), irrespective of surfactant concentration, stirrer speed, monomer concentration, and catalyst concentration (Tables 2 and 3). Note that, under a typical radical emulsion polymerization, one would expect the particle number to vary by several decades (typically from 10^{13} to 10^{18} part/L). Figure 2 illustrates the number of particles for 14 different experiments where both the monomer and the catalyst concentration are varied. We have also checked that the number of particles does not change when the surfactant is varied from below to above cmc, thus ruling out a micellar nucleation mechanism.[29] These results strongly suggest that a very efficient homogeneous nucleation mechanism is taking place, even when micelles are present.[29,39–45] These observations differ from the regular behavior of a radical polymerization in emulsion, yet it should also be pointed out that the active site in ROMP (the carbene) remains water-soluble during the reaction, whereas the radical changes in nature from water-soluble to oil-soluble. Further studies are effected in this direction in order to elucidate the nucleation mechanism.

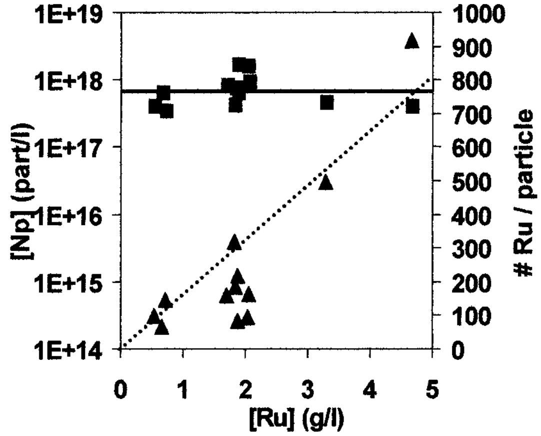


Figure 2. Particle number (left, plain line, squares) and number of ruthenium atoms per particle (right, dotted line, triangles) vs $RuCl_2(TPPTS)_2$ concentration (in g/L). Experimental conditions: 5 g ≤ NBE ≤ 34 g, H_2O = 150 g, SDS = 1.27 g, stirrer speed = 400 rpm, T = 80 °C.

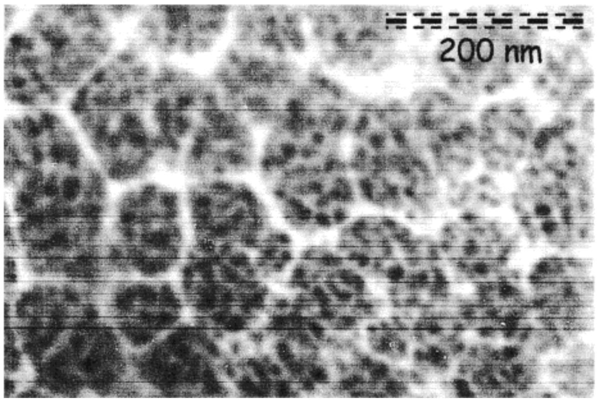


Figure 3. TEM picture of PNBE latex. The latex characteristics can be found in the last entry of Table 2.

Particle size distribution of the PNBE latex is analyzed by a variety of different methods. Routinely, dynamic light scattering with a set of five different angles (from 30° to 150°) is effected on the latex, to yield an average particle size and the half-width of particle size distribution. The result is often biased toward the larger particle sizes.[46] The complete distribution can be observed by optical methods such as electron microscopy. Although the T_g of PNBE latex is measured at 38 °C by differential scanning calorimetry, the particles quickly form a film under the electronic beam. After a slow drying period at room temperature, the particles appear as nonspherical irregular objects (Figure 3). The apparent morphology of the particles is quite surprising, as there seems to be numerous black grains, thus imparting a leopard skin like texture. Scanning electron microscopy (Figure 4), where the sample is quenched and metallized at liquid nitrogen temperature, confirms this observation: numerous small particles of typical size 25 nm can be seen on top of latex particle size (70 nm). The particle size distribution is also conveniently analyzed by flow FFF (Figure 5), with little difference from microscopy observations and dynamic light scattering. A putative explanation for particle formation is that the polymer chain starts to grow in water, where it eventually precipitates, forming a primary particle containing only one macromolecule. Because of the highly ionic character of the catalytic chain end (it is 6 times negatively charged), the primary particle is nearly

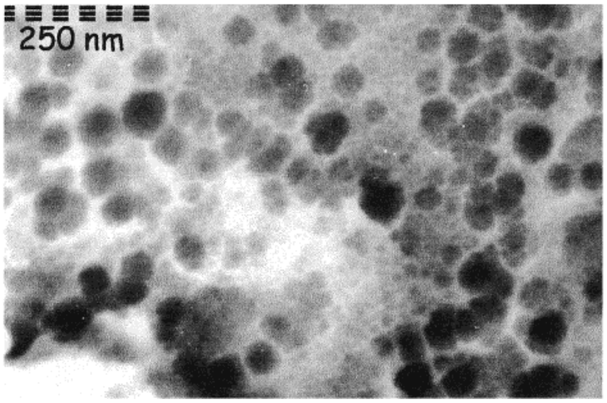


Figure 4. SEM picture of PNBE latex. The latex characteristics can be found in the seventh entry of Table 2.

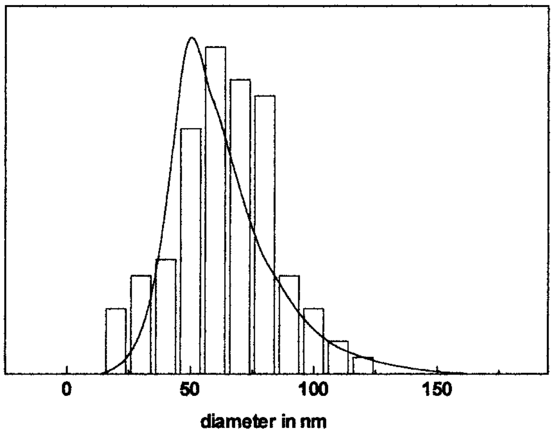


Figure 5. Particle size distribution obtained by flow FFF[47] (continuous line) and by particle enumeration[48] from TEM pictures (bar chart) for an emulsion PNBE latex. Mean diameter determined by flow FFF is 57 nm, with a standard deviation of 29 nm; mean diameter by microscopy is 70 nm with a standard deviation of 28 nm. Latex characteristics can be found in the seventh entry of Table 2.

stable (high surface charge). The latex particle grows by precipitation of these primary particles. Darker regions in the TEM picture (Figures 3 and 4) might therefore correspond to the imprint of a primary particle (ruthenium-rich region) and lighter regions to interstitial regions where pure PNBE has diffused.

Molecular weights of PNBE are extremely high, ranging from 2×10^5 to 2×10^6 g/mol, and in certain cases, the polymer cannot be dissolved in THF (the eluent used for GPC). We believe that because of the very high density of double bond, spontaneous cross-linking of the polymer might occur, in the presence of trace amounts of oxygen. Even in the presence of a radical inhibitor added during the polymerization, such as 2,5-di-*tert*-butyl-4-methylphenol, the cross-linking process cannot be avoided.

High solid latexes (as high as 46%) can be obtained in quantitative yield, if Dowfax 3B2 is used as surfactant (see Table 2). We believe this surfactant more strongly adsorbs onto the particle surface than SDS, resulting in improved stabilization. Ongoing work concentrates on measuring adsorption isotherms of the surfactant on the latex. Using the high solids latex, a PNBE containing coatings will be formulated. Because of the excellent sound dampening properties of PNBE, a sound proof paint will thus be generated.

Scheme 3. Polymerization of COD with Catalyst 3

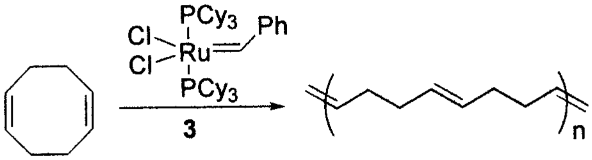


Table 4. NBE Plymerization Catalyzed by 3 Dispersed through the Use of a Miniemulsion[a]

surf	surf (g/L)	[mon]/ [cat.]	conv (%)	particle size (nm)
	0	1585	91	no latex
SDS	5	1820	88	652
SDS	7.5	1580	93	391
Dowfax 3B2	7.5	1710	97	251

[a] NBE = 100 g/L, $T = 80$ °C, reaction time = 5 min. The first entry of the table corresponds to a bulk polymerization under similar conditions.

Table 5. COD and COE Polymerizations Catalyzed by 3, Dispersed through the Use of a Miniemulsion[a]

mon	toluene (g/L)	[surf] (g/L)	[mon]/ [cat]	react time (min)	conv (%)	particle size (nm)
COD		0	800	60	98	no latex
COD		3	755	60	56	>1 μm
COD	60	6	690	60	69	583
COD	27	10	550	300	52	263
COE	33	10	400	300	27	191

[a] COD/COE = 100 g/L, $T = 80$ °C.

Miniemulsion Polymerizations of COD and COE. We found that both catalysts **1** and **2** are ineffective for the emulsion polymerization of cyclopentene, 1,5-COD and COE. With catalyst **2**, the yield is virtually zero, whereas with catalyst **1**, the yield, under the same conditions as NBE polymerization, does not surpass 10%. More active catalysts can be obtained by using very hydrophobic phosphines, such as tricyclohexylphosphine (catalyst **3** in Scheme 3). Since the catalyst is not water-soluble, using it in emulsion polymerization results only in floc formation. To perform the polymerizations, we have used a miniemulsion process.[49−53] In an emulsion process, the monomer droplets are colloidally unstable, due to Ostwald ripening that provides a driving force toward coagulation. By adding a hydrophobic component (cosurfactant, usually hexadecane) and after suitable treatment (sonication, microfluidization), the droplets become thermodynamically stable: this corresponds to the formation of a miniemulsion. The size of the droplets is typically in the range 100−400 nm. In radical chemistry, it is usually the monomer that is emulsified by such a process. If no renucleation and no coagulation occurs,[54] the polymer particles are then direct 1 to 1 replicas of the initial monomer droplets (miniemulsion polymerization). In ROMP emulsion, we have not dispersed the monomer, but catalyst **3**, dissolved in a minimum amount of organic solvent (toluene). The resulting catalytic droplets are then set into contact with a mixture of monomer, water, and, eventually, additional surfactant. The monomer diffuses through the aqueous phase to the catalyst droplets, where polymerization occurs. The measured size of the final polymer particle does not match the size of the catalyst droplet (Tables 4 and 5). When the final size is much larger than the initial size, growth of the particle by monomer diffusion and/or coagulation through Ostwald ripening has occurred. On the other hand, when a high concentration of surfactant is used, particles smaller than the initial droplets are formed. Although we might attribute this behavior to particle renucleation, it difficult to

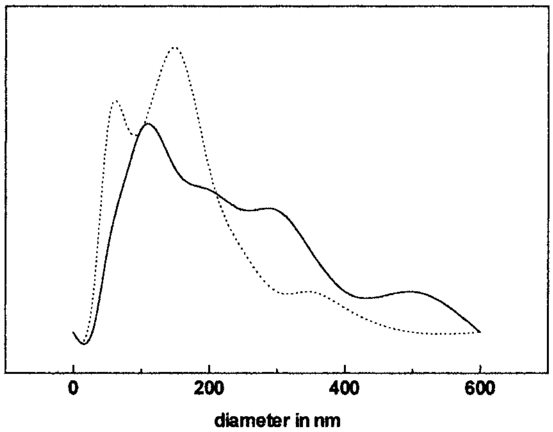


Figure 6. Particle (plain line) and droplet (dotted line) size distribution for a miniemulsion polymerization of COE. The miniemulsion average diameter is 160 nm (standard deviation is 93 nm), and the latex average diameter is 190 nm (standard deviation is 72 nm). This latex corresponds to the last entry of Table 5. The droplet and particle size distribution was obtained by flow FFF.

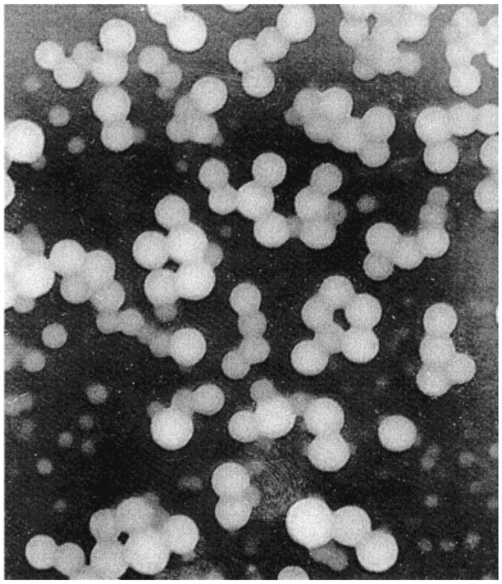


Figure 7. Electron microscopy picture of a polybutadiene latex obtained by polymerizing COD (entry 3 in Table 5).

believe that a catalyst as hydrophobic as **3** can diffuse through the aqueous phase. Another explanation might be that the miniemulsion is entirely reorganized upon contact with monomer. In most cases, the particle size is somewhat shifted toward higher diameters relative to droplet size distribution (Figure 6). This is quite expected, since monomer is continuously polymerizing inside the catalyst containing droplets, thus increasing their volume.

In general, NBE miniemulsions do not drastically differ from emulsion processes: high conversions are reached in a small amount of time (Table 4). However, the resulting latex is prone to flocculation. COD and COE miniemulsion polymerizations are characterized by lower yields and slower kinetics. Under similar conditions, polymerization in bulk gives high yield (first entry of Table 5). It seems that the miniemulsion yield is increasing with the amount of organic solvent used to disperse the catalyst and with the size of the catalyst droplets. We assume that, when dispersed into small droplets, **3**, although solubilized in toluene, might be poisoned by neighboring water. In larger droplets (more solvent), or less dispersed state, the catalyst is not in direct contact with water, and the poisoning effect is less predominating.

For COD, soluble high molecular weight polymers are formed. For example, for entry 2 of Table 5, a M_n = 155 000 g/mol polymer is obtained, with a polydispersity index of 1.6. NMR characterization indicates that the polymer is 60% cis. To our knowledge, this is the first time a completely 1,4 soluble polybutadiene latex is synthesized (Figure 7). For COE, the polymer (last entry of Table 5) is also entirely soluble and is characterized by a M_n of 90 000 g/mol with PDI = 1.5.

Conclusions

It is possible to synthesize PNBE and polybutadiene latex through ROMP in emulsion. Water-soluble catalysts can be used very efficiently for ROMP of NBE: high solid latexes can then be synthesized, using Dowfax 3B2 as a surfactant. Hydrophobic catalysts are conveniently used if they are encapsulated in toluene droplets, using a miniemulsion process. In this case, COD and COE can also be polymerized. Ongoing work now concentrates on the ROMP of cyclopentene in emulsion. PNBE and polycyclopentene aqueous borne coatings will be formulated and characterized, in terms of their mechanical and rheological properties.

Acknowledgment. We thank Dr. Brigitte Emelie (Dow Deutchland) for the generous gift of Dowfax 3B2.

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MA001570M