Catalytic Emulsion Polymerization of Olefins: Surfactant Effects in the ab Initio Polymerization of Norbornene

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ABSTRACT: The polymerization of olefins in aqueous media by late transition metal catalysts has created new opportunities to produce latex particles based on ethylene and its olefinic derivatives. In this work, we have concentrated on creating water-based latices from the strained cyclic olefin, norbornene. This has been done as ab initio batch emulsion vinyl polymerizations using allyl palladium catalysts and a lithium-based activator, supported by a variety of surfactants. The role of surfactants in traditional emulsion polymerization is to assist in particle nucleation and/or to stabilize latex particles. We studied the role of several classes of surfactants in the emulsion vinyl polymerization of norbornene with Pd catalysts, both with and without the activator LiFABA. In the catalytic emulsion polymerization of norbornene, some of these surfactant classes were found to act as weakly coordinating anions with the Pd-based catalysts to promote vinyl polymerization. When the base latex recipe already contains an activator specifically designed to work effectively with Pd in organic media (e.g., LiFABA), certain classes of surfactants (e.g., sulfates) act to provide an alternative pathway for polymerization and latex particle formation. Other surfactants (e.g., cationics) can actually suppress all or part of the polymerization by destructively interfering with either the catalyst or the separately added activator. Alkyl sulfates and sulfonates were both effective activators of allyl Pd catalysts and produced latex particles (ca. 40−50 nm) without significant amounts of coagulum. This activity is significantly dependent on the alkyl chain length, and alkyl sulfate anions are more active than the equivalent alkyl sulfonate anions. Cationic, fatty acid, and nonionic surfactants produced variable, but ineffective, results in our studies.

Introduction and Background

The vinyl polymerization of olefins using late transition metal catalysts in aqueous emulsions is possible and has begun to receive some attention in the literature.[1−10] For the most part, these studies have utilized the mini-emulsion polymerization route and often used substantial amounts of hexadecane to retard Ostwald ripening of the particles during polymerization. In those studies reported thus far, sodium dodecyl sulfate (SDS) has been the main surfactant employed. Chemtob et al.[11] reported examining four other surfactants, but used SDS for the bulk of the experiments. Regarding the emulsion vinyl polymerization of norbornene and its derivatives, very few studies have been reported. It is to be noted here that norbornene can also be polymerized via a ring-opening mechanism. That resultant polymer contains a residual double bond and is used as a specialty rubber. On the other hand, when it is polymerized through the vinyl polymerization mechanism, the resultant polymer is saturated and has a high glass transition approximating 300 °C. Puech et al.[12] were the first to report the aqueous polymerization of norbornene via vinyl polymerization. Their catalyst was $PdCl_2$ and produced low molecular weight oligomeric polynorbornene. They found that an increase in their surfactant (SDS) level increased the molecular weight of the polymer and that the latex particles formed were only 10−20 nm in diameter. Lipian et al.[13] reported the vinyl polymerization of butyl-norbornene in aqueous media using $[(\eta^3\text{-allyl})Pd(Cl)]_2$ catalyst precursor, $P(m\text{-}C_6H_4SO_3Na)_3$ ligand, and $Li[B(C_6F_5)_4 \cdot 2.5Et_2O]$ (LiFABA) activator with SDS as surfactant. They claimed that high catalyst activity is obtained with coordination of a phosphine to a cationic palladium center in the presence of the weakly coordinating LiFABA anion. Chemtob used the same catalysts, ligands, and activators as Lipian, as well as a PCy_3 ligand, to polymerize norbornene via mini-emulsion with hexadecane as a co-stabilizer and SDS as surfactant. Chemtob could not measure the molecular weight of the polymer because it would not dissolve in any of the solvents they tried. When they omitted the hexadecane, they reported that the conversion was still 100% but the particle size was greater than 1 μm. The amount of coagulum was more than 20 wt %.

We have recently reported some results from our study on the ab initio batch emulsion vinyl polymerization of norbornene using two Pd-based catalysts.[14] In that paper, we concluded that there is a major competition for polymerization reactions between the latex particles (on the order of 50 nm in diameter) and the emulsified droplets (ca. 10 μm in diameter). The use of a Li-based activator (LiFABA) promoted polymerization in both the emulsified droplets and the aqueous phase; the former produced great amounts of coagulum, and the latter produced stable latex particles. When using SDS as the surfactant, we achieved overall conversion levels of about 75%, and about one-half of the polymer was produced as coagulum. The coagulum was identified as massive agglomerates of ~10 μm particles and thought to have come from reaction in the emulsified droplets. In an attempt to reduce/eliminate the coagulum in these lattices, we subsequently varied the type of surfactant used in the basic recipe and studied the resultant reactivity, overall conversion, and coagulum levels. Anionic, cationic, and nonionic surfactants were used alone and in combination. The purpose of this Article is to report those results for norbornene monomer and to comment on the possible mechanisms of polymerization and particle formation as they are affected by the surfactants employed in the recipe.

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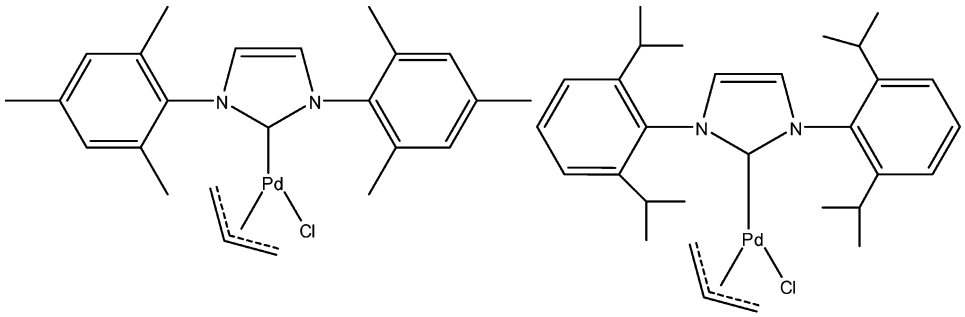

(a) (b)

Figure 1. Structure of catalysts. (a) TMP, (b) DPP.

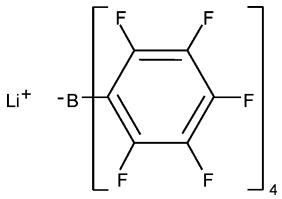

Figure 2. Structure of the activator, LiFABA.

Table 1. Standard Polynorbornene Polymerization Recipes

emulsion recipe	
DI water	95 g
norbornene	5 g
acetone	0.5 g
SDS	0.25 g
catalyst	3.2 mg
activator	5.6 mg
THF	1 g
temperature	60 °C

Materials. Norbornene (99%, Aldrich) was used as received. Allylchloro[1,3-bis(2,6-di-*i*-propylphenyl)imidazol-2-ylidene] palladium (97%, Strem Chemical) (henceforth referred to as DPP) and allylchloro[1,3-bis(2,4,6-tri-methylphenyl)imidazol-2-ylidene] palladium (Rohm and Haas) (henceforth referred to as TMP) were the catalysts and were also used as received. The structures of catalysts are shown in Figure 1. Lithium tetrakis(pentafluorophenyl) borate (LiFABA) (Boulder Scientific) was the activator and was used as received. The structure of this activator is shown in Figure 2. The catalysts and activators are oxygen sensitive and were kept in an MBraun glove box to ensure stability. Sodium decyl sulfate (Acros) (SDS), sodium dodecyl sulfate (99%, Alfa Aesar) (SDDS), sodium tetradecyl sulfate (95%, Acros) (STDS), sodium hexadecyl sulfate (99% Alfa Aesar) (SHDS), and sodium octadecyl sulfate (93% Aldrich) (SODS) were used as received. Rhodapex CO-436 (Rhodia), sodium stearate (99% Sigma), tetrasodium pyrophosphate (TSPP) (≥95%, Sigma), dodecyl benzene sulfonic acid (Acros) (DBSA), sodium 1-hexadecane sulfonate (98%, Avocado Research Chemicals), Aerosol OT (EM Chemicals), and cetyltrimethylammonium bromide (CTAB) were used as received. Igepal CO-520 and CO-997 (Rhône Poulenc) and Igepal CO-720 and CO-890 (Aldrich) were used as received. The deionized water from a Corning Mega Pure D2 water purification system was used in all experiments. Acetone (99.5%, EMD Chemicals), tetrahydrofuran (99.9%, EMD Chemicals), and cyclohexane (99.9%, Fisher Scientific) were used as received.

Latex Preparation. Deionized water was boiled and purged with argon for 30 min to eliminate the oxygen. Norbornene was dissolved in acetone in a ratio of 9:1 to ease the transfer of norbornene to the reactor because it is solid at room temperature. All surfactants were also dissolved in water to ease the transfer into the reactor. Both solutions were purged with argon for 10 min. The reaction was carried out in a 125 mL, three-neck, water-jacketed glass reactor equipped with a magnetic stirring bar. The reaction temperature was controlled by means of a water bath, and the reactor was evacuated and purged with argon. The above solutions were cannulated into the reactor using argon pressure, and then the reactor was brought up to 60 °C. The catalysts, activator, and THF were stored in the glove box. The catalyst and activator were dissolved separately in 0.5 g of THF, to produce solutions of 0.013 and 0.016 M, respectively, and sequentially injected into the reactor (catalyst first). The reaction was allowed to proceed for 3 h when catalyst and activator were used, and 5 h when only catalyst was used. After the reaction process was complete, the polymer latex was filtered through eight layers of cheesecloth to separate coagulum present in the latex. A standard polynorbornene recipe is shown in Table 1. We note that by our choice the amount of SDS in the base recipe was slightly less than its critical micelle concentration at the 60 °C reaction temperature. In our earlier work,[14] we found that the latex particle size was not sensitive to variations in surfactant levels both moderately above and slightly below the CMC.

Latex Characterization. Latex conversion was measured gravimetrically after evaporating the volatile compounds in a conventional oven at 60 °C. The total coagulum level was determined from the combination of the amount of polymer left in the reactor (i.e., wall scale) after removal of the latex and that separated by filtration of the whole latex through cheesecloth. The overall conversion was calculated as the sum of the latex conversion and the coagulum conversion. Particle size distributions of the final lattices were measured by light scattering (Microtrac Nanotrac 250) and capillary hydrodynamic fractionation (Matec CHDF2000) as well as compared to scanning electron microscopy (Amray 3300FE) (SEM) images. The SEM samples were sputter-coated with ∼50 Å of platinum.

Results and Discussion

A useful backdrop for this discussion is to describe the set of reaction mechanisms that we proposed in our recent paper.[14] There we suggested that with either the TMP or the DPP catalysts in the presence of LiFABA activator there is an opportunity to have latex particle nucleation and simultaneously have reaction in the large, emulsified droplets. The latter leads to massive agglomerates of ∼10 μm particles and the formation of coagulum. In the beginning, our testing of a large number of surfactants arose from our desire to eliminate the coagulum, and in the end we have begun to gain a more complete picture of the role of surfactants as either positively or negatively interacting with the catalysts and/or the LiFABA activator. Figure 3 shows that when SDS is used (this was our "reference" surfactant against which to judge the performance of others), there may be three mechanisms responsible for the polymeri-

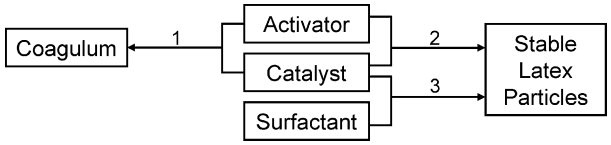

Figure 3. Proposed reaction pathways for norbornene polymerization using DPP or TMP catalysts with or without LiFABA activator.

zation. The first is the migration of the catalyst and the LiFABA through the water and into the emulsified droplets to produce large polymer particles (eventually coagulum), and the second is to have the same catalyst and activator produce colloidally stable latex particles (ca. 40 nm in size). A third possibility is that of the surfactant acting as a weakly coordinating anion and activating the catalyst in the water phase leading to latex particle formation. These pathways are numbered 1−3, respectively, and are depicted by the various arrows in Figure 3. These reaction steps are meant to be occurring simultaneously. It appears to us that the final characteristics of the latex are determined by the dominant reaction pathway that is specific to the recipe and temperature conditions used in the experiment. Indeed, our goal eventually became to influence the competition between the various potential mechanisms.

Another interesting reference point is that of a latex recipe without any surfactant at all. Standard emulsification of monomer in water using mechanical stirring produces droplets around 10 μm or greater in diameter. When the catalyst and activator were sequentially added to our reactor containing only water and dispersed monomer, a rapid reaction ensued and an overall conversion of 70% was obtained. However, 92% of that polymer was in coagulum form, although there was a small amount (ca. 5%) of latex conversion. The stable latex particles had a broad size distribution of 50−300 nm. This indicates that there was some water phase polymerization even without the presence of surfactant. It now becomes interesting to observe what happens as various other surfactants are added to the recipe, both with and without the LiFABA activator.

For discussion purposes, the surfactants are separated into classes: sulfates, sulfonates, cationic, fatty acid soap, and nonionics. The overall polymer conversion resulting from the use of various surfactants can be found in Table 2. All of the experiments using LiFABA activator employed the DPP catalyst. The set of experiments that did not use the LiFABA activator used the TMP catalyst. The polymers produced were not soluble in a number of different solvents, and thus we were not able to obtain molecular weight data for any of the experiments at this time.

Sulfate Series. Because SDS, in the presence of our catalysts and activator, was able to enhance the production of latex particles and provide a new pathway that can effectively compete with reaction pathways 1 and 2 in Figure 3, we suspected that other alkyl sulfate surfactants would provide interesting results. Our conclusion that the alkyl sulfate anion provided a weakly coordinating pair with the Pd cation is supported by the work of Lapinte et al.[15] They used $PdCl_2$ as the catalyst to polymerize octene in aqueous emulsion and determined that the alkyl (C-12) sulfate anion coordinated with the Pd cation to effect the polymerization of the octene. Although our Pd catalyst is different, it appears to also be activated by the same sulfate anion.

Our first experiment utilized sodium sulfate (Na_2SO_4) salt instead of surfactant to test the unlikely possibility of the simple sulfate anion coordinating with the Pd cation to activate the catalyst without the LiFABA activator present. It did not do so, as no polymer was formed when LiFABA was not added. As previously mentioned, "normal" 70% conversion was obtained when no surfactant was added and catalyst and activator were present. The Na_2SO_4 salt without activator yielded no polymer, which is similar to the experiment where neither surfactant nor activator was used.

We then used sodium alkyl sulfates of varying carbon chain lengths, ranging from 10 to 18. Figure 4 shows the results for sodium alkyl sulfates when LiFABA was used, and Figure 5 displays similar data for the experiments in which the LiFABA was omitted from the recipe. Figure 4 uses the DPP catalyst, and Figure 5 uses the TMP catalyst. As we showed in a previous paper,[14] the overall polymer conversion does not change when interchanging these catalysts. In Figure 4, it is striking to see as the alkyl chain length increased from 10 to 18 carbons that the conversion levels changed little while the coagulum levels dropped dramatically. This means that reaction pathway 3 became more and more prevalent with the increasing alkyl chain length and provided a highly competitive alternative to pathways 1 and 2 for polymerization. In particular, the hexadecyl sulfate effectively eliminated the tendency of the catalyst and the LiFABA to migrate to the large emulsified droplets and produce coagulum by providing a more rapid pathway for polymerization to produce small latex particles (ca. 40 nm). This interpretation of the results is supported by the fact that when the LiFABA is left out of the recipe (Figure 5), there is very little coagulum formed and monomer conversion is nearly as high as it was when the LiFABA activator was present to offer an additional pathway for polymerization. Also in Figure 5, it is seen that the C-10 alkyl sulfate surfactant does not appear to activate the catalyst. This is apparently why this surfactant allowed the LiFABA to induce the formation of massive amounts of coagulum, as seen in Figure 4. It is striking that adding two methylene groups to this alkyl chain, so as to produce SDS, results in a dramatic increase in the activity of the catalyst.

It appears from the data in Figures 4 and 5 that the positive trend seen with increasing the alkyl chain length does not extend beyond 16 carbons, as the C-18 sulfate surfactant seems to perform less well than the C-16 surfactant, both with and without the LiFABA activator. In a further test of the effect of the characteristics of the organic portion of the sulfate surfactant, we chose to use an ammonium salt of nonyl phenyl ethylene oxide (4 units) sulfate (Rhodapex CO-436) in experiments with and without the LiFABA activator. As seen in Table 2, the monomer conversions using Rhodapex CO-436 were the lowest in the sulfate series, although the surfactant clearly activated the catalyst (i.e., when the Rhodapex CO-436 was used without activator, 40% overall conversion was achieved, indicating that the surfactant can activate the catalyst). Because the number of carbons in this surfactant is 23, it may be that it is too large to be as effective as the C-16 sulfate. On the other hand, it may be that the ethylene oxide group adds an additional hydrophilic nature to the surfactant and in that way alters the association with the Pd catalyst.

We would have preferred to have additional experimental evidence, such as polymer molecular weight, to distinguish between the results of our experiments, and to compare to the results of other investigators. Yet, as discussed in our previous paper,[14] the polymers we made were not at all soluble in a wide range of solvents, and we have yet to be able to determine their chain lengths. Our experience is consistent with that of other investigators.[11]

Last, there was no correlation found between the latex particle size and the alkyl chain length. All of the experiments contained small particles around 30−80 nm as well as a few larger

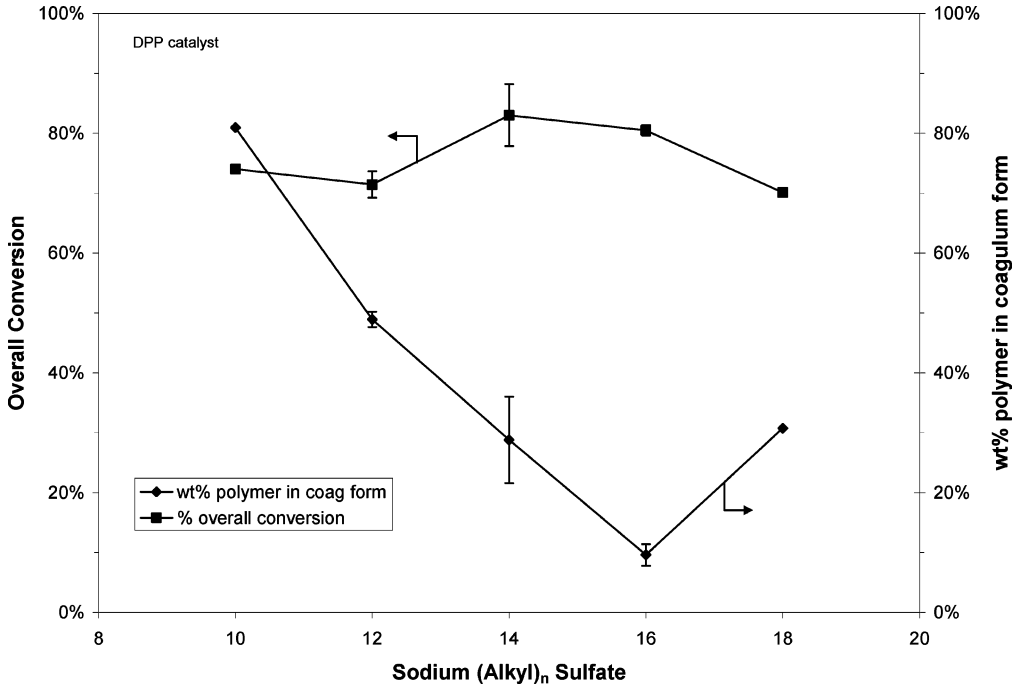

Figure 4. Overall polymer conversion of norbornene and coagulum level versus alkyl chain length (n = number of carbons in alkyl chain) of sodium sulfate surfactants for polymerization at 60 °C with DPP catalyst and with LiFABA activator.

Table 2. Overall Polynorbornene Conversion as a Function of Surfactant Type Using DPP Catalyst and LiFABA Activator[a]

	experiment number	wt % solids theoretical	wt % polymer in coagulum form	% overall conversion	[surfactant] $\times 10^{-3}$ (mol/L)	surfactant
a	DEC2-70	4.7%	92%	76.0%	0.00	no surfactant
b	DEC2-62	5.0%	83%	16.3%	9.21	DBSA
	DEC2-63	5.3%	33%	35.1%	6.60	Aerosol OT
	DEC2-66	5.6%	33%	64.1%	9.02	sodium hexadecane sulfonate
c	DEC2-73	5.5%	81%	57.9%	16.7	Igepal CO-520 (5 EO units)
	DEC2-75	4.6%	54%	30.2%	8.08	Igepal CO-520 w/ 8×10^{-3} M SDS
	DEC3-18	5.4%	23%	10.1%	8.63	Igepal CO-720 (12 EO units)
	DEC3-14	5.3%	30%	15.4%	3.18	Igepal CO-890 (40 EO units)
	DEC3-15	5.0%	19%	26.7%	2.06	Igepal CO-890 w/ 8×10^{-3} M SDS
	DEC2-74	4.7%	5%	11.1%	1.29	Igepal CO-997 (100 EO units)
	DEC2-76	4.8%	81%	43.9%	0.86	Igepal CO-997 w/ 8×10^{-3} M SDS
d	DEC2-80	4.7%	31%	2.0%	7.89	CTAB
	DEC2-55	5.1%	0%	0.0%	8.59	sodium stearate
e	DEC2-57	5.0%	0%	0.0%	8.59	sodium stearate + TSPP
f	DEC2-59	5.3%	36%	59.5%	9.58	Rhodapex CO-436
	DEC2-60	5.3%	50%	73.0%	9.40	SDS (C-12)
	DEC2-85	5.1%	48%	69.9%	8.89	SDS (C-12)
	DEC2-69	5.4%	81%	74.0%	8.94	SDecS (C-10)
	DEC2-64	4.8%	34%	79.4%	8.58	STDS (C-14)
	DEC2-67	5.3%	24%	86.7%	8.85	STDS (C-14)
	DEC2-79	5.0%	11%	79.9%	8.41	SHDS (C-16)
	DEC2-82	5.2%	8%	81.1%	8.12	SHDS (C-16)
	DEC2-68	5.0%	31%	70.1%	7.90	SODS (C-18)

[a] The nonionic surfactants were added at the same masses, while the remaining surfactants were added at $\sim 9 \times 10^{-3}$ M in water. (a) No surfactant; (b) sulfonated series; (c) nonionic series; (d) cationic; (e) stearate; (f) sulfate series; EO, ethylene oxide.

particles around 100−300 nm, irrespective of the surfactant. Figure 6 shows a representative SEM result for these latices. We also measured the particle sizes via light scattering (Microtrac Nanotrac 250) but found the data at the low end of the range (ca. 30−40 nm) to be questionable. The coagulum produced with the LiFABA was composed of agglomerates of ~ 10 μm particles (as shown in Figure 7) and had a character different from that of the small amounts of coagulum formed without LiFABA. The latter had the features of "normal" latex coagulum as usually found around the stir shafts and blades in latex reactors.

Sulfonate Series. Three surfactants were examined within the sulfonate series: sodium hexadecane sulfonate, dodecyl benzene sulfonic acid (DBSA), and Aerosol OT. These were chosen in an attempt to reduce the coagulum levels produced in reactions containing the LiFABA activator. They also serve to compare sulfonate surfactants to sulfate surfactants as potential weakly coordinating anions activating the Pd catalysts. Surprisingly, the overall conversions obtained in these three surfactant experiments (Table 2b) were considerably lower than those in the surfactant-free experiment. Sodium hexadecane sulfonate yielded the highest overall conversion at 64% with about one-third of that in coagulum form. The polymer formed with DBSA was mainly produced as coagulum, while the polymer formed with Aerosol OT had considerably less coagulum and a higher overall conversion level. Clearly, these

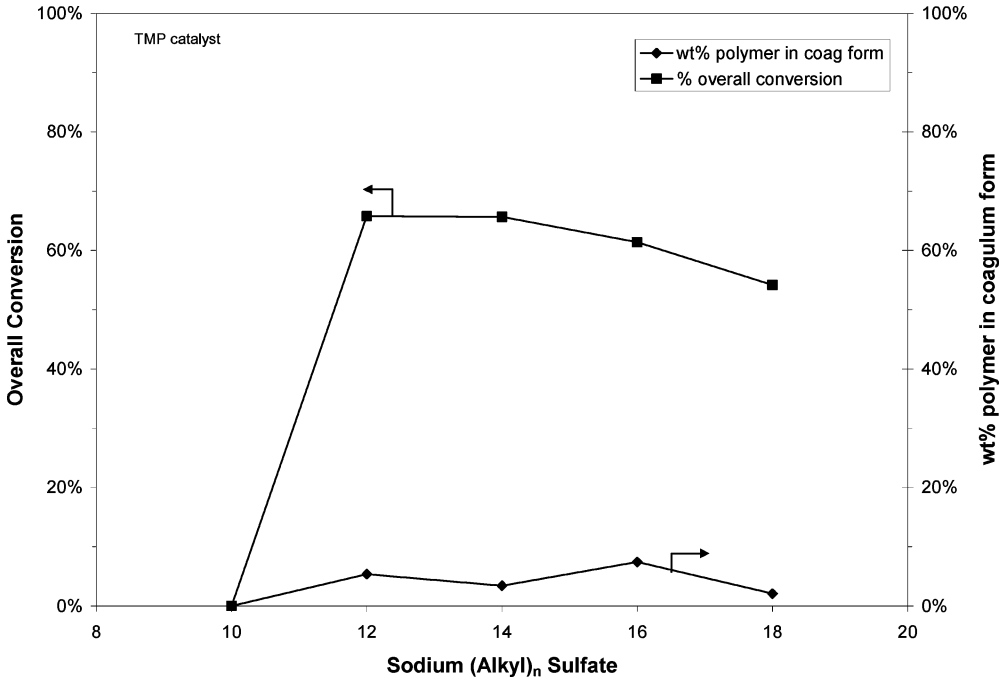

Figure 5. Overall polymer conversion of norbornene and coagulum level versus alkyl chain length of sodium sulfate surfactants for polymerization at 60 °C with TMP catalyst (without LiFABA activator).

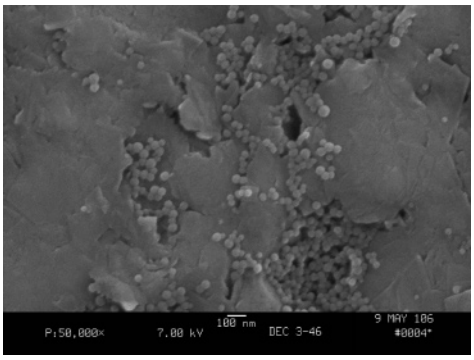

Figure 6. Representative SEM photo of PolyNB latex particles.

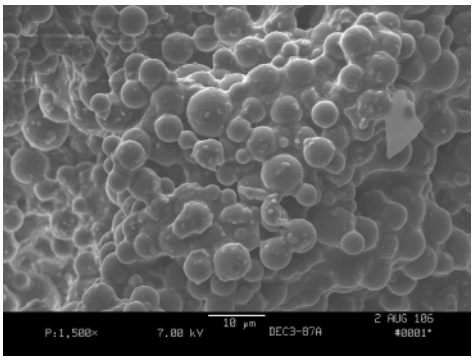

Figure 7. SEM photo of coagulum formed in polymerizations using LiFABA.

surfactants have affected the relative importance of the different pathways depicted in Figure 3. Sodium hexadecane sulfonate, similar to the C-16 sulfate except for the removal of one oxygen atom, yielded a total polymer conversion of 64%, with about a third of polymer in coagulum form. This is a decrease as compared to C-16 sulfate, which yielded 80% overall conversion. When the C-16 sulfonate was used without activator, 56% overall conversion was obtained. This indicates that the surfactant is able to activate the catalyst on its own. Both the C-16 sulfate and the sulfonate experiments without activator yielded similar overall reactions, 61% and 56%, respectively. This suggests a shift toward the enhancement of reaction pathway 3, but without the total diminution of the pathway to coagulum formation (when the activator is used).

The DBSA significantly hindered the polymerization as indicated by the low (16%) overall conversion. Because the surfactant is present in large molar excess of both the catalyst and the LiFABA, destructive interference with either or both could totally destroy the reactivity of the system. Achieving 16% conversion with nearly all of the polymer in coagulum form would suggest that pathway 1 in Figure 3 has been seriously diminished (as compared to the experiment with no surfactant) without any significant positive effect on the other two reaction pathways. Aerosol OT yielded a slightly higher conversion of 35% as compared to DBSA with significantly less polymer in coagulum form, 33%. This result suggests to us that pathway 3 has been enhanced at the expense of pathway 1 for this surfactant but the activity of the catalyst has decreased. It is not clear to us how these two results might happen at the same time.

Cationic. Cetyl trimethyl ammonium bromide (CTAB) was the only cationic surfactant used. The conversion level for the CTAB experiment was only 2%. Bromide is the anion of this surfactant, and it is very unlikely that it can act as a weakly coordinating anion with the catalyst. Pathway 3 in Figure 3 is not active as confirmed by Lapinte[15] who used a brominated cationic surfactant with $PdCl_2$ catalyst. Clearly, the CTAB had a catastrophic effect on the reactivity of our catalyst/activator system and even prevented this pair from migrating to the large emulsified droplets to produce polymer. We conclude that the cetyl trimethyl ammonium cation interferes with the LiFABA anion of the activator and effectively shuts down reaction pathways 1 and 2 in Figure 3, without providing an alternative pathway to polymerization.

Stearic Acid Soap. When we used sodium stearate as surfactant, we did so with and without the use of tetrasodium pyrophosphate buffer (TSPP). TSPP buffers the system at a pH of 9.0; without it the system operated at a pH of about 6, somewhat above the pK_a of the carboxylic acid group.[16]

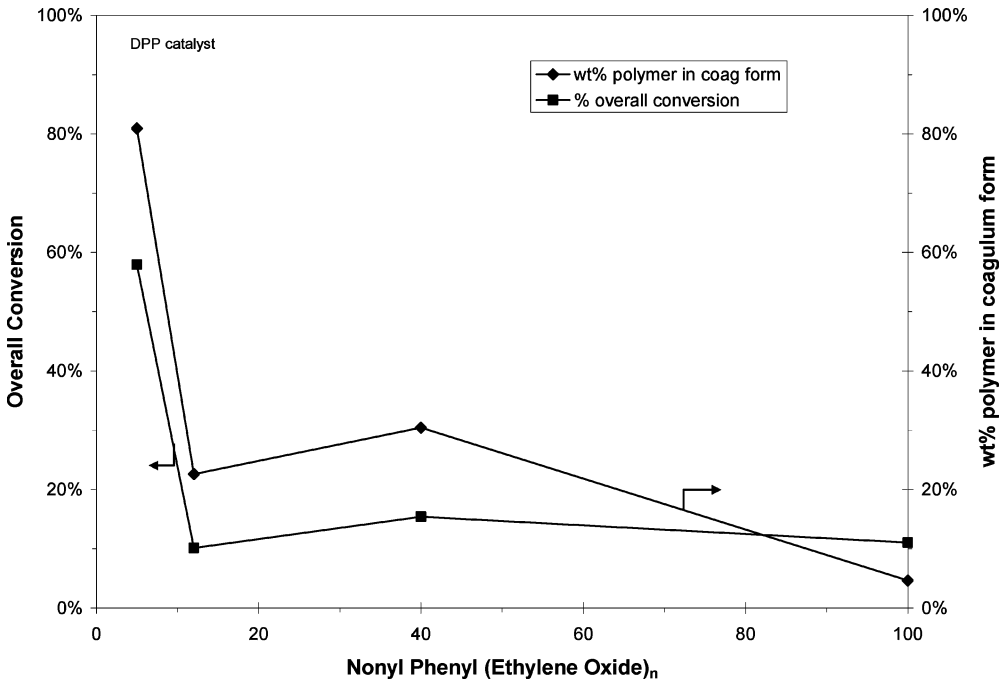

Figure 8. Overall polymer conversion and coagulum level versus ethylene oxide chain length of nonyl phenyl surfactant for norbornene polymerization at 60 °C with DPP catalyst and with LiFABA activator.

Absolutely no reaction was observed when using this surfactant with or without TSPP. Clearly, the reaction pathways 1 and 2 must have been eliminated by the C_{16} alkyl carboxylic anion. We suspect that this anion interacted with the Pd cation in a manner such that it eliminated the catalyst's ability to coordinate with the LiFABA. Because the molar concentration of the surfactant was so much higher than that of the catalyst, a strong, negative interaction with the catalyst would remove the catalyst from the system and eliminate any possibility of polymerization. Even without the TSPP, it would appear that the carboxylic group is ionized enough to interfere destructively with the catalyst.

Nonionic Series. Four nonyl-phenyl ethylene oxide surfactants were used with various ethylene oxide chain lengths. These nonionics were tested alone as well as with SDS. The polymer conversion and coagulum levels achieved with these surfactants are listed in Table 2, part c. These data are more dramatically summarized in Figure 8 where the conversion and coagulum levels are plotted as a function of the ethylene oxide (EO) chain length. We had expected that the nonionic surfactants might stabilize the particles that were formed without interfering with the polymerization reactions, but the data tell a very different story. As seen in Figure 8, the surfactant with 5 EO units produced slightly less polymer than the "no surfactant" experiment but again with nearly all of the polymer produced in coagulum form. Additional EO units resulted in dramatic decreases in the conversion levels to 10%, but the vast majority of the polymer was created as stable particles. By referring to the reaction pathways in Figure 3, we suggest that these nonionic surfactants may render the LiFABA activator to be inactive (as evidenced by essentially no coagulum formation) while slightly activating the catalyst to promote some limited latex conversion and the formation of stable latex particles. This apparent activity with low conversion level is consistent with that seen by Lapinte[15] with the use of Bri J 35 $[CH_3(CH_2)_{11}(OCH_2CH_2)_{23}$-OH], a nonionic surfactant.

Also entered into Table 2, part c, are some results using a dual surfactant system by adding SDS to several of the nonionic surfactants (those with 5, 40, and 100 EO units). We had anticipated that we might achieve at least the quality latex production obtained with SDS alone and perhaps some further enhancement due to the additional surfactant. The results are quite perplexing. At the 5 EO chain length, the two surfactants working together reduced the overall conversion level from that achieved with just the nonionic surfactant alone (30% vs 58%), yet also reduced the portion of the polymer produced as coagulum (55% as compared to 81%). When the same amounts of SDS were added to the Igepal with 40 and 100 EO units, the conversion levels were 27% and 44%, respectively; both results were improvements over those obtained with just the nonionic surfactant alone. However, the effect on the coagulum formation in these two experiments showed opposite trends. Thus, we see no consistency in the overall results of the nonionic surfactant study and do not offer any suggestions as to possible effects on the reaction pathways displayed in Figure 3.

Concluding Remarks

It is clear to us that a number of surfactants commonly used in standard emulsion polymerization of vinyl monomers can serve as weakly coordinating anions for Pd-based catalysts used to polymerize norbornene in aqueous emulsion. Both alkyl sulfate and alkyl sulfonate salts provide significant to excellent activation of the two forms of Pd catalysts used in our study. Additionally, there is a strong effect of the alkyl chain length on this activation capability when the number of carbons is less than 12 and some indication that the activation decreases as the number of carbons is greater than 16. The alkyl sulfate anions appear to be better activators than the alkyl sulfonate anions. When using such surfactants, it is not necessary to provide other means of activation of the Pd catalyst such as commonly done by the use of LiFABA. Cationic and fatty acid surfactants destructively interfere with the LiFABA activator and the Pd catalyst, respectively, and it is not clear why neither class of these surfactants was useful in suppressing the coagulum formation while allowing polymerization. The nonionic surfactants create a complicated set of interactions with either or both of the catalyst and LiFABA activator, but do not provide for an overall effective stabilizing system. The role of the surfactant

in activating the catalyst in norbornene emulsion vinyl polymerization sets it in striking contrast to the traditional role of the surfactant in standard, free radical emulsion polymerization where the surfactant can serve to nucleate and then stabilize the latex particles, but it does not influence the inherent activity of the initiator.

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