Catalytic Emulsion Polymerization of Olefins: Ab-Initio Polymerization of a Family of Norbornene-Derived Monomers

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ABSTRACT: The use of late transition metal catalysts for the polymerization of olefins in aqueous media has created new opportunities to produce latex particles based on ethylene and its olefinic derivatives. In this work we report on the production of water-based latices from a variety of monomers based on the strained cyclic olefin, norbornene. These have been carried out as ab-initio batch emulsion polymerizations using allylpalladium catalysts and a lithium borate activator as well as sodium dodecyl sulfate surfactant. We find that the *n*-alkylnorbornenes can be polymerized in aqueous emulsion and that the mechanisms for latex particle formation are likely the same as that for norbornene monomer alone. The latex particles created are small, averaging about 45 nm in diameter. As in the case of norbornene, large amounts of coagulum can be formed if the catalyst and activator are allowed to reach the emulsified monomer droplets and effect polymerization in that location. As the substituents on the norbornene become larger and nonpolar, it is necessary to consider their effect on the water solubility of the monomers in order to analyze the experimental results in an effective manner. Our studies included butyl- and decylnorbornene, vinyl- and butenylnorbornene, and methanol−norbornene.

Introduction and Background

In two recent papers,[1,2] we have described some of our studies on the catalytic emulsion polymerization of norbornene. In particular, we used two forms of allylpalladium chloride catalysts and an activator, LiFABA, a fluorinated borate. The chemical structures of these compounds have been detailed elsewhere,[1,2] and they function by forming an ion pair. This activation is strong in organic media and quite weak in an aqueous phase. Nevertheless, water does not deactivate the catalysts as evidenced by the rapid reaction of norbornene when the monomer is simply dispersed in water without a surfactant and the catalyst and activator are added to the aqueous phase. It appears that the Pd catalyst and LiFABA activator can migrate through the water to polymerize the norbornene in the dispersed droplets of about 10 μm in diameter.[1] This produces massive coagulum formation. When surfactants are added, as in standard emulsion polymerization, several different things happen depending on the type of surfactant used. In particular, the alkyl sulfate surfactants can act as weakly coordinating anions and activate the catalyst in the water so that small latex particles (~40 nm) are formed. Without the addition of LiFABA to the emulsion, conversion of norbornene at 60 °C reaches 70+% and little or no coagulum is formed.[2] When the LiFABA activator and the alkyl sulfate surfactants are present at the same time, there appears to be a competition for the activation of the catalyst by the LiFABA and by the surfactant. Such conditions produce variable ratios of coagulum to stable latex particles depending on the particular surfactant used, with the sodium hexadecyl sulfate surfactant resulting in almost no coagulum.

In the above manner, we have investigated the effects of catalyst level, temperature, ionic strength, and surfactant type on the production of polynorbornene latices.[1,2] We now extend our report to include a variety of substituted norbornene monomers. These studies were carried out in both organic solutions and in aqueous emulsions using the same catalysts and activators (LiFABA and surfactants) as described above. The monomers were all derivatives of norbornene with substitutions at the fifth position and included the butyl and decylalkyl derivatives, the vinyl and butenyl derivatives, and the methanol derivative, whose structures are shown later in Table 3. The reactivity of a number of these monomers has been studied by others in solution[3–7] as well as emulsion[7,8] polymerization using other Pd-based catalysts and then compared to the reactivity of norbornene. Because these monomers are commonly prepared via Diels–Alder reactions, such functionalized norbornenes consist of both *exo* and *endo* isomers.[9] Often the ratio of the *exo* to *endo* isomers is in the range of 25:75,[3] and it has been shown[3,9,10] that the *endo* form is moderately to substantially less reactive that the *exo* form. The purpose of our homopolymerization studies was also to compare the reactivities obtained with these monomers to that of norbornene itself, but in this case using aqueous emulsion polymerization systems. In addition, we were interested in whether or not the same mechanisms of reaction and latex particle formation were apparent for these substituted norbornene monomers as those found for norbornene.

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 solubility of norbornene and styrene at 25 °C are similar.[11] The melting point of norbornene is 45 °C; thus, all of the polymerizations were run at 60 °C, and the reactions were carried out at ambient pressure. The corresponding water solubilities of the other norbornene-based monomers are not known but can be rationalized on the basis of the polar or nonpolar natures of the substituted groups. All of the derivatized norbornene monomers were liquid at room temperature.

Materials. Norbornene (99%, Aldrich), 5-butyl-2-norbornene (Rohm and Haas), 5-decyl-2-norbornene (Promerus), 5-vinyl-2-norbornene (95%, Sigma Aldrich), 5-butenyl-2-norbornene, and 5-methanol-2-norbornene (95%, City Chemical) were used as received. Allylchloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]palladium (97%, Strem Chemical) (henceforth referred to

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Table 1. Standard Polynorbornene Polymerization Recipes

	polymerization recipes	
	emulsion	solution
DI water	95 g	
cyclohexane		95 g
monomer	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

as DPP) and allylchloro[1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]palladium (Rohm and Haas) (henceforth referred to as TMP) were the catalysts and also used as received. The structures of catalysts have been shown previously.[1,2] Lithium tetrakis(pentafluorophenyl)borate (LiFABA) (Boulder Scientific) was the activator and used as received. The structure has also been detailed elsewhere.[1,2] 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 (NB) 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. We note here that we carried out NB reactions without the acetone and found no effects. SDS was also dissolved in water to ease the transfer into the reactor. The other norbornene-derived monomers did not require any acetone to aid in transfer. Both solutions (monomer and surfactant) 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 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. The emulsion polymerizations reacted for 3 h, and the solution polymerizations reacted for 2 h (see our previous comments on polymerization kinetics[1]). After the reaction was complete, the polymer latex was filtered through eight layers of cheesecloth to separate coagulum present in the latex. A standard polymerization 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.

The SDS concentrations used in the emulsion polymerization experiments described here are slightly lower than the cmc at the reaction temperature. This avoided having micelles present for this particular study. Further discussion of the surfactant effect and level can be found in earlier work.[1,2]

Latex Characterization. Monomer conversion was measured gravimetrically after evaporating the volatile compounds in a conventional 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) as well as by scanning electron microscopy (SEM) (Amray 3300FE) images. The SEM samples (on polished carbon planchettes) were sputter-coated with ~50 Å of platinum. Molecular weight was determined using gel permeation chromatography (GPC) (Waters components with three HMW6E and one HMW7 Styragel column connected in series) and calibrated using polystyrene standards.

Results and Discussion

Solution Polymerization. Solution polymerizations were performed with three of the monomers to gauge their activity with the catalyst and what we presumed would be their maximum conversion levels. The reactions were performed in cyclohexane at 60 °C for a period of 2 h. The three monomers were norbornene (NB), 5-butyl-2-norbornene (NB-4), and 5-decyl-2-norbornene (NB-10). The results of the polymerizations of these monomers can be found in Table 2. Both TMP and DPP catalysts were used and the DPP catalyst with NB resulted in a continuously precipitating polymer that created a gelatinous mass within the reactor while reaching 100% conversion. The TMP catalyst with NB resulted in a viscous, opaque solution that only reached 57% conversion in the 2 h of reaction. The visual differences between the resulting solutions, as well as the polymer conversion, indicates that there may be a difference in polymer microstructure dependent on the catalyst used. Neither NB-4 nor NB-10 exhibited such dramatic visual or conversional differences between catalysts.

The polynorbornene formed using the DPP catalyst was a gelatinous mass which would not dissolve in chloroform. The polymer formed with the TMP catalyst dissolved in chloroform and the molecular weight determined by GPC was 555 000 g/mol. The expected molecular weight of the polymer, assuming one Pd atom per polymer chain and complete monomer conversion, is 750 000 g/mol. The experimental molecular weight is slightly lower than the theoretical, potentially indicating that all of the catalyst is not active. At the present time, molecular weight data range from 250 000 to 500 000 g/mol, with some polymers not soluble in chloroform. We are not aware of studies with these monomers and catalyst which suggest specific chain-stopping reactions.

NB-4 only reached low conversions (7–8%) with either catalyst, and those conversions were sensitive to the concentration of catalyst and activator. Raising the catalyst and activator concentrations by a factor of 4 increased the polymer conversion to 34 and 39% for the DPP and TMP catalysts, respectively. Even with this higher catalyst and activator concentration, the NB-4 conversion was still much lower than that for NB solution polymerization. A recent patent[12] describes the use of the TMP catalyst with LiFABA activator to polymerize NB-4 in toluene. With a catalyst concentration lower than the "standard" used in our studies (0.51 μmol/g NB compared to our "standard" 1.34 μmol/g NB, as shown in Table 1), the authors were able to achieve 91% conversion. Myagmarsuren et al.[3] and Funk et al.[10] found that NB-4 had a lower reactivity than NB due to the steric bulk of the butyl chain. Our results for NB-4 reactivity are significantly lower than that of Myagmarsuren and Funk and also much less than the reactivity of NB. We will discuss more about the NB-4 conversion characteristics in the emulsion polymerization section of this paper.

NB-10 showed slight final conversion dependence with catalyst type, although reasonably high conversions were achieved with both catalysts. The polymer formed using TMP did not dissolve in chloroform, but the polymer formed with DPP catalyst did dissolve in chloroform. The theoretical molecular weight of P(NB-10) at 78% conversion was 550 000 g/mol, but the measured molecular weight was 267 000 g/mol. Strangely, we did not observe clear glass transition temperatures (T_g) of the NB, NB-4, or NB-10 polymers, even upon heating to 400 °C in the DSC. Overall, these solution polymerization results have shown that the allyl Pd catalyst—LiFABA activator pair has good activity for NB and NB-10 monomers and relatively much poorer activity for NB-4. The NB-10 shows a higher reactivity than expected, in contrast to Myagmarsuren,[3] who found that as the alkyl chain length of the substituent increased, the monomer reactivity continually decreased.

Table 2. Monomer Conversions and Observations from Solution Polymerizations of Various Monomers Using Either TMP or DPP Catalyst with LiFABA Activator in Cyclohexane at 60 °C

expt no.	wt % solids theoretical	% total conversion	monomer	catalyst	observations	M_w (g/mol)	M_n (g/mol)	M_w/M_n
DEC3-25	5.08	100.0	NB	DPP	precipitated	insoluble in chloroform		
DEC3-26	5.21	56.8	NB	TMP	opaque	554523	373008	1.49
DEC3-27	5.08	7.2	NB-4	DPP	clear	284651	119867	2.37
DEC3-28	4.94	8.3	NB-4	TMP	clear	408980	244388	1.67
DEC3-29	5.07	33.6	NB-4	4×DPP	clear			
DEC3-30	5.29	38.8	NB-4	4×TMP	clear	insoluble in chloroform		
DEC3-23	5.06	78.2	NB-10	DPP	clear	267393	134223	1.99
DEC3-24	5.15	98.6	NB-10	TMP	clear	insoluble in chloroform		

Emulsion Polymerization. In this section of the paper we divide our discussions into those for the different classes of substituted norbornene monomers. As we do so, we note that in addition to the chemical structure differences between the monomers, there will also likely be differences in their water solubilities, something that is always important in emulsion polymerization. Indeed, as one looks at the various reaction pathways for norbornene catalytic emulsion polymerization with the surfactant acting as a weakly coordinating anion, as shown in Figure 1, it is apparent that the production of latex particles via pathways 2 and 3 (but predominantly pathway 3) will gain or lose importance as the water solubility of the monomer is higher or lower, respectively. As we indicated previously,[2] alkyl sulfate anions such as SDS interact favorably with the TMP catalyst to create small latex particles (via pathway 3) and establish a rate of polymerization that is quite competitive to that of the catalyst and LiFABA activator migrating to the emulsified droplets and producing large amounts of coagulum (agglomerates of ~10 μm polymer particles). We speculate that the TMP catalyst and the SDS form ion pairs to effect polymerization[2] and that latex particles are formed via a homogeneous nucleation process. Since norbornene has a water solubility of about that for styrene,[11] adding substituents to the norbornene monomer at the 5 position is very likely to decrease their water solubility. Octanol to water partition coefficients for the monomers were predicted using "property prediction software" from ChemSilico.[13] These results allowed us to rank the monomers by order of most to least water-soluble. As such we have MeOH−NB > NB > vinyl-NB > butenyl-NB > NB-4 > NB-10, as might be expected from the polar or nonpolar nature of the sustituents.

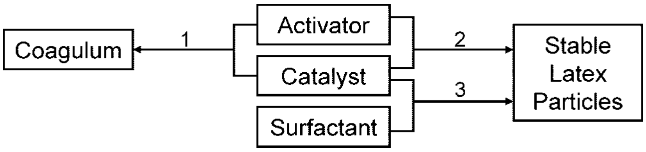
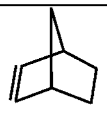
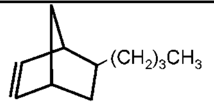
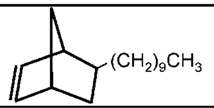
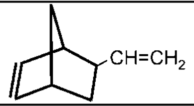
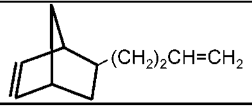
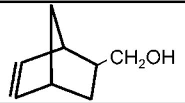


Figure 1. Proposed reaction pathways for norbornene polymerization using TMP catalyst and SDS, with or without LiFABA activator. Pathway 1 involves migration of the catalyst and LiFABA through the water and into the large emulsified droplets. Pathway 2 involves the aqueous phase reaction between the catalyst and the LiFABA to create stable latex particles. Pathway 3 involves the aqueous phase interaction between the catalyst and the SDS to create stable latex particles. The rates of pathways 2 and 3 will be dependent upon the aqueous concentration of the monomer.

The experimental results for the emulsion polymerization of the substituted norbornene monomers are displayed in Table 3. The results for the NB-4 and NB-10 are compared to those for NB itself in Figure 2, where we have plotted the overall monomer conversions and percent of polymer in coagulum form

Table 3. Emulsion Polymerization of Various Norbornene Derived Monomers Using Either TMP or DPP Catalyst with LiFABA Activator at 60 °C

Experiment Number	wt% solids theoretical	wt% of polymer as coagulum	% total conversion	Monomer		Catalyst
DEC2-37	5.73%	29.50%	71.80%	NB		TMP
DEC2-60	5.26%	49.80%	73.00%	NB		DPP
DEC2-85	5.13%	48.00%	69.90%	NB		DPP
DEC2-99	5.70%	30.60%	79.70%	NB		4x DPP
DEC3-20	5.41%	29.40%	82.80%	NB		4x DPP
DEC2-39	5.32%	55.50%	30.10%	NB-4		TMP
DEC2-81	4.95%	33.90%	39.90%	NB-4		TMP
DEC2-43	4.90%	44.20%	80.90%	NB-4		4x TMP
DEC3-44	5.11%	99.10%	93.40%	NB-10		TMP
DEC2-19	5.82%	88.90%	7.40%	Vinyl-NB		TMP
DEC2-20	5.42%	74.60%	9.60%	Vinyl-NB		TMP
DEC2-45	4.72%	22.10%	14.70%	Butenyl-NB		4x TMP
DEC2-41	5.24%	88.50%	48.80%	MeOH-NB		TMP

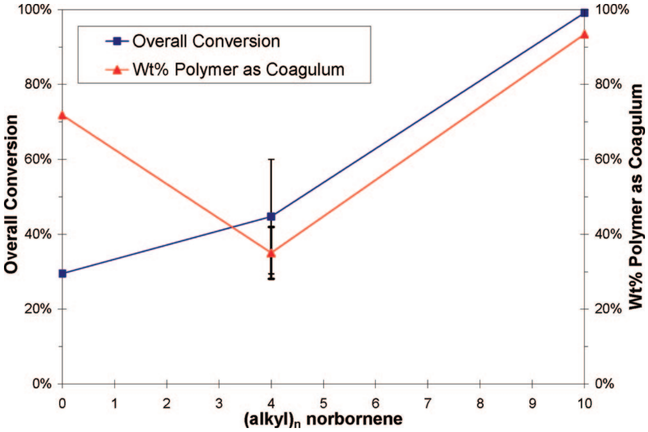


Figure 2. Overall conversion and amount of coagulum as a function of 5-alkyl-2-norbornene chain length in emulsion polymerization at 60 °C with TMP catalyst.

against the number of carbons in the substituted alkyl chain. When the final conversion (at the end of the 3 h reaction) is less than 100%, we use the conversion level as an indication of the reactivity of the monomer with the catalyst and activator. As expected from the work of others with Pd-catalyzed norbornene monomers,[3,10] NB-4 is substantially less reactive than NB, in this case only achieving half the conversion of NB in the same reaction time at the same catalyst levels. This is consistent with our solution polymerization results as discussed above, but the extent of the comparative decrease is much larger than that which others have reported in solution polymerization. Perhaps this is due to our particular catalyst system or an unusually high level of the *endo* isomer in the monomer. The latex particle sizes achieved were very nearly the same (45 nm via Nanotrac) for the two monomers, and SEM photos are shown in Figure 4a,b.

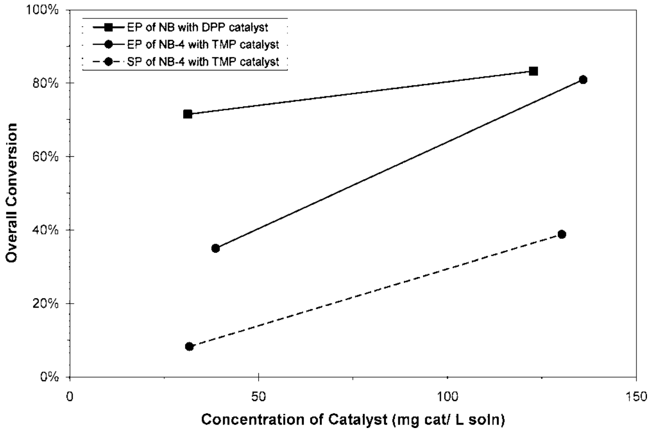
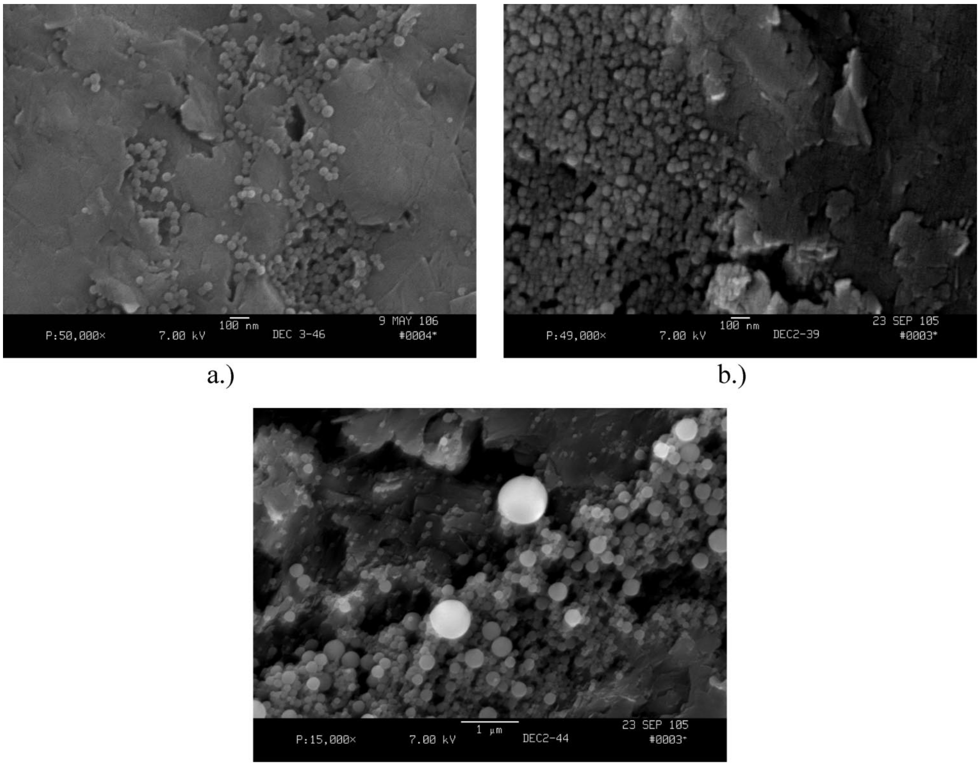


Figure 4. Overall conversion of NB and NB-4 in emulsion (EP) or solution (SP) as a function of either TMP or DPP catalyst concentration.

The polymerization of NB-10 obtained nearly full conversion in the emulsion, consistent with that found in our solution polymerization experiment. These results are quite in contrast to those found by others[3,10] in that the apparent reactivity is higher than norbornene itself and very much greater than that for the butyl derivative. Given the likely water insolubility of the NB-10, is not surprising that there was only a very small portion of the polymer formed as latex particles. However, those that were formed were somewhat larger than those from NB and NB-4, as noted in the SEM photo in Figure 3c. What is perhaps the most distinctive about the data for the NB-10 is that nearly all of the polymer formed was coagulum. As noted in Figure 1, we believe that this would be due to the majority of reaction taking place along pathway 1. In fact, as we view all of the coagulum data in Table 3 and Figure 2, we see that the ratio of the amount of coagulum to latex particle polymer

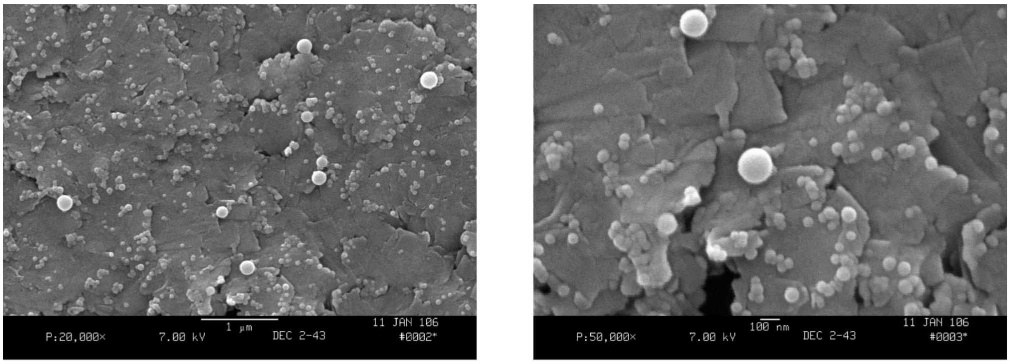


a.)

b.)

c.)

Figure 3. SEM images of (a) NB, (b) NB-4, and (c) NB-10 latex particles produced in aqueous emulsion using TMP catalyst. Particles were dried from latex on polished carbon planchettes, accounting for the uneven surfaces in the images.



a.) b.)

Figure 5. SEM images of P(NB-4) latex particles produced at 4 times the standard TMP catalyst concentration. Scale bars are different in (a) and (b). Particles were dried from latex on polished carbon planchettes, accounting for the uneven surfaces in the images.

increases as the alkyl chain length becomes higher. We speculate that this is due to the relative water solubilities of the monomers, which should decrease substantially as one moves from NB to NB-4 to NB-10, and its impact on reducing the importance of reaction pathways 2 and 3 (perhaps homogeneous nucleation of latex particles). As these pathways are adversely affected by the water solubility of the monomers, pathway 1 is unaffected.

Returning to the unexpectedly low conversion levels achieved with the NB-4 in both solution and emulsion polymerizations, we determined the effect of increasing the TMP catalyst (and associated LiFABA) concentrations, while conducting the reactions at the same 60 °C. Figure 4 shows these results (albeit with only two data points for each set), and it is quite clear that major increases in reactivity were achieved in both systems. The response for NB in emulsion polymerization is also shown in Figure 4 for reference. Further, the data in Table 3 show that the relative amounts of coagulum polymer to latex particle polymer were unchanged as the catalyst level was increased 4-fold. It appears to us that the relative importance of the various reaction pathways shown in Figure 1 is unchanged as we add more catalyst and LiFABA activator. Since the SDS is present in great molar excess of the catalyst, its concentration did not have to be increased to allow pathway 3 to be impacted favorably by the increase in catalyst concentration. Alternatively, the LiFABA concentration had to be increased in the same proportion as the catalyst to have pathways 1 and 2 appropriately impacted. In this manner, it is possible to understand why the conversion levels were higher but the fraction of polymer formed as coagulum remained constant. In addition, we found that the particle size at the higher catalyst loading was similar to the standard catalyst loading particles of 52 nm (via Nanotrac) and shown as SEM photos in Figure 5a,b.

We were interested in experimenting with vinyl-substituted norbornenes as a means to obtain norbornene-type latices that contained pendant vinyl groups on the polymer chains. One can imagine that these latex particles might serve as seed particles for the creation of composite latex particles (perhaps with acrylics) and that the pendant double bonds might lead to the ability to form graft copolymers using free radical initiators. When we polymerized these monomers in emulsion (we did not perform comparative studies in solution), we found that the conversion level achieved for the 5-vinyl-2-norbornene (vinyl-NB) was only 8–9% in the 3 h reaction time. It seems the water solubility of this monomer should not be greatly lower than that for NB and thus that the suppression of the reactivity was likely due to the *endo* isomer retarding the polymerization rate. For the 5-butenyl-2-norbornene (butenyl-NB), we increased the catalyst and LiFABA concentrations by a factor of 4 in order to achieve high conversion, but only achieved 15%. Given the discussion in the literature about the suppression of reaction rates by the substituent groups on the norbornene ring, we had thought that the butenyl-NB might not retard the rate as much as the vinyl-NB due to the possibility of chelation via a six-membered ring in the latter and not in the former. At this point we cannot offer any further analysis of the results for these two monomers.

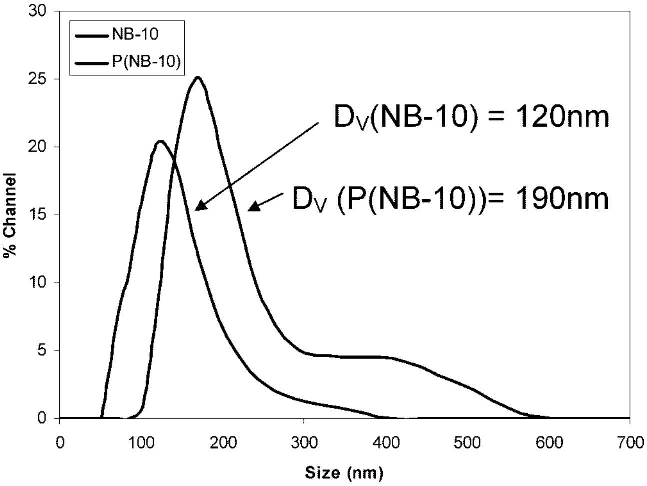


Figure 6. Nanotrac particle size results of sonified NB-10 monomer and the resulting P(NB-10) latex.

A last new monomer experiment was conducted with 5-methanol-2-norbornene (MeOH−NB) in an attempt to change the polar nature of the substituted group. Oxygen-containing side groups on the norbornene (e.g., carboxylic acid) are known to seriously degrade the reactivity of the monomer in solution polymerization,[9,10] and thus we expected a retardation in our emulsion polymerization rate with this monomer. Table 3 shows that we only achieved 48% conversion with this monomer. Puech et al.[4] polymerized MeOH−NB to 80% conversion using $PdCl_2(TPPTS)_2$ catalyst in water over a reaction time of 24 h. Perhaps an extension of our reaction time would have improved the conversion level. In contrast to the other monomers described in this paper, the 48% conversion figure is not nearly as poor as some of the others, being about two-thirds as active as NB. However, the vast majority of the polymer was produced as coagulum. Taken together with all of the results for the monomers shown in Table 3, those for MeOH−NB do not offer any significant clues as to the effect of monomer polarity on reactivity in these emulsion polymerizations.

Miniemulsion of Decylnorbornene. As we showed above, this very hydrophobic monomer could be polymerized to a high extent with catalyst and activator in aqueous emulsion; however, 99% of the polymer was formed as coagulum. To show that the polymer particles could be stabilized by SDS if they were smaller, NB-10 was miniemulsified with SDS to produce 120 nm droplets of monomer, and then catalyst and activator were added to the reactor. The resulting particles were all stable latex particles with a diameter of 190 nm, as seen in the particle size distribution curves in Figure 6. We did not add any compound to prevent Ostwald ripening so we might have experienced some particle size increase by this mechanism. The sonified NB-10 resulted in 96% conversion with none of the polymer as coagulum. The catalyst and activator were apparently able to migrate to the monomer droplets to effect polymerization in that location. New particles were not nucleated during this experiment, which shows that we had a "true" miniemulsion where the polymerization occurred in the monomer droplets. These results complement those noted earlier—the catalyst and activator easily migrate through the water to penetrate small (miniemulsified) or larger (normally emulsified) monomer droplets and promote reaction within them. The SDS appears to stabilize the 190 nm particles while it does not stabilize micron-sized polymer particles. This result is promising, and future work should include using miniemulsion for all of the monomers listed in Table 3.

Concluding Remarks

It is quite evident that substituted norbornene monomers have lower catalytic reaction rates than the parent norbornene, as shown previously by others in solution polymerization. Our results have further demonstrated that this is also true in emulsion polymerization when using a consistent Pd-based catalyst and activator system as one moves from solution to emulsion polymerization systems. In contrast to other studies, our results do not show a continual decrease in the reactivity of *n*-alkyl-substituted norbornenes over the range of 0–10 carbons in the chain. The reactivities of these alkyl norbornenes are affected by the catalyst concentration in both solution and emulsion systems, as might be expected. We speculate that the apparent mechanisms for latex particle formation for these substituted norbornene monomers is the perhaps the same as that for norbornene and that large amounts of coagulum can be formed when the catalyst and activator are allowed to migrate to the emulsified monomer droplets and effect polymerization in that location. Such large polymer particles are not stabilized by SDS. Alternatively, the very nonpolar decylnorbornene can be polymerized to form a colloidally stable latex at ca. 200 nm particle size with the same level of SDS by using the miniemulsion polymerization process.

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