Macromolecules **2007,** *40,* 5743−5749

Catalytic Emulsion Polymerization of Olefins: Ab Initio Polymerization of Norbornene

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Received March 28, 2007; Revised Manuscript Received May 23, 2007

ABSTRACT: It has recently been shown that it is possible to polymerize homo- and copolymers of olefins in aqueous media by using late transition metal catalysts. This has opened a new set of opportunities to produce simple and composite latex particles based on ethylene and its olefinic derivatives. Here we report some of our experience in creating water-based latices from the strained cyclic olefin, norbornene. This has been done as ab initio batch emulsion polymerizations using two different allylpalladium catalysts and a lithium-based activator as substitutes for the free radical initiator in standard emulsion polymerization. Such experiments produce small latex particles (ca. 50 nm) and can be burdened with large amounts of coagulum. In studying the effects of catalyst levels, ionic strength, and temperature on the reaction rates, conversion levels, and particle size, we have determined that the coagulum is produced by the migration of the catalyst and activator to the emulsified monomer droplets, producing large agglomerates of ∼10 μm polymer particles. After separating out the coagulum, the latices are stable for over a year. It has also become clear that in the aqueous environment the lithium activator is not necessary to promote emulsion polymerization and that without it we eliminate the coagulum. Apparently, the surfactant (in our case SDS) works as a weakly coordinating anion with the Pd catalyst. This work has shown that Pd catalysts can tolerate direct injection into the water.

Introduction and Background

During the past decade, it has been demonstrated[1−10] that late transition metal catalysts are capable of producing some aqueous-based latices of polyolefins and their copolymers with a few vinyl monomers. The use of such latices as aqueous-based coatings with low VOC offers numerous possible advantages over free radically derived latices including low-cost monomers, well-defined polymer architecture, new ranges of mechanical properties, inherent UV resistance, etc. This opportunity has led us to begin a research program based upon the catalytic emulsion polymerization (Cat EP) of polyolefins with the objective of elucidating the independent and combined mechanisms of polymerization reactions and polymer particle nucleation and growth. In those efforts, we have tried to compare and contrast our findings and ideas to those inherent to traditional free radical emulsion polymerizations (FR EP).

The olefins of interest are α-olefins, such as ethylene, and strained-cyclic olefins, such as norbornene. Polyethylene has a low glass transition temperature, T_g, of −120 °C, whereas polynorbornene has an extraordinarily high $T_g \sim 300$ °C.[11] Copolymerizing these two monomers would allow the production of a large range of T_g's as well as obtaining highly durable and chemically resistance polymers. The ethylene homopolymer is crystalline and thus will not film-form when cast from a water-based latex. Copolymerization is likely to break the crystallinity of polyethylene and allow easy tailoring of the T_g for film-forming polymers. Additionally, there is a family of norbornenes, such as acetyl, butyl, decyl, etc., in which the substituents decrease the T_g of the polymer. This offers many opportunities to make latices with interesting and useful properties.

The mechanism of particle nucleation in FR EP is well-known to occur via micellar or homogeneous nucleation. The oligomers are formed in the water phase and enter either a micelle or precipitate. Once particles are formed, there are three places for polymerization to occur: water phase, particle surface, and inside the particle. Particle size is controllable by the temperature, the amounts of surfactant and initiator, and the amount of monomer added to the reactor. Once particles are formed, the resulting monomer will polymerize within those particles, barring the existence of micelles. The molecular weight increases through propagation and is stopped through chain transfer and termination reactions. In contrast, Cat EP produces active polymer chains that cannot terminate with another polymer chain like FR EP can, but rather the growing chains can be stopped through chain transfer reactions or deactivation of the catalyst. These contrasting mechanisms may result in differences in the mechanisms of particle nucleation and growth and molecular weight development between Cat and FR EP.

It has been shown that norbornene can be polymerized in *solution* with Ni- and Pd-based catalysts through vinyl polymerization in the temperature range of 25−75 °C.[12−16] The molecular weights reported were between 400 and 300 000 g/mol. Monomer conversions ranged from as low as 20% to as high as 100%. Only a few authors have polymerized norbornene or substituted norbornene monomers in aqueous based emulsions. Puech et al.[17] 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.[18] reported the polymerization of butylnorbornene in aqueous media. They used $[(\eta^3\text{-allyl})Pd(Cl)]_2$ catalyst precursor, $P(m\text{-}C_6H_4SO_3Na)_3$ ligand, and $Li[B(C_6F_5)_4{\cdot}2.5Et_2O$ (LiFABA) activator for the polymerization and obtained 89% conversion at 65 °C over a period of 4 h. The M_w of the polymer was 1.03 million, and the M_n was 384 000. Lipian claims that high catalyst activity was obtained

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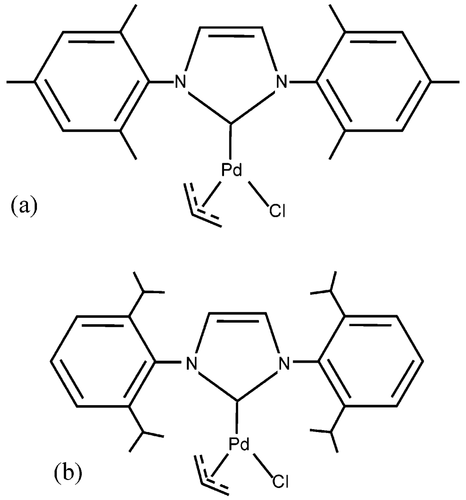

Figure 1. Structure of catalysts (a) TMP and (b) DPP.

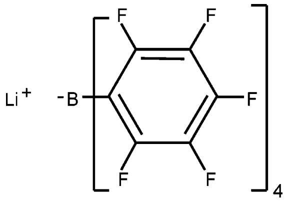

Figure 2. Structure of the activator LiFABA.

Table 1. Standard Polynorbornene Polymerization Recipes

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

with coordination of a phosphine to a cationic palladium center in the presence of the weakly coordinating FABA anion. Chemtob et al.[19] used the same catalysts, ligands, and activators as Lipian as well as a PCy_3 ligand to polymerize norbornene via miniemulsion with hexadecane as a costabilizer. Chemtob obtained 100% conversion but could not measure the molecular weight of the polymer because it would not dissolve in any of the solvents they tried. In one experiment, they omitted hexadecane, and the conversion still was 100% but the particle size was greater than 1 μm. The amount of coagulum was more than 20 wt %.

The goal of the present article is to assess the possibility of producing stable polynorbornene latices with certain allylpalladium catalysts and to do so under conditions common to FR EP. Using ab initio batch emulsion polymerization conditions, we have studied the effect of Pd catalyst structure, the use of a lithium-based activator, and the influence of catalyst, temperature, surfactant, and ionic strength levels. Where possible, we comment on the apparent site of polymerization and the formation of the latex particles.

Experimental Section

The experiments were designed to be similar to typical free radical, batch emulsion polymerizations. Water, surfactant, and monomer were initially charged to the reactor. The catalyst and activator take the place of the normal free radical initiator. More care was taken to eliminate the oxygen from this system because metal catalysts, especially palladium, are quite sensitive to oxygen. The water solubilities of norbornene and styrene at 25 °C are similar: 130 and 310 mg of monomer/L of water, respectively.[11] The melting point of norbornene is 45 °C; thus, all of the polymerizations were run at 50 °C or above, and the reactions were carried out at ambient pressure.

Materials. Norbornene (99%, Aldrich) was used as received. Allylchloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] palladium (97%, Strem Chemical) (henceforth referred to as DPP) and allylchloro[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] palladium (Rohm & Haas) (henceforth referred to as TMP) were the catalysts and also used as received. The structures of catalysts are shown in Figure 1. Lithium tetrakis(pentafluorophenyl)borate (LiFABA) (Boulder Scientific) was the activator and 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 glovebox to ensure stability. Sodium dodecyl sulfate (99%, Alfa Aesar) was used as received, and 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. Distilled 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. SDS was 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 temperature, typically 60 °C. 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 then transferred out of the glovebox. The catalyst solution was injected into the reactor followed by the activator solution. After the reaction 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. Solution polymerizations were also carried out by following the same procedure as above but removing the SDS and replacing the water with cyclohexane.

Latex Characterization. Latex conversion was measured gravimetrically after evaporating the volatile compounds in an air convection oven at 60 °C. The total coagulum level was determined from the amount of polymer left in the reactor after removal of the latex (i.e., wall scale) and that separated by filtration through cheesecloth. The overall conversion was calculated as the sum of the latex conversion and the coagulum conversion. Particle size distributions of the final latices 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. Reaction rates were observed by sampling the latex as a function of time.

Results and Discussion

While the bulk of our experiments were carried out in latex form, we also used the catalysts and activator in solution polymerization to judge the inherent activity of the catalysts. The discussion below begins with this aspect of the work.

Solution Polymerization. Table 1 shows the recipe for these experiments conducted at 60 °C and for a duration of 2 h. For the TMP catalyst system an optically clear and continuously increasing viscous solution was produced during the first hour. During the second hour, the solution turned slightly opaque,

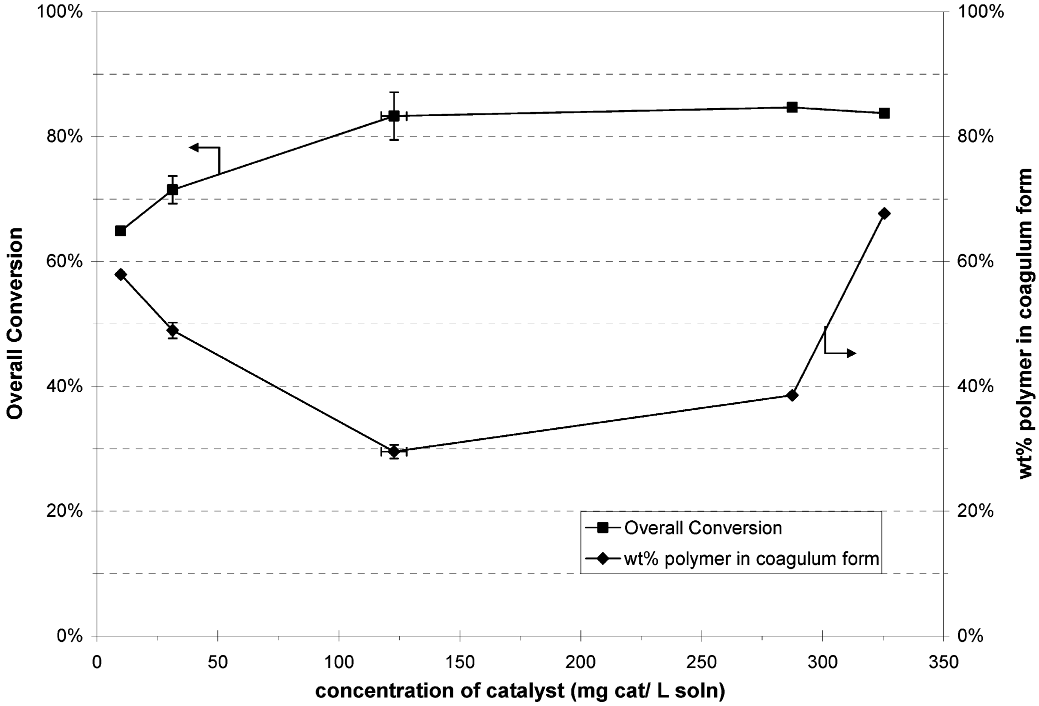

Figure 3. Overall polymer conversion vs catalyst concentration of norbornene polymerization at 60 °C with DPP catalyst.

Table 2. Oxygen Sensitivity of Norbornene Emulsion Polymerization

experiment no.	wt % solids theoretical	wt % polymer in coagulum form	% total conversion (latex + coag)	comments	
DEC2-60	5.26	49.8	73.0	thorough O_2 purging	DPP catalyst
DEC2-85	5.13	48.0	69.9	thorough O_2 purging	DPP catalyst
DEC2-92	5.04	33.8	67.2	moderate O_2 purging	DPP catalyst
DEC2-96	4.98	24.3	70.1	moderate O_2 purging	DPP catalyst
DEC2-37	5.73	29.5	71.8	thorough O_2 purging	TMP catalyst
DEC2-95	5.09	30.6	67.5	moderate O_2 purging	TMP catalyst
DEC2-97	4.93	45.8	67.1	moderate O_2 purging	TMP catalyst

indicating that some of the polymer had precipitated out of solution. The final conversion of monomer to polymer was only 60%. The DPP catalyst system resulted in a continuously precipitating polymerization process creating a completely gelatinous mass within the reactor while reaching 100% conversion. While the reaction rates were not measured directly, the visual aspects of the reactor contents indicated that the polymerization continued for much of the 2 h period. This set of experiments was our first indication that the polymer microstructure produced by the two different catalysts might be different enough to have contrasting solution properties.

The above experiments were repeated without the addition of activator, and as expected, no polymerization reactions occurred. This is to be contrasted with the results described in the next section.

Emulsion Polymerization. Our goal in this portion of the work was to contrast ab initio Cat EP to that using the standard FR EP process, albeit for a very different type of monomer. As such, we wanted to keep the sequence of addition of materials to the reactor the same and to study the effects of catalyst level, temperature, ionic strength, and surfactant level (and type) on the resultant latex characteristics. The following discussion is related to the results obtained for the first three variables. We will report a large study on the effect of surfactant type and level in a subsequent communication.

Catalyst and Surfactant Levels Used for Base Conditions. Both of the catalysts are activated by the removal of the chloride ion to form a vacant site. The LiFABA activator is used to abstract the chlorine as well as to leave the weakly coordinating FABA anion to associate with the palladium. Palladium has four bonds, and the allyl group associates with two of them. Both the catalyst and the activator are soluble in water. The catalyst and activator concentrations were designed to yield a molecular weight of ~750 000 g/mol, assuming there would be one catalyst molecule per polymer chain (i.e., no chain transfer). This resulted in a catalyst concentration of 32 mg of catalyst/L of water (6.7×10^{-5} M) for a 5% polymer solids latex. The molar ratio of palladium to lithium was normally 1:1, but we also performed experiments with no activator.

We chose to use sodium dodecyl sulfate (SDS) as the surfactant in this portion of the study and to add it at the level of 2.5 g/L of water. At 60 °C, this represents a surfactant concentration just slightly below the critical micelle concentration. We recognized that this would not enhance micellar nucleation of particles (if such a mechanism exits for Cat EP). In addition, we performed all of the experiments in the batch mode of operation.

One of our initial concerns was the potential high sensitivity of the catalysts to degradation by oxygen. In standard FR EP, we are careful to exclude oxygen by purging the reactor after water addition with standard grade nitrogen gas and usually remove oxygen from the water prior to adding it into the reactor. No other materials are deoxygenated prior to adding them to the reactor, but we keep a slow flow of nitrogen to the reactor throughout the reaction. In our initial catalyst experiments, we swept the empty reactor with argon, added deoxygenated water to the reactor from a Schlenk flask using argon, purged the norbornene/acetone solution with argon, and added it in the same manner as the water. We prepared the catalyst and activator solutions in a glovebox and injected them into the reactor. In contrast, we conducted additional separate experiments with both catalysts in which we used standard grade nitrogen gas and followed the procedure noted above for the "standard" FR EP, but maintained the injection of the catalysts and activator to the reactor. The results for these contrasting experiments are displayed in Table 2. It is seen that the extra care to exclude oxygen did not significantly affect the overall conversion levels, and the coagulum levels (a significant problem for many of the reactions described in this paper) showed no clear trend. Thus, it appears that the usual oxygen purging precautions employed in emulsion polymerization might also be applicable to such reactions using the catalysts of Figure 1. Nonetheless, we conducted most of the experiments reported below under the more stringent conditions.

Experiments with Variations in Catalyst/Activator Levels. The DPP catalyst concentration was varied to determine whether the polymer conversion, the latex stability, and the polymer molecular weight were affected by the amount of catalyst. The activator was also varied with the catalyst to keep with the molar ratio of palladium to lithium 1:1. For this series of experiments, the conversion and amount of coagulum are shown as a function of catalyst concentration in Figure 3. The conversion and coagulum data were quite reproducible. The overall conversion appears to increase somewhat with catalyst level until a concentration of about 120 mg of catalyst/L. Continued catalyst concentration increases showed no further improvement in conversion level. In addition, as the conversion increased, the amount of coagulum decreased markedly, and the minimum amount of coagulum corresponded to the maximum conversion at 120 mg of catalyst/L. The coagulum level markedly increased at a catalyst concentration of 325 mg/L. Although the catalyst and activator are both ionic, the combined ionic strength of the catalyst and activator is only 1.5×10^{-3} M. This ionic strength would have a negligible effect on colloidal stability in normal (i.e., free radical) styrene or acrylate latices. While the data suggest that there is an optimum range of catalyst concentrations to minimize coagulum formation, we did not expect such a result and cannot at this time offer a useful explanation.

The T_g of polynorbornene is high (~300 °C),[12] and with the reaction temperature at 60 °C, the Fox equation suggests that the highest conversion that might be attained before the glass effect prevents further polymerization is ~70%. However, at high catalyst concentrations, the computed limiting conversion of 70% is surpassed and 80% conversion is experimentally attained. Despite this disparity, we think that it is very likely that a lack of mobility of the polymer chain connected to the catalyst and/or very low diffusivity of the residual monomer causes incomplete conversion at 60 °C.

In these experiments we expected the polymer molecular weight to decrease as the catalyst concentration was increased. Polynorbornene did not dissolve in several solvents, even when produced at high catalyst concentrations. Others have also noted that polynorbornene does not dissolve in a number of solvents[15,19] while others note that it does.[12,13] The mentioned solvents (i.e., 1,2-dichlorobenzene, bromobenzene, cyclohexane) did not dissolve our polynorbornene, and since we were not able to get polynorbornene in solution, there are no molecular weight data to report at the present time.

The experiment with 32 mg of catalyst/L of water yielded almost 50% coagulum. The resulting latex was examined via SEM, and the results are shown in Figure 4a. The particle size contains mainly small particles around 30−80 nm and a few larger particles around 100−300 nm. Just as there were solubility differences between the two catalysts in solution polymerization, there is an apparent difference in particle size distributions they created. There are fewer large particles when the TMP catalyst is used as seen in Figure 4b.

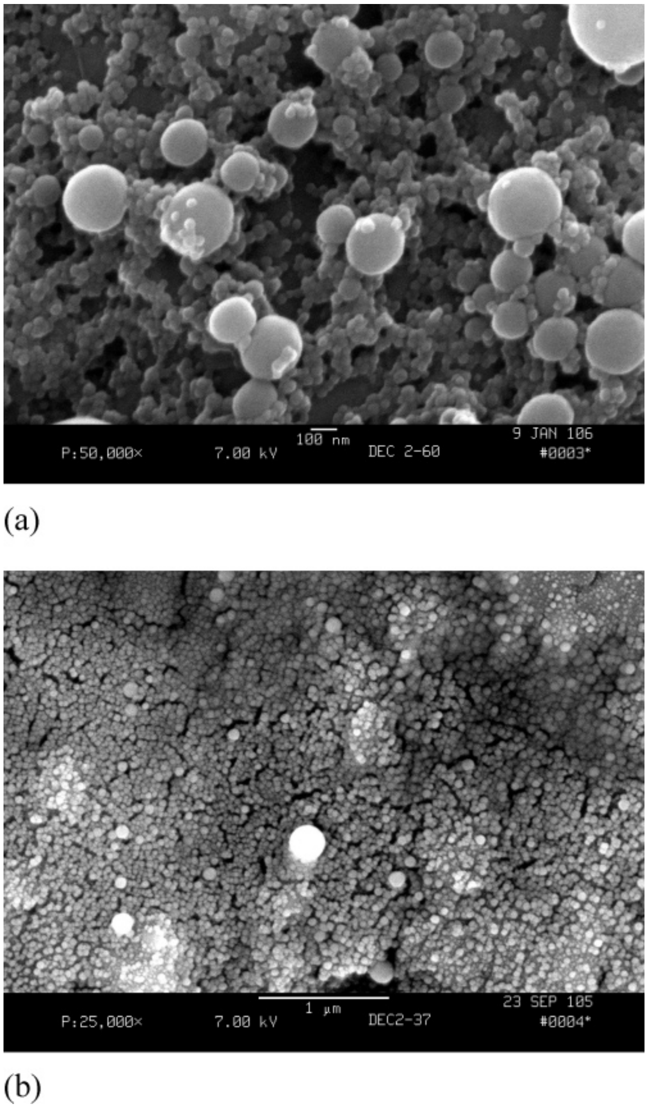

Figure 4. SEM image of polynorbornene particles made via (a) DPP catalyst scale bar equals 100 nm and (b) TMP catalyst scale bar equals 1000 nm, both with LiFABA activator.

Variations with Temperature. If the glass effect limits final conversion levels, then in the absence of competing effects the conversion should increase slightly at higher temperatures and decrease slightly at lower temperatures. Figure 5 is a plot of polymer conversion vs reaction temperature over the range of 50−80 °C for the standard polymerization recipe conditions listed in Table 1 using the DPP catalyst. The amount of coagulum drastically increased as the temperature increased; the instability occurred immediately after the activator was added to the reactor and worsened with time. Surprisingly, over the same temperature range, the overall conversion decreased slightly. While the effect on coagulum might be an expected result of decreased colloidal stability at higher temperatures, the apparent effect on the extent of reaction is mysterious.

Ionic Strength Effects. Both the catalyst and the activator are ionic species. The lithium from the activator is thought to abstract the chloride from the catalyst, leaving a cationic vacancy on the catalyst.[18] The activator anion is weakly coordinated with

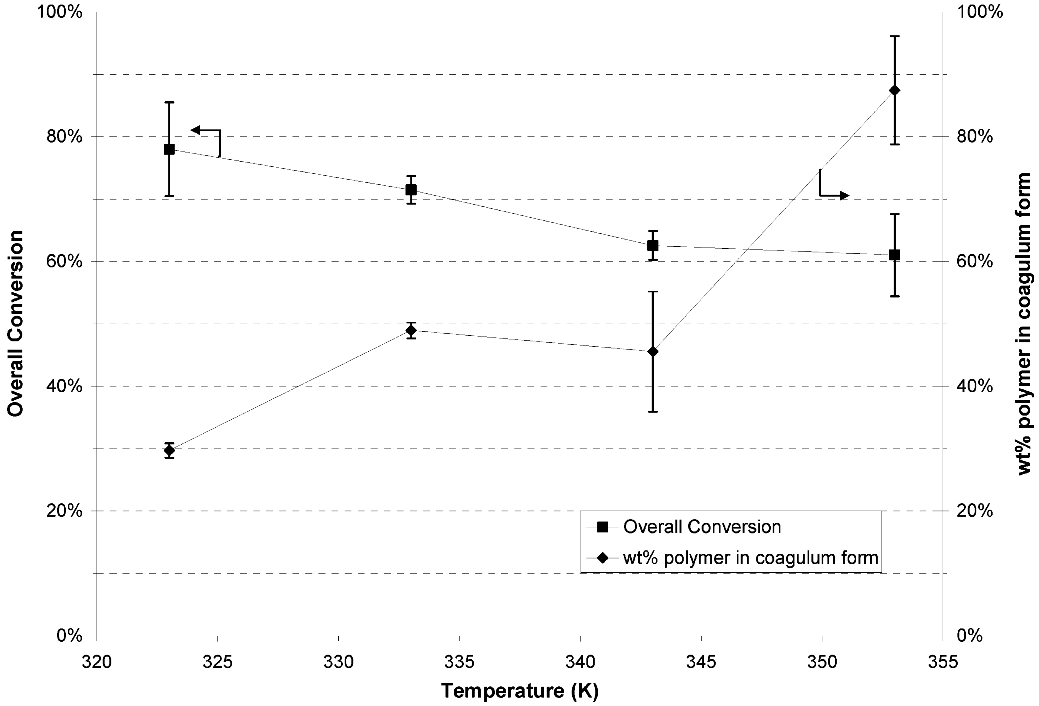

Figure 5. Overall polymer conversion vs reaction temperature of norbornene polymerization with DPP catalyst.

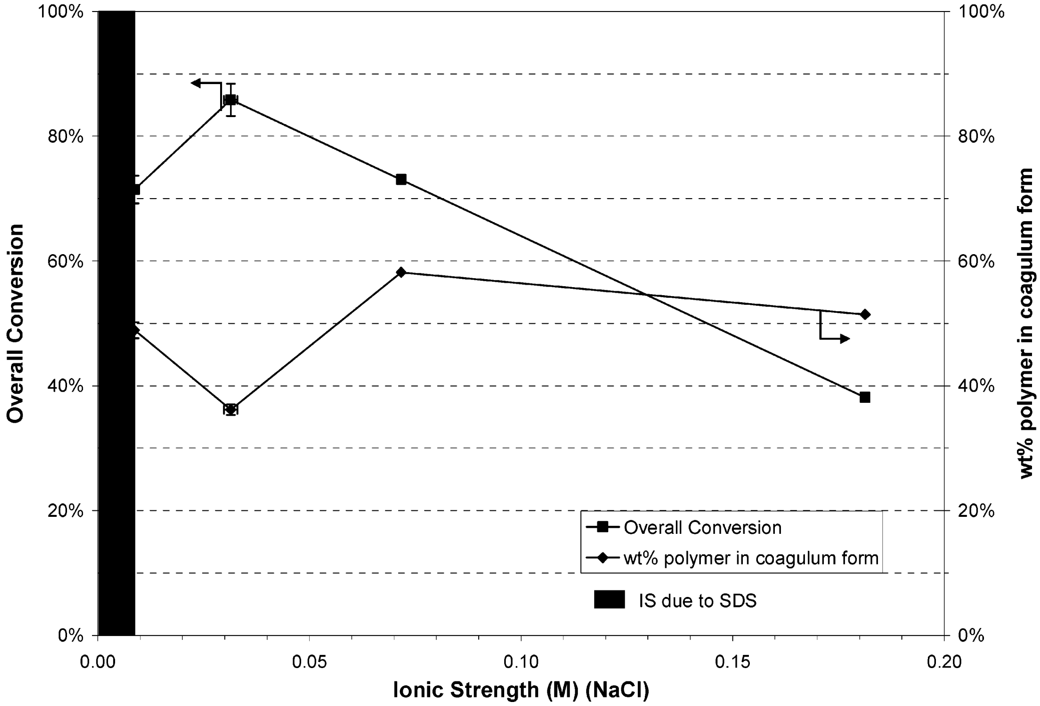

Figure 6. Overall polymer conversion vs ionic strength of norbornene polymerization at 60 °C with DPP catalyst.

the vacancy and is the site of polymerization. If the vacancy becomes too strongly coordinated, monomer will not easily access the vacant site and polymerization will be hindered or prevented. In this sense, we wondered whether the overall ionic strength of the aqueous phase would affect the catalytic activity. Monovalent buffers, such as sodium bicarbonate, are frequently used in FR EP. When there are too many ions in such emulsion polymerization systems, the polymer particles may destabilize and coagulate. In our study, we wanted to examine whether the catalyst efficacy and the amount of coagulum would be affected by variations in ionic strength (using NaCl). Figure 6 is a plot of overall conversion and coagulum level as a function of the total salt level and takes into consideration the ionic strength that is contributed by the SDS. The latter is depicted by the shaded box on the plot. The polymer conversion initially increased with ionic strength, from 72% at 0.01 M to 86% at 0.03 M. Under the same conditions the coagulum level surprisingly decreased from 49% to 36%. These data at 0.03 M ionic strength, while apparently reproducible, are most curious, especially for the conversion result. This increase in polymer conversion was unexpected because we thought that the increased chloride ion concentration might interfere with the catalyst site. When the ionic strength was increased further to 0.07 M, the overall conversion did decrease (back to the

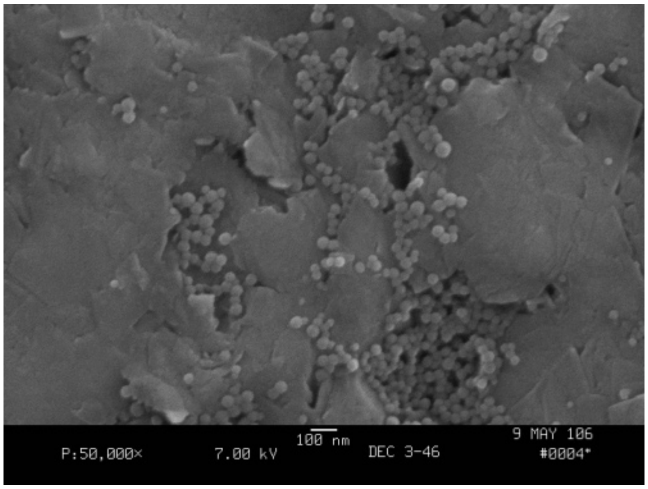

Figure 7. SEM image of polynorbornene particles using only TMP catalyst (no activator). Scale bar equals 100 nm.

original level of 72%) while the percentage of coagulum slightly increased. Going further, the overall conversion decreased drastically at an ionic strength of 0.18 M. Thus, it appears that there is eventually a significant deleterious effect of salt content on the polymer conversion. Interestingly, the coagulum level seemed to have been relatively unaffected by the addition of NaCl.

Experiments without Activator. If the lithium ion in the activator is thought to abstract the chlorine from the catalyst to produce an active site, could something else activate the catalyst as well? To probe this question, we were interested in seeing whether the catalyst could be activated and polymerization achieved without the LiFABA. A series of emulsion polymerization experiments were conducted with the same concentrations of TMP catalyst and surfactant of Table 1, but without the activator. As previously noted, when the catalyst and activator were used together, the overall conversion was 72% and the coagulum level was 30%. The latex particle size distribution included small particles (50−100 nm) as well as a few larger particles (200−500 nm), as seen in Figure 4b. In contrast, when no activator was used, an overall conversion of 66% was obtained. Thus, it appears that in this latex system it is not necessary to have the LiFABA activator to achieve reasonable polymerization. There was also a drastic decrease in the coagulum level to 4%, confirmed with replicate runs. This coagulum was markedly different in physical form than the coagulum formed with activator, as will be discussed later. The particle size distribution was limited to particles in the 30−70 nm diameter range, as seen in Figure 7. While we did not accurately measure the *rates* of polymerization, we did find that those with activator present were faster (2 h to completion) than those without activator (4 h to completion).

Given the above results in emulsion polymerization, we tried the same reaction in solution polymerization. We again used the recipe in Table 1, and in this case, we got no polymerization at all—a result that we fully expected. Going a bit further, we tried the latex recipe *without surfactant* but *with activator*. In this case, we achieved “normal” conversion of about 76%, but as might be expected, we obtained essentially complete coagulum (93% of the polymer in coagulum form). Leaving the activator and the surfactant out of the emulsion polymerization recipe (thus having just water, monomer, and catalyst) resulted in no polymerization. Taken together, these results offer clues as to the chemical reaction mechanisms involved in these experiments.

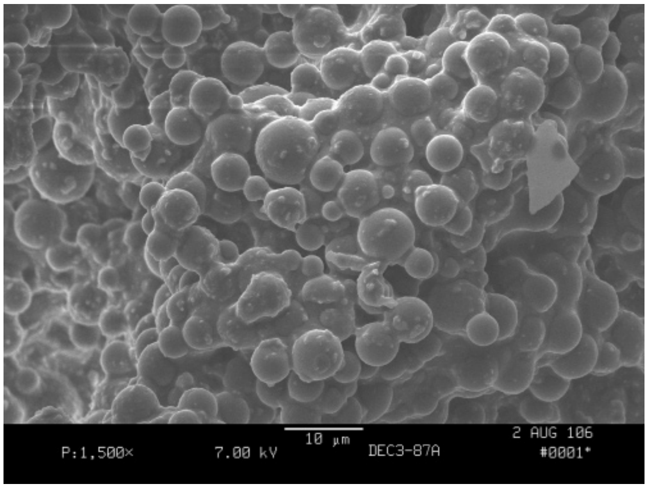

Figure 8. SEM image of the coagulum produced in the emulsion polymerization recipe of Table 1 with the TMP catalyst. Scale bar equals 10 μm.

Competitive Reactions during Catalytic Emulsion Polymerization of Norbornene. Clearly, the amount of coagulum formed in most of the reactions described above is far greater than any acceptable value and certainly well above that commonly experienced in FR-based emulsion polymerizations. This led us to investigate the nature of the coagulum formed in the Cat EP reactions via electron microscopy. A typical example is shown in the SEM image of Figure 8. It is very clear in this photo that the coagulum is composed of an agglomeration of polymer particles in the 10 μm diameter range. This is entirely consistent with the size of emulsified monomer droplets in normal batch FR EP that serve as reservoirs of monomer to supply the reactions that take place in the growing polymer particles (which are 2 orders of magnitude smaller than the emulsified droplets). Such coagulum forms to varying, but to very large, degrees in all of the Cat EP reactions utilizing activator described above. It does not form when we eliminate the LiFABA activator. Noting that we achieve roughly normal levels of overall conversion and the usual small latex particles without the use of activator, we now speculate that it is possible that the coagulum produced in systems utilizing the LiFABA activator results from the catalyst and activator migrating to the emulsified droplets and promoting rapid polymerization within them, much as in the solution polymerization reactions described earlier. Without activator present, we know that polymerization does not take place in solution polymerization or in the bulk polymerization of the norbornene. It appears to us that without the LiFABA activator the Cat EP takes place in the aqueous environment and creates latex particles in the 50 nm size range and that these particles are stabilized by the SDS surfactant in the normal fashion. Considering the Cat EP experiment without activator or SDS, which showed no polymer formation, it appears that the SDS surfactant may play a larger role than simply stabilizing particles. This leads us to further speculate that the allyl Pd catalyst is somehow activated by the SDS surfactant, perhaps acting as a weakly coordinating anion. We will comment more extensively on this in a future report.

Concluding Remarks

With the above thoughts, we reflect upon the overall results presented in this paper. It now appears to us that, in the standard latex formulations expressed in Table 1, we create a situation in which there is a significant competition for reaction in distinctly different regions of the overall reaction medium. For batch emulsion polymerization reactions there is always that period of time in which reaction can take place in the aqueous phase and also possibly in the emulsified monomer droplets. In FR EP, reaction in the large droplets is not important relative to the much faster reactions in the aqueous/micellar environment. However, in the Cat EP of norbornene that appears not to be the case. Here we think that when the LiFABA activator is present, reaction happens in both the aqueous environment and the large emulsified droplets—to an extent that nearly equal amounts of polynorbornene are produced in both places. When the activator is left out of the recipe, polymerization in the emulsified droplets is eliminated because catalytic reactions in those droplets requires the presence of the LiFABA activator in order to create a vacancy on the Pd to induce polymerization. It appears that the LiFABA activator is not required to promote polymerization in the water and surfactant environment. Clearly, there are likely to be other complications to understanding the mechanisms of polymerization and especially latex particle formation that have not yet been addressed here, but the ideas presented above appear to us to be a start on that task.

Acknowledgment. We are indebted to the scientific exchange of ideas with Brian Goodall and Lester McIntosh of Rohm and Haas and Jerome Claverie of UNH. We thank the Rohm and Haas Company for the supply of allyl Pd catalyst and greatly appreciate the financial assistance provided by the National Science Foundation via Grant Award CTS-0354825.

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MA070751M