ABSTRACT: We demonstrate for the first time spherically propagating frontal polymerization that also exhibits spin modes. We have developed an interesting system using the amine-catalyzed Michael addition of a trithiol to a triacrylate to create a rubbery gel. The gel suppresses convection and bubble formation during front propagation. A peroxide is also present to act as a thermal initiator. The front propagates via free-radical polymerization of the remaining triacrylate after being initiated photochemically in the center of the reactor. It is possible to prepare the rubbery gel in any shape and then initiate thermal frontal polymerization. So-called spin modes have been observed for the first time in spherically propagating fronts in which waves of polymerization propagate on the expanding spherical front. A system using a diacrylate dissolved in dimethyl sulfoxide with added silica gel and with persulfate as the initiator supports spherical fronts but does not exhibit spin modes. © 2006 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 44: 1387–1395, 2006

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INTRODUCTION

Frontal polymerization is a process in which the reaction propagates directionally through the reaction vessel. The three types of frontal polymerizations are thermal frontal polymerization (TFP), which uses an external energy source to initiate the front,1–4 photofrontal polymerization, in which the localized reaction is driven by an external UV source,5–9 and isothermal frontal polymerization, which relies on the Norrish–Trommsdorff or gel effect,10,11 which occurs when the monomer and initiator diffuse into a polymer seed (small piece of polymer).12

TFP begins when a heat source contacts a solution of a monomer and thermal initiator. Alternatively, a UV source can be applied if a photoinitiator is also present.13 The area of contact (or UV exposure) has a faster polymerization rate, and the energy from the exothermic polymerization diffuses into the adjacent region, raising the temperature and increasing the reaction rate in that location. The result is a localized reaction zone that propagates down the reaction vessel as a thermal wave.1–4 The simplest example is a front propagating down a glass tube (Fig. 1).

The overwhelming majority of work with TFP has been on free-radical systems, but other chemistries can be used. Begishev et al.14,15 studied the frontal anionic polymerization of ε-caprolactam, and epoxy chemistry has been used as well.16–20 Mariani et al.21 demonstrated frontal
ring-opening metathesis polymerization. Fiori et al.\textsuperscript{22} produced polyacrylate–poly(dicyclopenta
diene) networks frontally, and Pojman et al.\textsuperscript{23} studied epoxy–acrylate binary systems. Polyur-
ethanes have been prepared frontally\textsuperscript{24,25} as well as polyurethane–nanosilica hybrid nanocompo-
sites.\textsuperscript{26} Frontal atom transfer radical polymeriza-
tion has been achieved\textsuperscript{27} as well as frontal poly-
merization with thiol–ene systems.\textsuperscript{28} Crivello et al.\textsuperscript{29,30} developed photoactivated cationic fron-
tal polymerization, which can be performed in thin layers.

A current comprehensive bibliography of fron-
tal polymerizations can be obtained at the web-
site listed in ref. 31.

Spin Modes

Thermal fronts have been used in a process discov-
ered in 1967 by Merzhanov and Borovinskaya\textsuperscript{32} and called self-propagating high-temperature syn-
thesis (SHS) to prepare technologically useful cerami-
cs and intermetallic compounds.\textsuperscript{33–38}

Fronts do not have to propagate as simple pla-
nar fronts. Analogously to oscillating reactions, a
steady state can lose its stability as a parameter is
varied and exhibit periodic behavior, either as pul-
sations or spin modes in which a hot spot propa-
gates around the reactor as the front propa-
gates, leaving a helical pattern. This mode was
first observed in SHS.\textsuperscript{39} SHS fronts demonstrate
a rich variety of dynamical behavior, including
planar fronts, spin modes,\textsuperscript{40–43} and chaotic reac-
tion waves.\textsuperscript{44} Many examples of beautiful pat-
terns spontaneously formed by frontal polymeri-
zation have been discovered.\textsuperscript{4,45–49}

A linear stability analysis of longitudinally propa-
gating fronts in cylindrical adiabatic reactors with one overall reaction predicts that the ex-
pected frontal mode for the given reactive medium and diameter of the reactor is governed
by the Zeldovich number ($Z$):

$$Z = \frac{T_m - T_o}{T_m} \frac{E_{\text{eff}}}{R T_m}$$

The planar mode is stable if $Z < 8.4$ and is unsta-
ble if $Z > 8.4$. Through the variation of $Z$ beyond
the stability threshold, more complicated spin
mode instabilities can be observed. Polymeriza-
tion is not a one-step reaction, so the previously
shown form of $Z$ does not directly apply. It does
indicate that there are three ways to increase the
probability of observing spin modes: lower the ini-
tial temperature, raise the front temperature,
and increase the energy of activation. The front
temperature is limited by the energy released per
mass of the monomer, so a lower molecular
weight is advantageous. (This is also true for
achieving frontal polymerization at all.\textsuperscript{13})

The most commonly observed case with frontal
polymerization is the spin mode in which a hot
spot propagates around the front. A helical pat-
ttern is often observed in a sample. The first case
was with the frontal polymerization of $\varepsilon$-caprolac-
tam,\textsuperscript{14,15} and the next case was discovered in a
methacrylic acid system in which the initial tem-
perature was lowered.\textsuperscript{45}

An interesting problem arises in the study of
fronts with multifunctional (meth)acrylates. At
room temperature, fronts with monomers such as
1,6-hexanediol diacrylate (HDDA) and triethyl-
enene glycol dimethacrylate (TGDMA) exhibit spin
modes. In fact, if an inert diluent such as di-
methyl sulfoxide (DMSO) is added, the spins modes
are more apparent even though the front temper-
ate is reduced. Masere and coworkers\textsuperscript{46,47}
found spin modes in the frontal polymerization of
a diacrylate at room temperature. The overall
energy of activation for multifunctional acrylates
increases with conversion and is a stronger func-
tion of conversion the higher the functionality is
of the monomer.\textsuperscript{50,51}

Other geometries allow other modes. Matkow-
sky and Volpert\textsuperscript{52} analyzed the problem of an
expanding front in a disk in which hot spots in the front traced out Archimedean spirals. Pojman et al.\textsuperscript{49} studied propagation modes in square reactors and in funnels.

Frontal polymerization shares many similarities with SHS, but a significant difference is that the monomers are usually transparent, whereas the starting materials used in SHS are opaque. This difference affords the possibility of observing a type of propagation that cannot be observed in SHS, namely, a spherically propagating front that expands from an initiating source.

**Convection**

Because of the large thermal and concentration gradients, polymerization fronts are highly susceptible to buoyancy-induced convection. Garbey et al.\textsuperscript{53,54} performed a linear stability analysis for the liquid–liquid and liquid–solid cases. Experimental work was done and confirmed the analysis.\textsuperscript{55,56} An interesting issue is that a descending front with a solid product is more susceptible to spin modes if the monomer has a low viscosity. The first experimental confirmation that gravity plays a role in spin modes in a liquid–solid system came in a study of descending fronts in which the viscosity was significantly increased with silica gel. Masere et al.\textsuperscript{47} found that silica gel significantly altered the spin behavior; the addition of silica gel suppresses spin modes in some systems. Pojman et al.\textsuperscript{49} made a similar observation in square reactors.

To achieve a spherical front, the reactant solutions must be sufficiently viscous to suppress buoyancy-driven convection. The first approach was to use a multifunctional acrylate dissolved in DMSO with ammonium persulfate as the initiator. This initiator does not produce volatile byproducts that can cause bubbles or lead to explosions in large reactors. However, even for a triacrylate such as trimethylolpropane triacrylate (TMPTA-N), spin modes were not observed in test tubes when silica gel was added.

We can create spherically propagating fronts using liquid–solid systems. By adding silica gel, we can suppress convection but still have an initially transparent system. Figure 2 shows such a system in which a drop of photoinitiator was injected into the center of an HDDA–DMSO–persulfate solution that contained enough silica gel to make it highly viscous. By the exposure of the system to 365-nm radiation, the front ignites in the center.

**Challenges for Spherical Fronts**

Bubbles and an increase in pressure come from the volatility of the monomer, dissolved gas, and water and volatile byproducts produced by the thermal initiator.\textsuperscript{4} The initiator gas problem can be solved with a tetra-alkyl ammonium persulfate\textsuperscript{57} or with DMSO as a solvent for the acrylate and ammonium persulfate. As we discuss later, diluting the monomer in DMSO with persulfate does not present conditions favorable to spin modes but offers a relatively simple system for achieving spherically propagating fronts.

Luperox 231 produces half as much gas per molecule as typical peroxides or nitriles. Bubbles can be suppressed in test tubes with screw caps.\textsuperscript{47} However, if larger reactors are used, the pressure can rupture the reactor. Therefore, some method must be used to suppress bubbles. Goldfeder et al. employed a custom-built pressure reactor (up to 30 atm) that allowed temperature control and video observation of the fronts.\textsuperscript{58} Its diameter was 10 cm, which limited the range of sizes of spherical fronts that could be studied. More importantly, the reactor was inconvenient to use.

Pojman et al.\textsuperscript{4} noticed that if a multifunctional acrylate containing a peroxide was allowed to remain at room temperature for several days, gelation could occur without complete conversion. The system could support frontal polymerization, although it was not possible to make gels this way in less than a day, and the results were not reproducible. Nonetheless, the remarkable feature of these partially reacted and gelled diacrylates was that no bubbles formed. We attribute this to the high free energy of bubble nucleation in a gel.

We tried to allow a multifunctional acrylate to slowly polymerize at room temperature in a water bath. Once the system gelled, the polymerization always accelerated because of the Norrish–Trommsdorf effect. Thus, we need a system that can be gelled by one type of chemical reaction and...
frontally polymerized by another. The system must also be transparent, and the polymer must possess sufficient optical contrast from the monomer. The system must also have a pot life of at least an hour.

**Thiol–Ene System**

Hoyle et al.\(^5^9\) recently reviewed thiol–ene polymerizations. There are three mechanisms by which polymers can be formed with these materials. In all cases, the mechanism is step growth. If a dithiol and a diene are used, a linear polymer results. At least one of the components must have functionality greater than two to achieve a cross-linked polymer.

If an electron-rich ene, such as an allyl ene, is used, then the only mechanism is a free-radical step-growth mechanism; an initial source of free radicals is required. The ene cannot homopolymerize. If an acrylate is used, the thiol undergoes the step growth process, but the acrylate also homopolymerizes via a free-radical chain growth mechanism.

A thiol can add to an acrylate through a base-catalyzed Michael addition. Tertiary amines or tetra-alkyl ammonium hydroxides are effective catalysts. We selected a trithiol and a triacrylate. We had demonstrated frontal polymerization via a free-radical mechanism with a thiol and allyl ether and with a diacrylate and noted that spin modes occurred.\(^2^8\) The strategy was to have an acrylate-to-thiol ratio greater than one. By the addition of a tertiary amine, the thiol would react slowly with the acrylate and would form a gel near the complete consumption of the thiol. The rest of the acrylate could then polymerize via a free-radical mechanism for there would be a thermal initiator present.

For step-growth polymerization, the critical conversion (\(p_c\)) for gelation can be calculated as follows:\(^6^0\)

\[
p_c = \frac{1}{\sqrt{r(f_A - 1)(f_B - 1)}}
\]

where \(r\) is the stoichiometric ratio between the two monomers, which is always \(\leq 1\), and \(f_A\) and \(f_B\) are the functionalities of the thiol and acrylate, respectively.

We want all the thiol to react via the amine-catalyzed Michael addition and still leave as much acrylate as possible to react via a free-radical chain growth mechanism. We solve \(p_c\) for the value of \(r\) that will yield the unit conversion, given \(f_A\) and \(f_B\):

\[
\text{ratio} = \frac{1}{f_A f_B - f_A - f_B + 1}
\]

To increase the chance for observing spin modes, we wanted a system that would have a large front temperature. For a triacrylate with a trithiol, the critical ratio for gelation is 4:1 triacrylate/trithiol. For a diacrylate with a trithiol, the ratio is 2:1. Only 25% of the triacrylate double bonds will be consumed by the thiol versus 50% for the diacrylate. This means that the triacrylate system should have a higher front temperature. Also, earlier work had shown that higher functionality acrylates have faster front velocities\(^1^3\) and show more complex dynamic behavior.\(^4^6\)\(^,\)\(^4^7\) We investigated TMPTA-N with trimethylolpropane tris(3-mercaptopropionate) (TT1) with triethyl amine as the catalyst and Luperox 231 as the free-radical initiator.

**EXPERIMENTAL**

**Materials**

TMPTA-N was obtained from Cytec Surface Specialties. TT1, 1,1-bis(terbutylperoxy)-3,3,5-trimethylcyclohexane (Luperox 231P75), and triethyl amine were purchased from Aldrich. 1-Hydroxycyclohexyl-phenylketone (Sarcure SR1122) was purchased from Sartomer. All the chemicals were used without purification.

HDDA (90% technical grade), ammonium persulfate, and DMSO were used as received from Aldrich.

**Experiments with HDDA in DMSO**

An 8.0 mM solution of ammonium persulfate was prepared fresh daily by the addition of 0.072 g of ammonium persulfate to 40 mL of DMSO. An aliquot of 30 mL of this solution was transferred to a 150-mL beaker and stirred with 20 mL of HDDA. Then, 2.7 g of Cab-O-Sil was slowly stirred until all the powder was dispersed. The photoinitiator solution consisted of 0.33 g of Irgacure 184 dissolved in 10 mL of HDDA, to which 0.67 g of Cab-O-Sil was dispersed. The HDDA–DMSO solution with silica gel was added to half of the reactor. A small amount of the photoinitiator solution was injected into the HDDA–DMSO solution. The
reactor was then completely filled with the HDDA solution. To prevent cracking, diethyl phthalate was used. The optimal solution was 35% HDDA, 53% DMSO, 12% diethyl phthalate, and 6.7% Cab-O-Sil.

To ignite the front, a 3-mW, 365-nm UV light source was shone on the sample until polymerization began in the center.

**Thiol–Ene System**

**Gel Formation**

Initially, we had trouble obtaining gels without the rest of the triacrylate polymerizing, especially for larger containers. If the thiol–acrylate reaction raises the temperature high enough for the peroxide to initiate chain-growth polymerization, thermal runaway will occur. The system is very sensitive to the concentration of the amine catalyst. However, maintaining the system in an ice-water bath is essential.

TMPTA-N (303 mL) and 123.48 mL of TT1 were mixed inside a 1000-mL screw cap, wide-mouth glass jar with a stir motor equipped with a three-bladed propeller at 430 rpm. The jar was kept inside a 0 °C ice–water bath during the mixing. TMPTA-N and TT1 were mixed for 1 min. After 1 min, the stirrer was turned off, and 6.48 mL of 1,1-bis(terbutylperoxy)-3,3,5-trimethylcyclohexane and 2.16 mL of triethyl amine were added to the mixture and mixed with the same stirrer and propeller at the same speed. After the mixing, a vacuum was applied to the solution for 1 h to remove dissolved gas. After the vacuum was applied, the jar was kept inside the cooling bath for 3.5 h more, and then it was taken out of the cooling bath. The initiator gel (1 cm³), which contained a photoinitiator and a thermal initiator, was held in the center of the solution with a needle, and the solution was left to gel for 1.5 h. The solution gelled after 6 h from the beginning of the application of the vacuum. After those 6 h, the gel was exposed to 365-nm radiation from a Novacure lamp, which had an intensity of 16 mW cm⁻², for 2 min to ignite the front in the center. The light guide was placed over the jar 10 cm from the center of the gel.

**Initiator Gel**

TMPTA-N (25.25 mL), 10.29 mL of TT1, 0.36 mL of 1-hydroxy-cyclohexyl-phenylketone, 0.74 mL of 1,1-bis(terbutylperoxy)-3,3,5-trimethylcyclohexane, and 0.092 mL of triethyl amine were mixed inside a 100-mL glass beaker with a magnetic stirrer for 5 min. The beaker was kept inside the ice–water bath for 5 h, after which it became a gel. After gelation, 1 cm³ of this gel was placed in
the center of the gel that contained only the thermal initiator.

RESULTS

With HDDA and persulfate, spherically propagating fronts were achieved (Fig. 2). The system was relatively easy to prepare, but no spin modes were observed. Cracking of the polymer was not observed until the front reached the walls or a free interface.

The thiol–ene system is much more sensitive to preparation, especially with scale-up: the thiol–acrylate reaction is exothermic, and it is essential that the solution not get too hot and decompose Luperox 231. This system readily supports spherical fronts. Figure 3 shows images of such a front. With a cube of gel containing a photoinitiator, it is possible to initiate fronts with different initial geometries (Fig. 4).

Not only does this system support spherical propagation, but spin modes can also be observed. A sequence of images is shown in Figure 5 for a descending front in a test tube. Figure 6 shows how the spin modes appear as waves of propagation along the surface of the expanding front. The arrow points to the leading edge of a spin mode, which is propagating toward the top of the sphere. Video images do not do justice to their ele-

Figure 4. Initiating fronts under nonspherical initial conditions with a cube of initiating gel. The diameter of the reactor was 8 cm.

Figure 5. Spin mode in a descending front of the thiol–ene system in a 1.5-cm-diameter test tube. The horizontal arrow indicates the direction of the spin mode. The vertical arrow indicates the direction of the overall front propagation.
gance; the human eye is far better at discerning the slightly raised region on the expanding polymerization front. Spin modes on the opposite side of the sphere also show through. We are currently working on methods to improve the imaging and characterization.

Another advantage of this system is that the gel can be cast in any shape to allow fronts to propagate in unusual geometries. Figure 7 presents a front propagating in a rectangular slab.

Why do spin modes occur in the thiol–acrylate system but not in the HDDA–DMSO system? We propose several factors. Persulfate was used to prevent bubbles with HDDA, being soluble in DMSO. We do not know how its energy of activation compares to peroxides such as Luperox 231. If it is lower, then that is a factor against spin modes. DMSO works against spin modes by lowering the front temperature and diluting the polymer so that the network forms at a higher conversion. We propose that the effective energy of activation for polymerization is thus reduced.

Although the thiol consumes some of the acrylate and thus reduces the front temperature, the remaining acrylate polymerizes in a gel, and this means its termination is reduced and the overall energy of activation is increased. Further studies are underway to test how the acrylate/thiol ratio affects the dynamics.

One limitation of this system is the cracking that occurs after the front propagates about a centimeter. The addition of plasticizers (phthalates) did not provide relief. Using more flexible monomers may reduce cracking, but an increase in the molecular weight/acrylate reduces the front temperature. However, because the cracking appears after the front passes, it should be possible to scale up the experiment to observe spin modes in even larger systems.

**CONCLUSIONS**

We have developed a novel system that supports spherically propagating thermal polymerization...
fronts. A gel is prepared by the reaction of a tri-thiol with a triacrylate in a 1:4 molar ratio by an amine-catalyzed Michael addition. A small piece of gel containing a photoinitiator can be inserted into the mixture as it gels. When gelation is complete, fronts are initiated by UV illumination and propagate from the center. The gel can be cast into different shapes. This approach works much better than using a multifunctional acrylate in DMSO with dissolved persulfate, which does not produce bubbles. The thiol–triacrylate gel prevents the appearance of bubbles from the peroxide initiator.

Spin modes were observed on the surface of the spherical fronts; this was a novel phenomenon never before observed with thermal fronts in condensed media. With a gel containing a photoinitiator, it was possible to initiate a front under rectangular initial conditions. The gel could be formed in rectangular slabs to observe fronts in quasi-two-dimensional media.

Future work will focus on determining the factors that affect the spin modes.

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REFERENCES AND NOTES