Free-Radical Frontal Polymerization with a Microencapsulated Initiator: Characterization of Microcapsules and Their Effect on Pot Life, Front Velocity, and Mechanical Properties

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ABSTRACT: In this study, microcapsules containing a cumene hydroperoxide (CHP) core were produced by interfacial polymerization and tested in a variety of free-radical frontal polymerization systems. It was observed that the microcapsules could be used successfully in number of systems, and comparisons were made with typical frontal polymerization systems. The effect of encapsulation of CHP on the pot life was tested in a variety of systems, and it was observed that systems containing microcapsules underwent a dramatic increase in pot life, from hours to weeks in certain systems and from a few days to several weeks in other systems. Polymer samples that were produced from 1,6-hexanediol diacrylate (HDDA) systems with and without microcapsules were tested for modulus and toughness. It was observed that the use of CHP microcapsules resulted in an increase in the modulus and toughness (up to 2×) of polymer samples.

Introduction

In frontal polymerization, a monomer is converted into a polymer by a localized front of polymerization that propagates through the system, leaving behind polymer in its wake and polymerizing unreacted monomer in its path. The front, also known as the reaction zone, propagates through the coupling of thermal diffusion and Arrhenius kinetics. Frontal polymerization was discovered in 1972 by Chechilo et al. in their studies of systems consisting of methyl methacrylate monomer and benzoyl peroxide initiator.[1] The extensive work from Russia was reviewed by Davtyan et al.[2]

Pojman and co-workers performed an extensive study of the macrokinetics and dynamics of frontal polymerization, in which properties such as front velocity, conversion, and the effect of different system components were studied.[3−7] They recently studied frontal copolymerization.[8] Several different materials have been made by frontal polymerization, including thermochromic composites,[9] interpenetrating polymer networks (IPNs),[6] polymer-dispersed liquid crystal materials (PDLC's),[10] functionally gradient materials,[11−13] large composites,[14] and hydrogels.[15]

The vast majority of frontal polymerization systems that have been studied have been free-radical polymerization systems; however, frontal polymerization has been demonstrated in other types of systems as well. Begishev et al. studied frontal anionic polymerization of ϵ-caprolactam,[16,17] and epoxy chemistry has been used as well.[18−21] Mariani et al. demonstrated frontal ring-opening metathesis polymerization of dicyclopentadiene using Grubbs catalyst.[22] Fiori et al. produced polyacrylate−poly(dicyclopentadiene) networks frontally using methyl methacrylate and tri(ethylene glycol) dimethacrylate as acrylate components in the respective systems,[23] and Pojman et al. studied epoxy−acrylate binary systems.[24] Polyurethanes have recently been prepared frontally.[25−27] Frontal atom transfer radical polymerization has been achieved[28] as well as frontal polymerization with thiol−ene systems.[29] Recent work has been done using frontal polymerization to prepare microporous polymers,[30−32] polyurethane−nanosilica hybrid nanocomposites,[33] and segmented polyurethanes.[34] Vicini et al. developed a frontal polymerization method for the consolidation of stone.[35] Nason et al. recently investigated UV-induced frontal polymerization of (meth)acrylates.

The free-radical frontal polymerization of several different monomer/initiator systems has been reviewed in detail by Pojman et al.[5] and by Washington and Steinbock.[36] The velocity dependence on the initiator concentration has been studied for several systems[3,37,38] and follows a power function dependence on the initiator concentration. Three different classifications of monomers polymerizable by free-radical frontal polymerization were made.[5]

Fortenberry and Pojman studied frontal polymerization of acrylamide without solvent using powdered acrylamide and persulfate.[7] They found that the initial or "green" density of the systems affected the front velocity. Such behavior is quite normal for self-propagating high-temperature synthesis with inorganic components.[39−45]

Frontal polymerization is often not useful for application in real-world applications because the monomer/initiator systems can suffer from a limited pot life, meaning that over a period of time the systems will polymerize homogeneously before they can be used. This happens due to decomposition of the initiator into radicals while the system is stored and the reaction of these radicals with monomer molecules. We sought to address this issue by microencapsulating a free-radical initiator in order to separate it from the monomer and prevent any radicals formed from initiator decomposition from coming into contact and reacting with monomer molecules. A frontal polymerization system was made by microencapsulating cumene hydroperoxide and dispersing the capsules throughout a mixture of 1,6-hexanediol diacrylate (HDDA) and silica gel.[46] Because the initiator was sequestered from the monomer, it could not initiate polymerization until the capsule burst open upon heating. Frontal polymerization was achievable with the CHP microcapsules and also when cobalt naphthenate was dissolved in the monomer, where it could react with the CHP in a redox reaction to produce free radicals. Initial indications were that these systems also

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had a longer pot life than in systems in which CHP was not encapsulated.

Experimental Section

Materials. 1,6-Hexanediol diacrylate (99%) (HDDA), trimethylolpropane triacrylate (99%) (TMPTA), and trimethylolpropane ethoxylate triacrylate (99%) (TMPETA) were obtained from UCB and used as received. Cumene hydroperoxide (88%) (CHP) and cobalt naphthenate in mineral spirits (8% cobalt) were obtained from Aldrich and used as received. Butyl acrylate (99%) was obtained from Aldrich and passed through a column of basic alumina to remove the inhibitor before use.

Preparation of Microcapsules. Microcapsules loaded with a cumene hydroperoxide core were prepared using an interfacial polymerization method. The shell materials consisted of a multifunctional amine and a multifunctional isocyanate. Triethylenetetramine (TETA, 60%, technical grade) was obtained from Aldrich and used as received. Mondur MRS (a polymeric isocyanate based on 4,4′-diphenylmethane diisocyanate) was obtained from Bayer Corp. and used as received. Poly(vinyl alcohol) (87−89% hydrolyzed) (PVA) was obtained from Aldrich and used as received.

A solution of the core material was made by dissolving 80 mL of CHP in 10 mL of Mondur MRS. The core solution was then emulsified in 250 mL of a 1.2% (w/w) aqueous poly(vinyl alcohol) solution with an IKA stir motor equipped with a three-bladed propeller. The emulsion contained dispersed-core droplets with sizes ranging from approximately 100 to 400 μm (measured by examination by light microscopy), which was achieved by mixing at 230 rpm for approximately 1−2 min. Once the desired droplet size range was achieved, a solution of 3.0−13.0 mL of a multifunctional amine in 12−30 mL of deionized water was added, and the mixture was heated to 50 °C in a water bath. The mixture was allowed to react for 4 h at 50 °C with continuous mixing at 230 rpm. After 4 h, the microcapsules were recovered by vacuum filtration and dried overnight with the aid of fumed silica (CAB-O-SIL, Cabot Corp.). The dried microcapsules were roughly spherical and had diameters in the approximate range of 100−400 μm. The microcapsules were composed of ∼80 wt % CHP and washed with heptane prior to use in order to remove any unencapsulated CHP from the outside of the shells.

Frontal Polymerization Experiments. We performed all frontal polymerization experiments in glass test tubes, 16 × 125 mm (VWR #72690-022), on which a plastic cap (VWR #60826-290) could be securely screwed. Polymerization was initiated by heating the top of the tube with a soldering iron. Fronts were performed using multifunctional acrylate systems containing unencapsulated CHP and encapsulated CHP. The front velocity was measured over a range of initiator concentrations; the CHP concentrations in the microcapsule systems were calculated using the core weight percentage of the capsules and the CHP density. To prevent the settling of the microcapsules, ultrafine silica gel (4% w/v) was added to the reaction medium. The same concentration of silica was also used in the unencapsulated CHP systems.

Determination of Pot Life. The pot lives of both encapsulated and unencapsulated systems were assessed by preparing tubes with the reactants, leaving them at ambient temperature and visually determining at what time they spontaneously polymerized. For the microencapsulated system, several tubes were prepared and their front velocities were determined after several days. The tubes contained a multifunctional acrylate, 4% (w/v) silica, and 2% CHP (v/v). In one sample set for each monomer, the CHP was encapsulated, and in another sample set the CHP was unencapsulated. An aliquot of 0.04% (v/v) cobalt naphthenate was added to one tube from each sample set. For the pot life studies approximately eight tubes of each system were prepared.

The pot life in butyl acrylate was determined by storage of initiator at ambient temperature in the presence of the redox accelerator cobalt naphthenate and at 50 °C without the accelerator. This was done in systems containing encapsulated and unencapsulated initiator, respectively. Samples of the systems were periodically observed with an Atago multiwavelength Abbe refractometer DR-M2 for changes in the refractive index of the system.

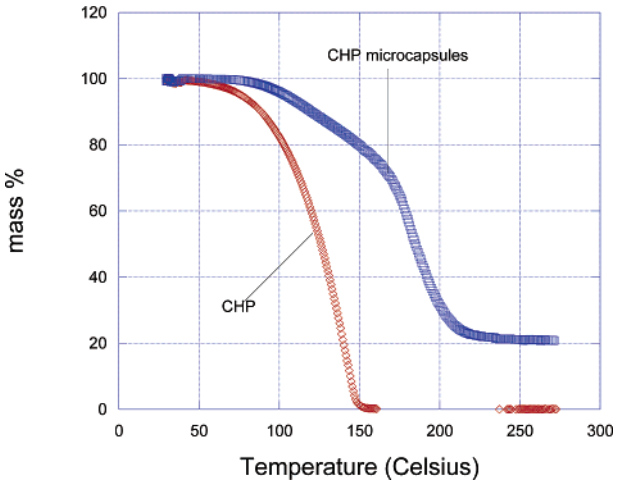

Figure 1. TGA comparison of CHP vs CHP-core microcapsules, ramped 20 °C/min.

Thermal Analysis. Thermal gravimetric analysis was performed on a TGA 2050 thermogravimetric analyzer from TA Instruments. Samples of 5−15 mg were analyzed in a nitrogen atmosphere. Samples were analyzed using a 20 °C/min ramp up to 300 °C and isothermally at 50 and 85 °C.

Microcapsules were examined by light microscopy while they were heated to 300 °C using a 20 °C/min ramp on Mettler Toledo FP82HT heated microscope stage. The heating rate was controlled by a Mettler Toledo FP90 central processor.

Temperature profiles of frontal polymerization reactions were gathered by inserting type K thermocouples (0.010 mm in diameter) into the middle of the reaction medium and securing by tightening the screw top lid of the test tube. The thermocouples were connected to an Omegaette HH314 humidity/temperature reader, taking one temperature reading per second. The temperature and time were measured using Testlink SE-310 software. The temperature vs time profiles were converted to temperature vs distance profiles by multiplying the time data (in minutes) by the front velocities (cm/min).

Measurement of Mechanical Properties. The modulus and toughness of the polymers produced in frontal polymerization experiments were tested using an Instron materials testing machine equipped with a 225 lb load cell. Samples were clamped and pulled apart at a rate of 0.5 in./min. Approximately three to five specimens of each sample were tested.

Results and Discussion

Thermal Properties of the Microcapsules. To determine the feasibility of using the initiator-core microcapsules in frontal polymerization, an examination of the thermal stability of the microcapsules was necessary. A typical polymerization front in a multifunctional acrylate propagates with a temperature on the order of 250 °C. To be effective, the microcapsules must release the core initiator either partially or completely below the front temperature. However, the microcapsules must have sufficient thermal stability to resist excessive leakage at elevated temperatures in order to make frontal polymerization applicable to a wide range of applications. An analysis of the thermal release properties was needed, so the microcapsules were tested by thermogravimetric analysis (TGA).

The first step was to compare TGA readings for CHP-core microcapsules with those of unencapsulated CHP. A rapid ramp of 20 °C/min was performed for CHP and for CHP microcapsules (Figure 1).

Unencapsulated CHP exhibited a rapid decrease in mass as the temperature reached ∼75 °C as it was thermally decomposed

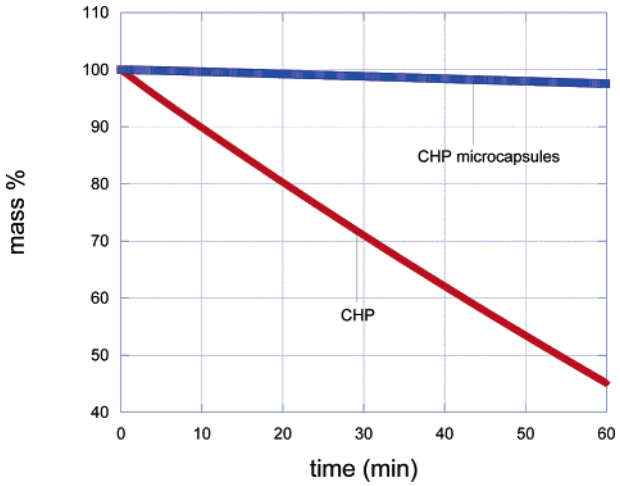

Figure 2. TGA comparison of CHP vs CHP-core microcapsules, held isothermally at 50 °C for 60 min.

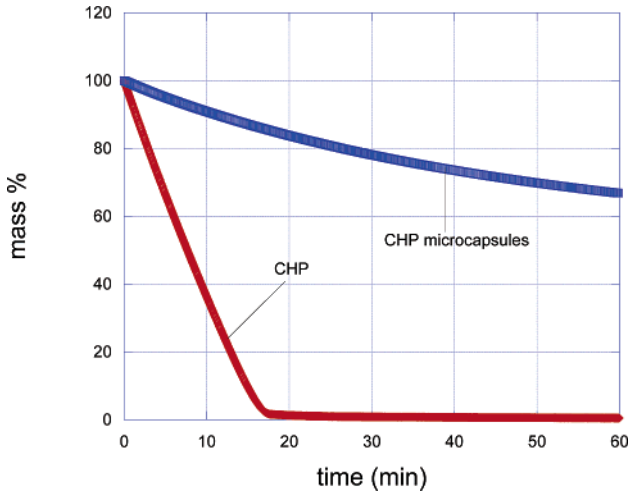

Figure 3. TGA comparison of CHP vs CHP-core microcapsules, held isothermally at 85 °C for 60 min.

into volatile products such as methane, acetophenone, benzaldehyde, and cumyl alcohol by β-scission. By the time the temperature reached 150 °C all of the CHP had decomposed. The microcapsule sample did not begin to exhibit a rapid decrease in mass until the temperature had reached ∼100 °C; the microcapsules had released the entire core CHP at ∼225 °C. It is seen that the presence of the microcapsule shell not only delayed the release of the CHP, but the mass loss occurred more gradually over a wider temperature range than with the unencapsulated initiator. This indicates that the microcapsules successfully offer a degree of protection from thermal release; however, they still release the CHP at temperatures attainable in a polymerization front.

The protection of the CHP from elevated temperatures in microcapsules can be demonstrated further by comparing encapsulated vs unencapsulated CHP samples in isothermal TGA tests. Figure 2 shows a comparison of these two samples held isothermally at 50 °C for 1 h.

This shows a considerably more dramatic effect of the microcapsule shell. Unencapsulated CHP undergoes a steady decomposition and after 1 h had lost 55% of its mass. Encapsulated CHP proves to be quite stable at 50 °C in comparison, losing only ∼2.5% of its mass. The microcapsules had a core mass percentage of ∼80%, so that corresponds to an approximately 3% loss of total CHP present in the microcapsule samples, considerably less than when the CHP was not encapsulated. This trend is also exhibited at higher temperatures. Figure 3 shows a comparison of encapsulated vs unencapsulated CHP held isothermally at 85 °C for 1 h. Unencapsulated CHP decomposed rapidly and after ∼18 min had completely decomposed. The CHP-core microcapsules were able to withstand the entire 60 min run, exhibiting a total mass loss of 33%, corresponding to a loss of ∼41% of the total CHP with the capsule sample.

TGA testing indicated that the exothermic polymerization of a multiacrylate would be sufficient to burst the capsules and cause them to release their initiator core. A preliminary test was conducted to test this; a system of HDDA and CHP-core microcapsules was prepared and examined by heated-stage microscopy as the temperature was ramped 20 °C/min. Figure 4 shows images of the system at various stages of the experiment. The system started out equilibrated at 30 °C; this is shown in Figure 4a. As the system was heated, the microcapsules gradually showed signs of leakage, and the monomer immediately around the capsules showed sign of reaction. Figure 4b shows the system when it had reached 150 °C; the area around the periphery of the microcapsules is seen to be fuzzy as opposed to the first image, due to an increased opacity caused by polymerization around the capsule edges. At 160 °C, the increased opacity is seen across the entire sample as the cross-linked polymer was rapidly formed (Figure 4c).

Comparison of Frontal Polymerization Systems with and without Microcapsules. There was initially some doubt about whether a system containing microcapsules could support a front because of factors such as additional energy required to provide core release, the presence of capsule shells acting as a filler and removing heat from the reaction front, and distortion in the shape of the reaction front caused by inhomogeneous dispersal of the microcapsules in the monomer. However, initial results showed that an HDDA system containing CHP-core microcapsules could support a polymerization front, and a comparison was made between systems in which CHP was encapsulated and systems in which it was dissolved.[46] It was found that increasing the concentration of CHP-core microcapsules increased the front velocity, just as increasing the concentration of dissolved CHP increases the front velocity in traditional frontal polymerization systems. The ratio of the front velocities (dissolved/encapsulated) was approximately 3:1 at the lowest concentration, but the ratio gradually got smaller as the CHP concentration was increased.

The effectiveness of the microcapsules was tested in frontal polymerization systems that consisted of trimethylolpropane triacrylate (TMPTA) and trimethylolpropane ethoxylate triacrylate (TMPETA) as monomers. It was discovered that TMPTA systems would support a polymerization front when CHP was encapsulated, but TMPETA systems would not. The presence of ethoxy units in the TMPETA molecules serves to reduce the number of double bonds present per unit of volume, thus reducing the amount of heat that is produced in the reaction front. Nason et al. recently found that TMPETA fronts were very slow using a less stable peroxide,[47] and so the microcapsules so reduced the front velocity that no front could propagate. In the TMPTA systems, an increase in CHP concentration caused an increase in front velocity when either dissolved or encapsulated. At lower concentrations of CHP, the ratio of the front velocities (dissolved/encapsulated) was approximately 4.4:1 and gradually decreased until the CHP concentration reached 5%, when the ratio spiked at approximately 4.8:1. A comparison of frontal velocities in HDDA and TMPTA systems is shown in Figures 5 and 6, respectively.

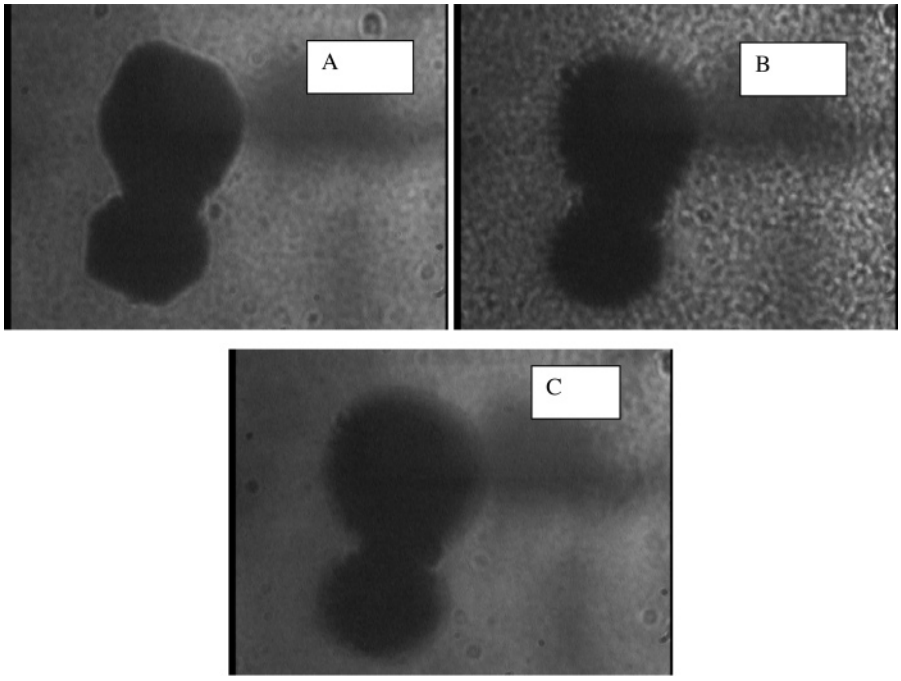

Figure 4. Heated-stage microscope images of CHP-core microcapsules in HDDA. The microcapsule size range was 300−400 μm. Temperatures were as follows: (A) 30, (B) 150, and (C) 160 °C.

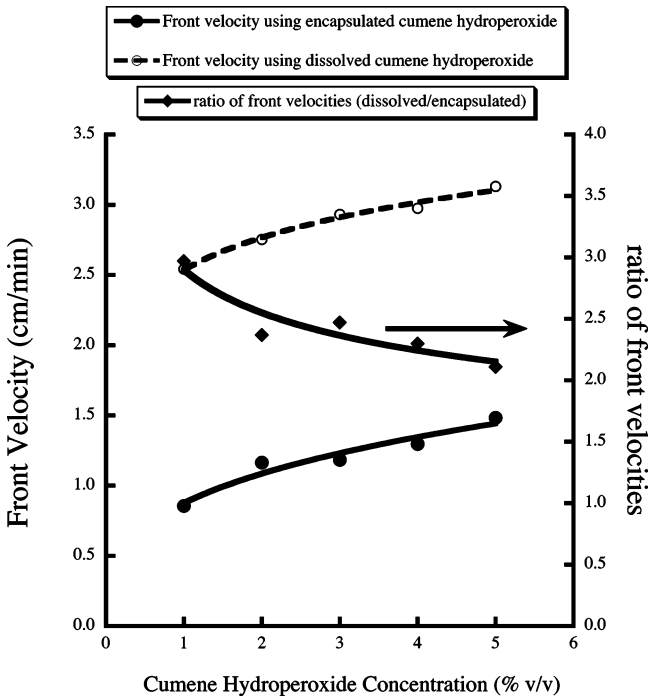

Figure 5. Front velocity as a function of the amount of cumene hydroperoxide, encapsulated and dissolved in the monomer and the ratio of the velocities in HDDA systems. Curves are power function fits to the data.

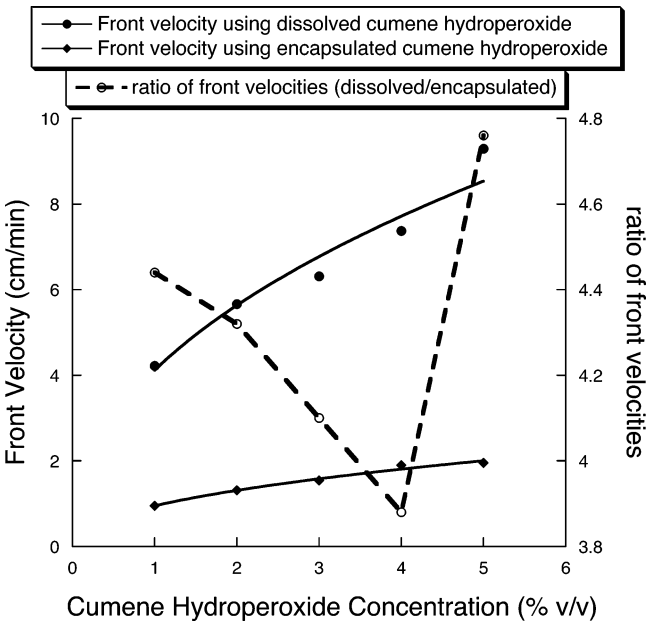

Figure 6. Front velocity as a function of the amount of cumene hydroperoxide, encapsulated and dissolved in the monomer and the ratio of the velocities in TMPTA systems. Curves are power function fits to the data.

It was initially assumed that the addition of a redox promoter such as cobalt naphthenate would always increase the front velocity of the system due to an accelerated production of initiator radicals at the reaction front. However, there were situations in particular when microcapsules were used, in which this was not the case. Figure 7 shows the dependence of the front velocity on cobalt naphthenate concentration at a constant CHP concentration in different frontal polymerization systems. A marked increase in the front velocity is seen in HDDA systems using dissolved CHP as the concentration of the promoter is increased; there is a large spike as the concentration is raised from 0 to 0.2% (v/v), after which a more gradual increase is seen. The increase in reactivity was even more dramatic in TMPTA with dissolved CHP; the addition of 0.04% (v/v) cobalt naphthenate caused the systems to become so reactive that the fronts propagated in an unstable manner with excessive amounts of gas produced, resulting in explosion. Front velocities were not measurable for these systems.

A different trend was seen in systems utilizing encapsulated CHP, however. In the HDDA systems there appeared to be an optimal ratio of initiator to promoter at which an acceleration of the front velocity was observed; a gradual increase in front velocity was seen up to a cobalt naphthenate concentration of

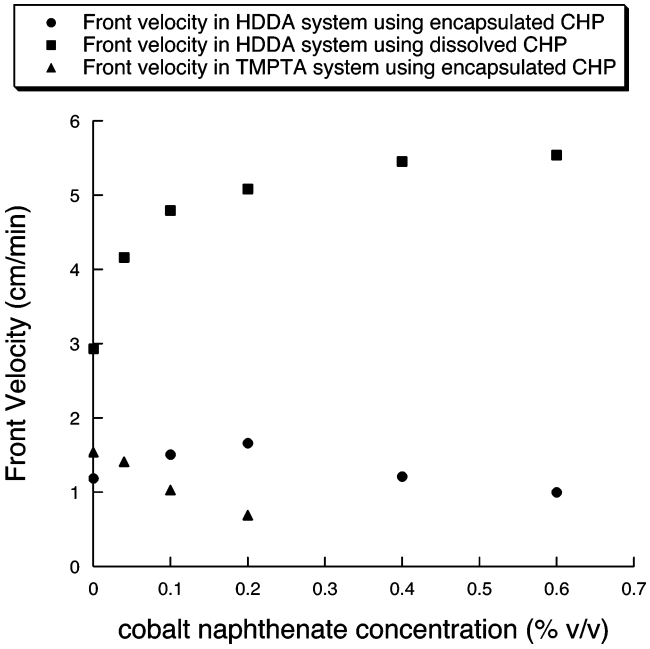

Figure 7. Effect of increasing cobalt naphthenate concentration at a constant CHP concentration (3% v/v) for HDDA and TMPTA systems.

0.2% (v/v). Upon further increase in promoter concentration, however, the front velocity was seen to decrease. The TMPTA systems containing CHP-core microcapsules showed a totally opposite effect from systems using dissolved CHP. In these systems, there was a dramatic decrease in front velocity as more cobalt naphthenate was added. When more than 0.2% (v/v) cobalt naphthenate was added to these systems, the front would not propagate. The reason for this observed inhibition in systems containing microcapsules is not immediately clear. One possibility could be a further reduction of radicals in the reaction zone by excess Co^{2+} to anions, thus reducing radical concentration and reducing the velocity of the front. This could be seen in systems with capsules if the capsules in the reaction zone undergo a slow release instead of an immediate burst; in this instance it is conceivable that a situation could exist in which there is an excess of Co^{2+} in relation to CHP radicals in the reaction zone, thus causing inhibition.

It was observed that in TMPETA systems using dissolved CHP, there was a general increase in front velocity as cobalt naphthenate was added (Figure 8). Because of this, it was thought that TMPETA systems with CHP-core microcapsules might support a polymerization front if enough promoter was added. This was not the case; a polymerization front was not observed in any TMPETA/microcapsule systems, regardless of the promoter concentration.

Because the presence of the microcapsule shells can act as a filler, it was hypothesized that the front temperature in systems containing CHP-core microcapsules would be lower than in traditional systems containing dissolved CHP. This was tested by comparing the temperature profiles for HDDA systems containing dissolved and encapsulated CHP (Figure 9). The shells indeed appear to act as a heat sink, as the front temperature in the system with dissolved CHP spikes about 20 deg higher. The depression caused by the presence of shell filler is not enough to adversely affect core release but can explain some of the decrease in the front velocity; the temperature for thermal fronts usually scales with the square of the front velocity.

Results of Pot-Life Studies. Table 1 shows the observed pot life of different thermosetting monomers containing dissolved

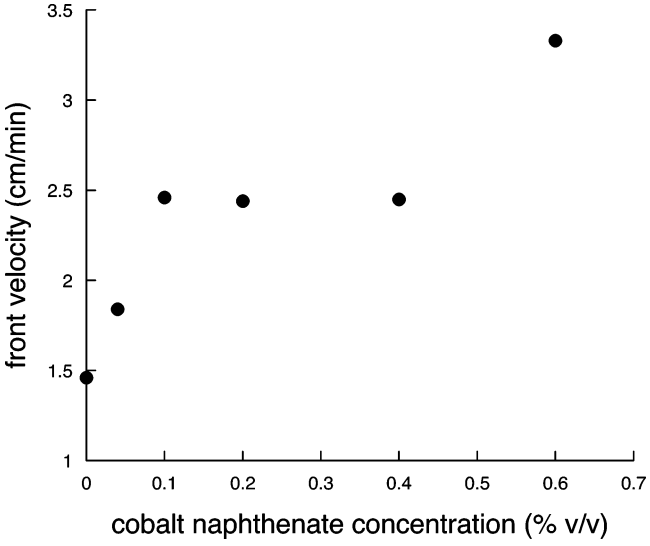

Figure 8. Effect of increasing cobalt naphthenate concentration at a constant dissolved CHP concentration (3% v/v) for TMPETA systems.

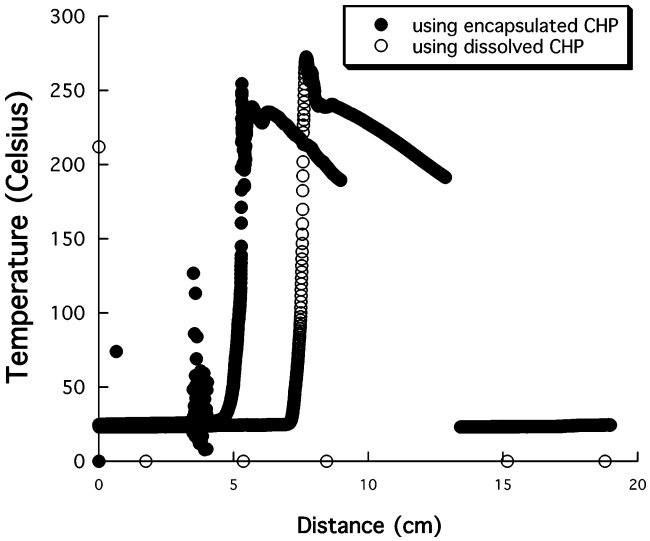

Figure 9. Temperature profiles of 5% v/v CHP in HDDA, both encapsulated and dissolved.

Table 1. Pot Lives of Thermosetting Monomers Containing Dissolved CHP under Various Storage Conditions

	2% CHP, 0.04% cobalt naphthenate, stored at room temp	2% CHP, stored at 50 °C
HDDA	1 h	6 days
TMPTA	5−7 h	5 days
TMPETA	3 h	7 days

CHP under different conditions. Pot life was determined by visually observing the systems for a change in opacity caused by the rapid polymerization of the monomers due to the gel effect. These pot lives were taken as base values on which it was the goal to improve upon using CHP-core microcapsules. It was observed that in accelerated systems at room temperature that the pot life of each system was a few hours, while systems at an elevated temperature of 50 °C had pot lives of 5−7 days.

Monomer systems corresponding to those described in the above table were prepared in which the dissolved CHP was replaced with CHP-core microcapsules, with the concentrations of each component remaining the same, and the pot life of each system was observed. The results are seen in Figure 10.

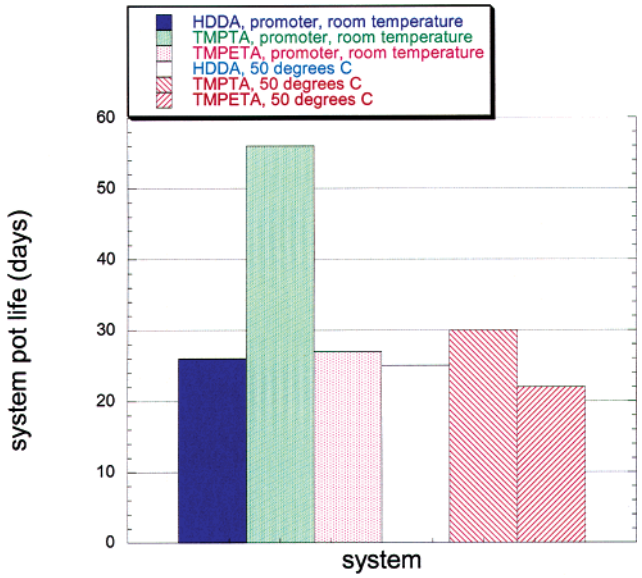

Figure 10. Pot lives of thermosetting monomer systems containing 2% CHP (encapsulated), in various storage conditions.

A major increase in pot life was observed for all the promoted systems. Whereas previous promoted systems only lasted for a matter of hours, the systems utilizing encapsulated CHP each lasted over 3 weeks before polymerizing. The TMPTA system lasted the longest, 56 days, before polymerizing. This was not surprising, given the low reactivity of TMPTA/encapsulated CHP/promoter frontal systems that was observed earlier.

A substantial increase in pot life was also observed in the unpromoted systems stored at 50 °C, increasing from 5−7 to 20−30 days. Although the least reactive of the three monomers, TMPETA was observed to have the shortest pot life of the three monomer systems. This could be a result of leakage of the monomer into the capsules, causing them to burst. Because TMPETA contains ethoxy groups within its monomer molecules, it is more polar than HDDA and TMPTA, which do not have these ethoxy groups. It is possible that the capsule shells are more permeable to the more polar TMPETA molecules than the less polar monomer molecules, resulting in swelling and capsule leakage. It was expected that the TMPTA would polymerize before the HDDA due to its higher reactivity, but this was not the case.

It was thought that capsule leakage over storage time could possibly be measured analytically by measuring the front velocity. If the core initiator was leaking out, it would make sense that the front velocity would increase as more leakage occurred. For each of the pot life setups described earlier, a front was run periodically and the velocity recorded for comparison. The front velocities were observed as a function of time using the same batch of microcapsules in two different multifunctional acrylates, HDDA and TMPTA. Tests were conducted in accelerated systems stored at room temperature and in unpromoted systems stored at 50 °C. The results are seen in Figures 11 and 12.

While Figure 11 shows a large initial increase in front velocity after 2 days of storage in the HDDA system, no such increase is seen in the TMPTA system. This is not surprising due to the apparent inhibition of front velocities of promoted TMPTA/microcapsule systems that was described earlier. An increase in velocity was not seen until day 14 when more CHP had leaked out. It appears from this and from the pot life data that promoted TMPTA systems tend to cause less capsule leakage than promoted HDDA systems.

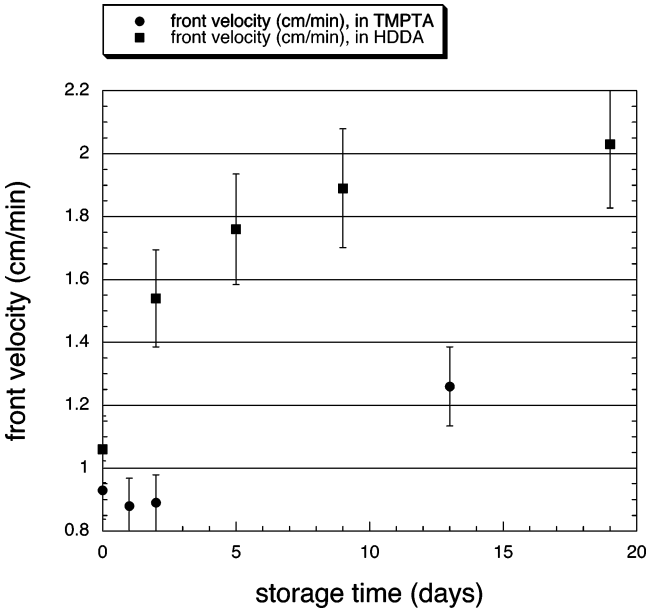

Figure 11. Measurement of front velocity as a function of storage time in accelerated monomer systems stored at room temperature, each using CHP-core microcapsules.

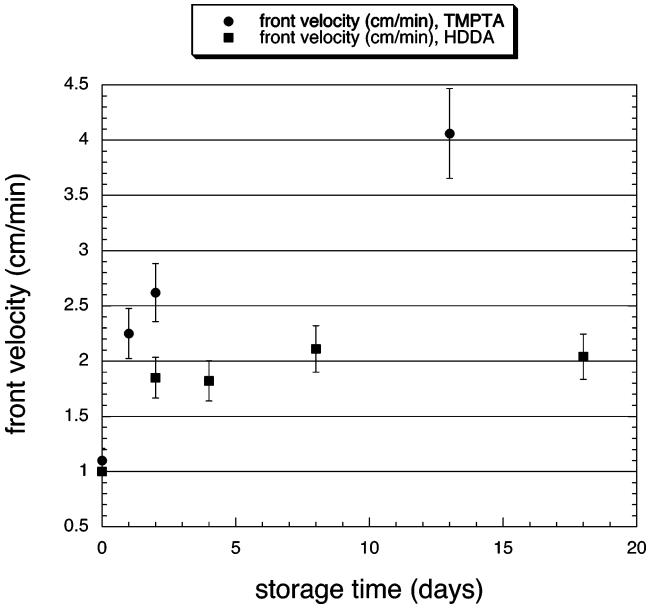

Figure 12. Measurement of front velocity as a function of storage time in unaccelerated monomer systems stored at 50 °C, each using CHP-core microcapsules.

TMPTA also appears to cause less capsule leakage in the unpromoted systems held at 50 °C. Whereas the largest increase in front velocity with HDDA systems occurred within the first 1−2 days of storage followed by a plateau, in TMPTA there is a smaller initial increase, and the velocity continues to increase substantially as storage time is increased.

To obtain a more quantitative analysis of general behavior of capsule systems vs systems containing dissolved CHP, the refractive index of butyl acrylate systems with and without encapsulated CHP was measured over time in different storage situations. As butyl acrylate polymerized, the refractive index increased with increasing conversion and was compared to a standard curve to determine percentage conversion for each system. The results are seen in Figure 13. The accelerated system containing dissolved CHP polymerized to ∼90% conversion after a storage time of ∼40 days; in comparison, the promoted

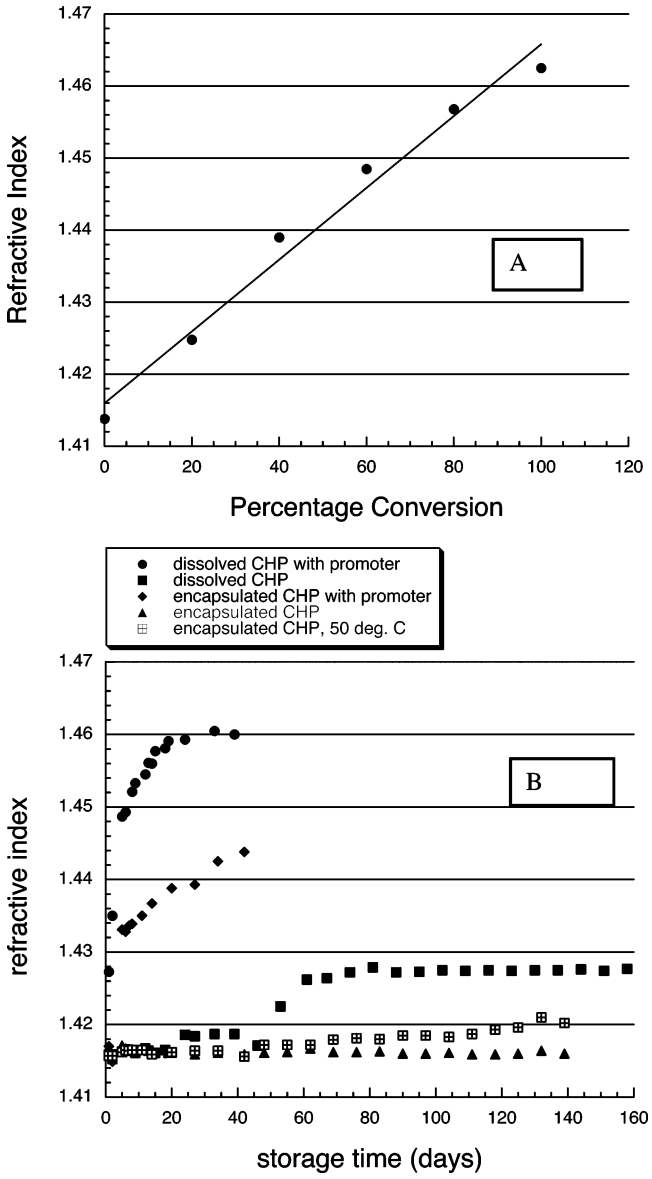

Figure 13. (a) Standard RI curve for butyl acrylate polymerization. (b) Measurement of the refractive index of various butyl acrylate systems under different storage conditions.

system that used encapsulated CHP had polymerized to <60% conversion. Unpromoted systems containing dissolved and encapsulated CHP respectively had respective conversions of ~25% and 1−2% after ~140 days of storage. When these systems were stored at 50 °C, a dramatic effect was observed. The conversion of the system containing encapsulated CHP only rose to ~10% after 140 days of storage, while the system with dissolved CHP (not shown on the graph) was observed to have completely polymerized by the second day. Again it was demonstrated that encapsulating the CHP had a positive effect on pot life in different storage situations.

Mechanical Properties. It is important to determine the effect that the presence of microencapsulated initiator will have, if any, on the polymer that is produced by the frontal polymerizations. Properties of particular interest included toughness and modulus. Tests were performed on polymers prepared from HDDA systems containing different combinations of dissolved or encapsulated CHP, promoter, and empty microcapsule shells used as filler. Because the microcapsule shells could affect the mechanical properties, so two extra tests were included using empty capsule shells. Polymers tested were prepared from

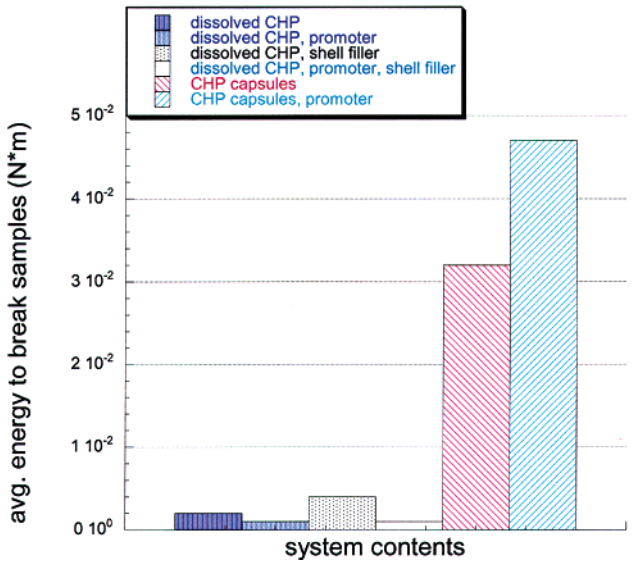

Figure 14. Toughness of poly(HDDA) samples produced from various systems.

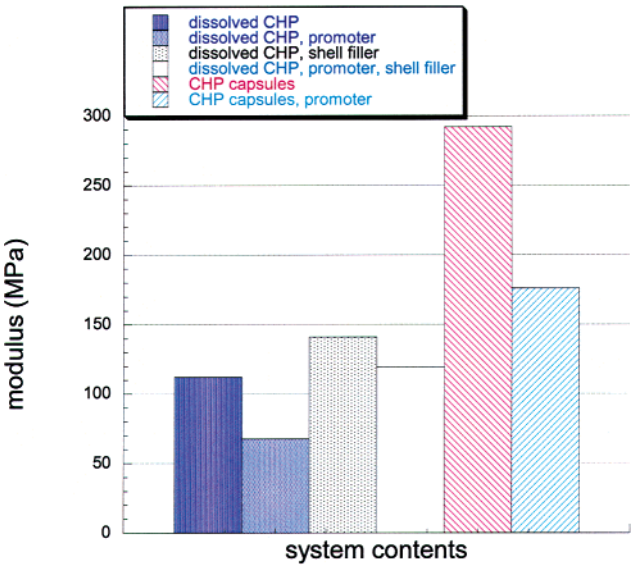

Figure 15. Modulus of poly(HDDA) samples produced from various systems.

HDDA systems containing the following: (1) dissolved CHP (2% v/v), (2) dissolved CHP + promoter (0.04% v/v), (3) dissolved CHP + promoter + empty shells, (4) dissolved CHP + empty shells, (5) CHP capsules, and (6) CHP capsules + promoter. All systems contained 4% (w/v) fumed silica. Results showing the toughness of each system are shown in Figure 14, and results showing the modulus of each system are shown in Figure 15.

The samples that were tested were quite brittle to the touch, so not surprisingly they did not exhibit particular toughness. There is little variation in toughness of the samples prepared from dissolved CHP, even with the addition of empty shell as filler. However, when encapsulated CHP was used, a dramatic increase in toughness was observed. Samples prepared with encapsulated CHP were an order of magnitude tougher than any samples prepared with dissolved CHP; when CHP capsules were used in conjunction with promoter, the toughness increased another 50%.

Similar results were seen in the modulus of each system, although not quite as dramatically. Samples prepared from

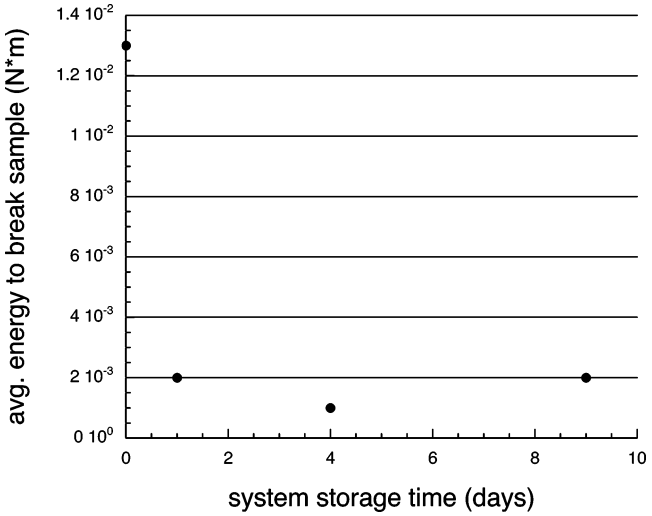

Figure 16. Toughness of polymer samples prepared from the same HDDA system containing encapsulated CHP, polymerized at different storage times.

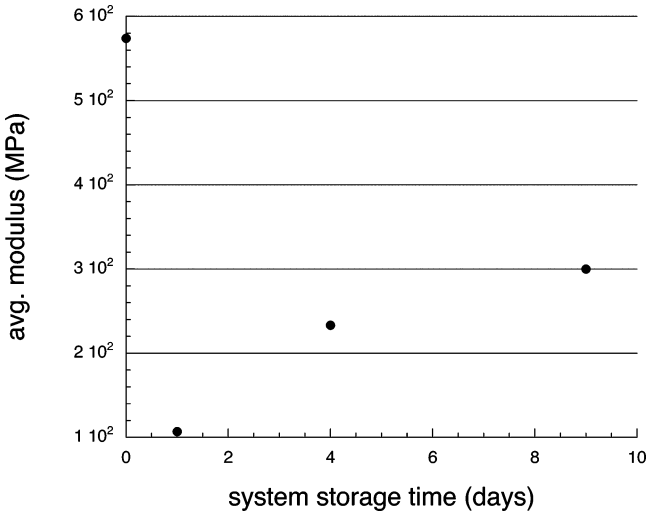

Figure 17. Toughness of polymer samples prepared from the same HDDA system containing encapsulated CHP, polymerized at different storage times.

systems containing dissolved CHP exhibited similar moduli, although it was observed that when a promoter was used in these systems the modulus (as well as the toughness) decreased. This was not surprising, as fronts in dissolved CHP/promoter systems seemed to produce more bubbles, causing distortions in the shapes of the fronts. These bubbles could have caused pockets in the polymer, thereby creating mechanical weakness. The modulus increased in systems in which encapsulated CHP was used. Samples prepared from systems containing encapsulated CHP along with promoter appeared to be tougher but less resistant to deformation than those prepared from systems containing CHP capsules and no promoter. This may reflect the absence of "spin modes", in which a nonuniform front propagates in a helical fashion, creating inhomogeneities in the sample.[5,48,49] Frontal polymerization with multifunctional acrylates is especially susceptible to such modes.[50−52] Although no spin modes were observed in this study, we cannot test our hypothesis without more detailed macrokinetic studies.

It was also of interest to observe the mechanical properties of a typical system containing CHP microcapsules as it was stored over time. Multiple samples were made of an HDDA system containing 2% (v/v) encapsulated CHP, and the samples were polymerized after different periods of elapsed time. The polymer samples were tested for the properties of toughness and modulus, and the results are shown in Figures 16 and 17, respectively.

The toughness of the polymer samples decreased dramatically upon 1 day of storage and remained at a very low value throughout samples made after further storage. The modulus of the polymer samples also decreased dramatically after 1 day of storage of the monomer system and remained low.

Conclusions

We have encapsulated the thermal free-radical initiator cumene hydroperoxide and found that these microcapsules can be used successfully to sustain propagating fronts of polymerization in both HDDA and TMPTA. These fronts propagated with lower velocities than in systems containing dissolved CHP, which was expected due to the extra required step of core release. Fronts were supported in systems with and without the presence of promoter cobalt naphthenate. In promoted systems, encapsulated systems provided a more stable front without the presence of excess bubbles that were present when dissolved CHP was used. An optimal cobalt naphthenate concentration appeared to exist in promoted HDDA/capsule systems at which greatest promotion occurred. The addition of further promoter tended to inhibit the system. TMPTA/capsule system front velocities were inhibited greatly by addition of promoter; addition of promoter to TMPTA/dissolved CHP systems greatly increased reactivity to explosive levels. CHP microcapsules would not support a polymerization front in TMPETA, regardless of whether promoter was used or not.

The use of encapsulated CHP in place of dissolved CHP proved to greatly improve the pot lives of frontal polymerization systems in TMPTA and HDDA. The pot lives of promoted systems improved from hours up to 25 days in HDDA, and unpromoted systems held at 50 °C experienced pot lives up to 4 times as long as when using dissolved CHP.

The use of microencapsulated CHP in lieu of dissolved CHP had an effect on the mechanical properties of the polymer produced in HDDA systems. Both the toughness and modulus of polymer samples were dramatically improved when the CHP was encapsulated. An effect of storage of the HDDA/capsule systems was seen as well; the toughness and the modulus dramatically decreased as the samples were polymerized after longer storage times.

The outlook is promising for future work in this area. We have demonstrated that CHP can successfully be microencapsulated and used in frontal polymerization systems; a logical next step is to determine the limits of initiator type that can be used in these systems. We plan to attempt encapsulation of initiators that are less temperature-stable than CHP, such as benzoyl peroxide and azobis(isobutyronitrile), to determine whether they can withstand the encapsulation process and to determine their overall effectiveness in frontal polymerization systems when encapsulated. We are also investigating the use of dual-capsules frontal polymerization systems in which both the initiator and monomer are microencapsulated.

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