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Free-Radical Frontal Polymerization with a Microencapsulated Initiator

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Introduction. Frontal polymerization entails the conversion of a monomer into a polymer via a localized exothermic reaction zone that propagates through the coupling of thermal diffusion and Arrhenius reaction kinetics. Frontal polymerization was discovered in Russia by Chechilo and Enikolopyan in 1972 using methyl methacrylate under high pressure.[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.[3–7] They recently studied frontal copolymerization.[8] Frontal polymerization has been used to prepare different materials, including thermochromic composites,[9] IPNs,[6] polymer-dispersed liquid crystal materials,[10] functionally gradient materials,[11–13] large composites,[14] and hydrogels.[15]

An overwhelming majority of work has been on free-radical systems, but other chemistries can be used. 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.[22] Fiori et al. produced polyacrylate–poly(dicyclopentadiene) networks frontally,[23] and Pojman et al. studied epoxy–acrylate binary systems.[24] Polyurethanes have recently been prepared frontally.[25,26] Frontal atom transfer radical polymerization has been achieved[27] as well as frontal polymerization with thiol–ene systems.[28]

Free-radical frontal polymerization has been discussed in detail by Pojman et al.[5] and by Washington and Steinbock.[29] The velocity dependence on the initiator concentration has been studied for several systems[3,30,31] and follows a power function dependence on the initiator concentration.

A significant issue for applying frontal polymerization to real-world applications is the issue of pot life, i.e., how long can the initiator–monomer solution remain at room temperature before reacting homogeneously. We sought to address this issue by microencapsulating a free-radical initiator, cumene hydroperoxide, and dispersing the capsules throughout a mixture of 1,6-hexanediol diacrylate (HDDA) and silica gel. 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.

Experimental Section. 1,6-Hexanediol diacrylate (80%, technical grade) (HDDA) was obtained from UCB

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and used as received. Cumene hydroperoxide (88%) (CHP) and cobalt naphthenate in mineral spirits (8% cobalt) were obtained from Aldrich and used as received.

Microcapsules loaded with a cumene hydroperoxide core were prepared using an interfacial polymerization method. The shell materials consisted of triethylenetetramine (TETA, 60%, technical grade) obtained from Aldrich and Mondur MRS (a polymeric isocyanate based on 4,4′-diphenylmethane diisocyanate) obtained from Bayer Corp. and were 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 0.5% PVA solution with a stir motor equipped with a three-bladed propeller. The emulsion contained dispersed-core droplets with a size ranging from 100 to 275 μm, which was achieved by mixing at 230 rpm for 2 min. Once the desired droplet size range was achieved, a solution of 6 mL of TETA in 12 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 gel (CAB-O-SIL, Cabot Corp.). The dried microcapsules were roughly spherical and had a size ranging from 150 to 300 μm. The microcapsules were composed of approximately 80 wt % CHP and were washed with heptane prior to use in order to remove any unencapsulated CHP from the outside of the shells.

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 HDDA 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 approximate core weight percentage of the capsules and 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.

The pot life was assessed by preparing tubes with the reactants and leaving them at ambient temperature and 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 HDDA, 4% (w/v) silica, and 2% CHP. In one sample set the CHP was encapsulated, and in another sample set the CHP was unencapsulated. An addition of 0.04% (v/v) cobalt naphthenate was added to one tube from each sample set.

Results and Discussion. The front position vs time data for all systems were linear, which indicates that constant velocity, self-sustaining fronts were achieved. Figure 1 shows images of a front in an encapsulated CHP system and of a front in an unencapsulated CHP system. In each of these systems the front is seen to
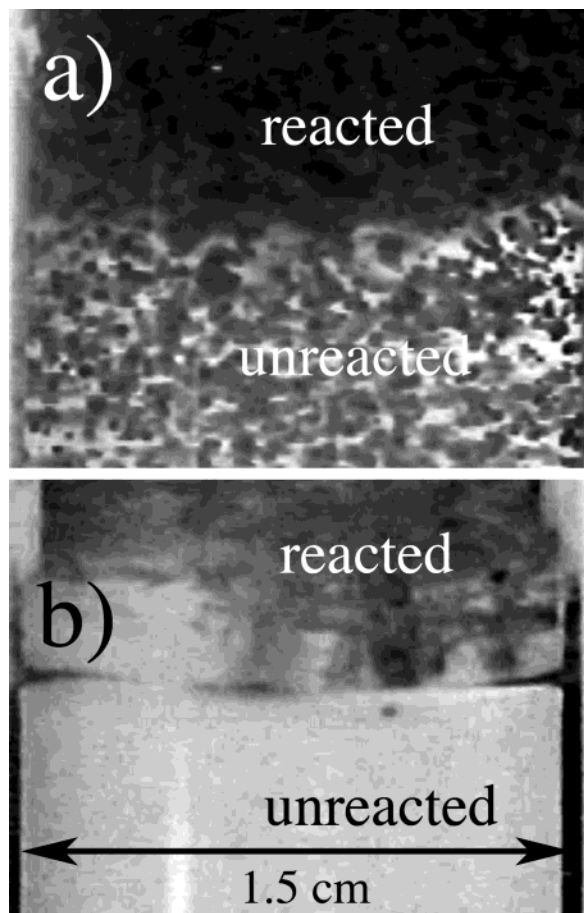
Figure 1. (a) Image of a front of HDDA polymerization, using 2% CHP (v/v) (encapsulated). (b) Image of a front of HDDA polymerization, using 2% CHP (v/v) (unencapsulated).

have a slight convex shape due to higher temperature in the center of the front and maintains this shape uniformly throughout the reaction. This is somewhat surprising in the case of the encapsulated CHP system, as we had supposed that heterogeneities in the capsule dispersion and/or core release could cause distortion of the front; this was not the case. At this point it is unclear exactly whether the core release from the shell is due to a sudden burst due to an internal pressure buildup, a gradual release from small stresses created in the shell by the temperature gradient, a glass transition of the polymer shell, or a combination of factors. However, the uniform shape and velocity of the front suggest that the release is most likely due to a sudden release of the core.

Because the initiator must release from the shell before it can initiate polymerization, we expected that the front velocity of systems using encapsulated CHP would be slower than in systems in which CHP was dissolved in the monomer. This was tested by running a series of fronts using increasing concentrations of both encapsulated and unencapsulated CHP. Figure 2 confirms that the front velocity of systems using encapsulated CHP is less than half that of systems using dissolved CHP. As has been seen in free-radical chain growth frontal polymerization, the velocity increases monotonically with the initiator concentration.[5,31]

The rate of decomposition of cumene hydroperoxide into radicals can be accelerated by addition of a metal ion, such as Co^{2+}. The cobalt ion can undergo a redox reaction with the hydroperoxide, which results in the
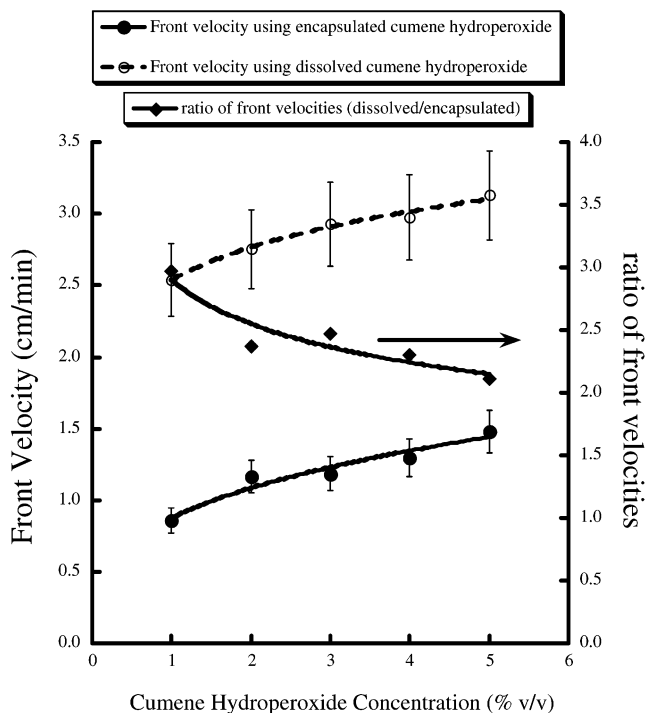

Figure 2. Front velocity as a function of the amount of cumene hydroperoxide, encapsulated and dissolved in the monomer and the ratio of the velocities. Curves are power function fits to the data.
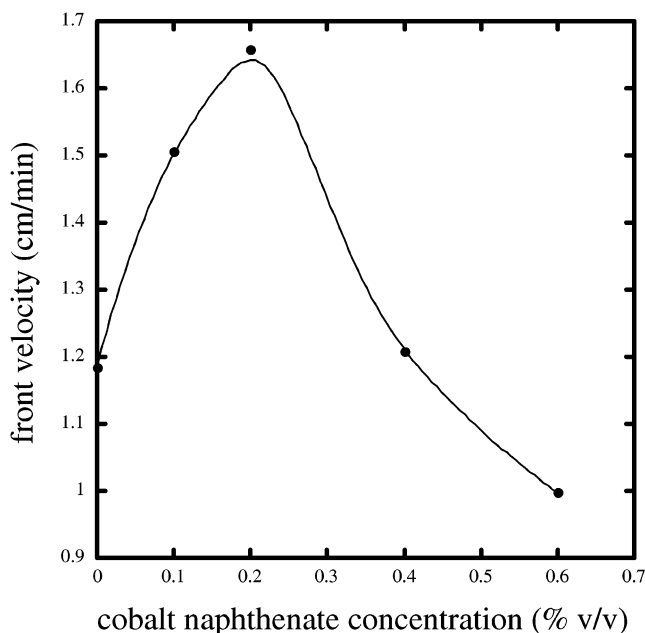

Figure 3. Front velocity vs cobalt naphthenate concentration for a fixed CHP concentration (3% v/v) (encapsulated). The curve is an interpolation.

formation of a Co^{3+} ion and a radical. We thought that addition of a cobalt naphthenate accelerator to frontal polymerization systems using encapsulated peroxide would result in an increased front velocity. This was tested by running a series of fronts using a constant concentration of encapsulated CHP and increasing concentrations of cobalt naphthenate accelerator. Figure 3 shows the velocity dependence on accelerator concentration. We can see that the addition of accelerator does increase the front velocity up to a point, but further addition of accelerator causes the front velocity to

decrease. This indicates that the ratio of initiator to accelerator must be optimized for each system. One possibility is that a high concentration of cobalt ions causes further reduction of radicals into anions before polymerization can take place.

The pot life of the samples was assessed by a combination of visual examination of the system for spontaneous polymerization and a measurement of front velocity of the samples after a period of storage. The tube containing unencapsulated CHP and a small amount of accelerator spontaneously polymerized after a storage time of 1.5 h. The tube containing encapsulated CHP and accelerator was stable for a period of 5 days, at which time it was tested to see whether a front would propagate. A constant velocity front of polymerization existed and propagated at a rate of 2.70 cm/min.

The samples without accelerator did not spontaneously polymerize during the storage period. In each sample set, the front velocity was recorded at the beginning of the storage period and after 5 days of storage. The samples containing unencapsulated CHP had an initial front velocity of 2.7 cm/min. After 5 days the velocity was the same. The front of the sample that was stored for 5 days was difficult to measure due to excessive bubble formation and nonuniformity of the shape of the front. The front quenched halfway down the tube. The samples containing encapsulated CHP had an initial front velocity of 1.3 cm/min. After 5 days of storage, the velocity had increased to 1.9 cm/min. This indicates there was a slight bit of leakage from the shells. The front remained uniform in shape and maintained a constant velocity after 5 days and did not show excessive bubble formation.

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 HDDA polymerization. The resulting fronts were of uniform shape and achieved a constant velocity, as seen using unencapsulated initiator. The uniform shape and constant velocity of the fronts seem to indicate a sudden release of the initiator from the capsule shell.

Fronts using encapsulated CHP have a velocity less than that of fronts using unencapsulated CHP, and this difference in velocity is seen to increase with increasing CHP concentration. The front velocity of the microcapsule system may be increased with the addition of cobalt naphthenate accelerator up to a point, at which further addition of accelerator causes an inhibitory effect most likely due to the further reduction of radicals to anions by excess cobalt ions.

Preliminary tests indicate that encapsulation of polymerization initiators can extend the pot life of frontal polymerization systems.

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