

Frontal Polymerization of a Cyanate Ester

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ABSTRACT: Thermal frontal polymerization is an exothermic process that uses a propagating wave to polymerize monomers via an external heat source, such as a soldering iron, to initiate front propagation. Herein, for the first time, the curing of a cyanate ester via thermal frontal polymerization is described with two different external heat sources. However, issues of bubbling due to vaporization of the amine catalyst generally resulted in incomplete frontal polymerization when a soldering iron was used as the external heat source. To counter this issue, dual-strip polymerization systems were used, wherein the heat from the exothermic polymerization of a free-radical system was used to initiate the frontal polymerization of a cyanate ester system with an amine catalyst. As a result, complete frontal polymerization occurred. Additionally, the effect of the width of the acrylate strip and its impact on the front temperature, initial velocity, and steady-state velocity of the adjacent cyanate ester system were studied. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Although frontal polymerization has been studied with different types of chemistries, including epoxy chemistry,^{1–4} polyurethanes,^{5,6} polyacrylate–polydicyclopentadiene networks,⁷ and thiolene chemistry,⁸ the frontal polymerization of a cyanate ester has not previously been investigated. Herein, cyanate esters were cured with two different types of frontal polymerization: thermal frontal polymerization and dual-strip frontal polymerization. In the first approach, cyanate esters with a liquid amine catalyst were cured with thermal frontal polymerization. Thermal frontal polymerization uses an external heat source to initiate a propagating front.⁹ Initially, different fillers and aniline catalyst concentrations were tested to determine the optimal reaction conditions for the frontal polymerization of the cyanate ester. Because bubbling was a major issue and hindered and quenched the propagating fronts, the effects of degassing the reactive components and adding a degasser also were evaluated.

Because the results were still inconsistent because of the vaporization of the amine catalyst in the first approach, a second approach, a dual-strip polymerization system, was developed. In this approach, one strip composed of one system (a free-radical acrylate system with a thermal initiator) self-propagates and releases enough exothermic heat to help initiate frontal poly-

merization in a second strip that contains the second system and that is adjacent to the first strip. The frontal polymerization of the cyanate ester with a liquid amine catalyst had inconsistent results when a soldering iron was used as the external heat source because of bubbling and void formation. The bubbling was due to the vaporization of the amine catalyst. To counter these issues, an external heat source with a known front temperature (i.e., the exothermic free-radical system) lower than that of the soldering iron, which was above 500°C in a matter of seconds, supplied enough heat to initiate frontal polymerization in the cyanate ester system with much less bubbling and voids. Less bubbling occurred because there was less vaporization of the liquid catalyst.

In a recent series of reports, Crivello and coworkers^{10–12} used frontal polymerization in a unique manner. They incorporated elements of cationic and photoinitiated polymerization together to cure epoxides. Like this study, they used one type of chemistry (cationic polymerization) to activate or help initiate a type of frontal polymerization. Herein, a multifunctional acrylate was used because multifunctional acrylates propagate at a much faster rate than monofunctional acrylates.¹³ The front temperatures of these systems can be as high as 250°C.¹⁴ The front velocities of the chosen acrylate, trimethylolpropane triacrylate (TMPTA-n), were faster than those of the corresponding

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cyanate ester resin systems because (1) TMPTA-n had a lower molecular weight per reactive functional group (99 g/mol per acrylate vs 132 g/mol per cyanate) and (2) the homopolymerization of the acrylate required fewer reactive functional groups to form one polymer unit (one acrylate and one initiator radical to form one polymer unit and three cyanate ester resins and one amine catalyst to form one triazine ring or polymer unit).¹³ Lower molecular weights per ene resulted in shorter initiation times.¹³

The front temperatures of these acrylate systems could be as high as 250°C.¹⁴ Previous work with ovens rather than thermal frontal polymerization and conducted by Bauer and Bauer determined that a temperature of 200°C was critical for the complete curing of cyanate esters. With a system with front temperatures in this range, the cyanate ester can be cured effectively without the formation of voids or bubbling observed when a soldering iron is used to initiate a front.

Because thermal diffusion is a key factor in thermal frontal polymerization, the initial amount of heat applied and/or the temperature of the external heat source affects the initial front propagation of the system. Additionally, the dimensions of the strip affect the front temperature. To determine how the width of the acrylate strip affected the front temperature, initial front velocity, and steady-state front velocity of the cyanate ester system, different widths of acrylate strips were tested.

EXPERIMENTAL

All reagents were used without further purification. Primaset LeCy (4,4'-ethylidenediphenyl dicyanate) was obtained from Lonza. Polygloss 90 and Cab-O-Sil (M-5, LM-150, and EH5) were obtained from Huber Materials and Cabot Corp., respectively. Aniline was obtained from Sigma Aldrich. BYK 060N was obtained from BYK Chemie.

Preparation of the Systems Used for the Homopolymerization of the Cyanate Ester

Initially, 1–8 g of aniline was dissolved in 100 g of Primaset LeCy to make 1–8 phr (parts per hundred resin) aniline in cyanate ester or 1–8 g of initiator per 100 g of monomer. To 10.0 g of this catalyst–monomer system was added 0.80–4.50 g of filler (Cab-O-Sil M-5, EH, or LM-150 or Polygloss 90). The resulting mixture was stirred thoroughly until a homogeneous putty was formed.

When the degasser, BYK 060 N, was added, about 0.1 g of it was added to 10.0 g of the monomer–catalyst solution before the addition of filler.

For some systems, the cyanate ester was degassed in a vacuum oven at room temperature for 2–24 h before use. Occasionally, the amine was degassed at room temperature in a vacuum oven for 2 h before use.

An example of a formulation is as follows: 10.0 g of 1 phr aniline in Primaset LeCy was mixed with 0.80 g of Cab-O-Sil M-5. Another example included 0.1 g of BYK 060 N being dissolved in 10.0 g of 4 phr aniline in Primaset LeCy. The resulting liquid

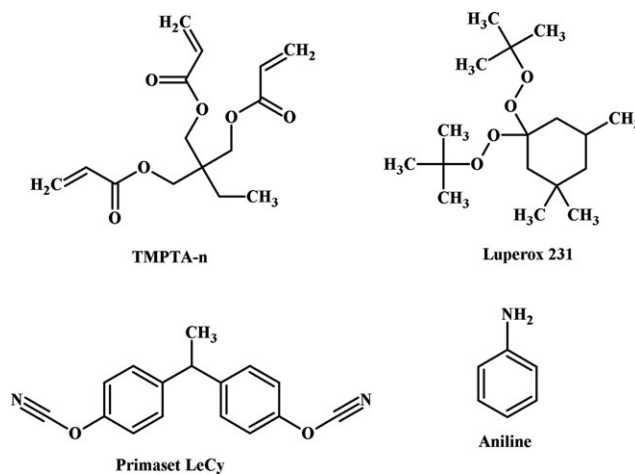


Figure 1. Structures of the reactants used.

solution was then mixed with 4.50 g of Polygloss 90 until a homogeneous putty was formed.

Ignition of the Propagation in Polymerizable Systems

The homogeneous putties were made into strips with dimensions of 2 cm × 4 cm × 5–7 mm and were placed on a 2-cm thick piece of wood surrounded by wooden barriers. A front was ignited at one end of the strip with a soldering iron. The soldering iron was applied (for times <30 s to 5 min) at one end of the strip until a propagating front was observed. The front temperature was measured with an 450 AKT Omega reader and a type K thermocouple wire situated in the center of the strip. Movies of some of the strips were recorded with an iSight camera connected to a PowerBook G4 Macintosh computer running iMovie. The front velocity was calculated by a plot of the distance versus time and with the slope of linear regression taken as the velocity.

Dual-Strip Preparation and Ignition

Initially, for the free-radical system, 10.4 g of Luperox 231 [1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane] was dissolved in 100 g of TMPTA-n to make 10.4 phr Luperox 231 in TMPTA-n. Next, 0.80 g of filler was mixed with 10.0 g of 10.4 phr Luperox 231 in TMPTA-n until a homogeneous putty was formed. In a second vial, 5.0 g of aniline was dissolved in 100 g of Primaset LeCy to make 5 phr aniline in Primaset LeCy. To 10 g of 5 phr aniline in Primaset LeCy was added 0.8 g of filler; the resulting mixture was stirred until a homogeneous putty was formed. The structures of the catalysts and monomers used are shown in Figure 1.

Strips with dimensions of 0.1–2.0 cm wide × 4.0 cm long × 5–7 mm thick for the free-radical system were placed adjacent to cyanate ester system strips that were 2.0 or 7.5 cm long × 5–7 mm thick × 4.0 cm wide with the 4.0-cm edge of each strip adjacent to and touching each other. An image of the basic setup, including the wooden barriers and point of contact with the soldering iron, is shown in Figure 2(a). An image of the setup showing how the fronts propagated is shown in Figure 2(b).

A soldering iron was applied briefly (<10 s) at the juncture where the two strips met. The front temperature was

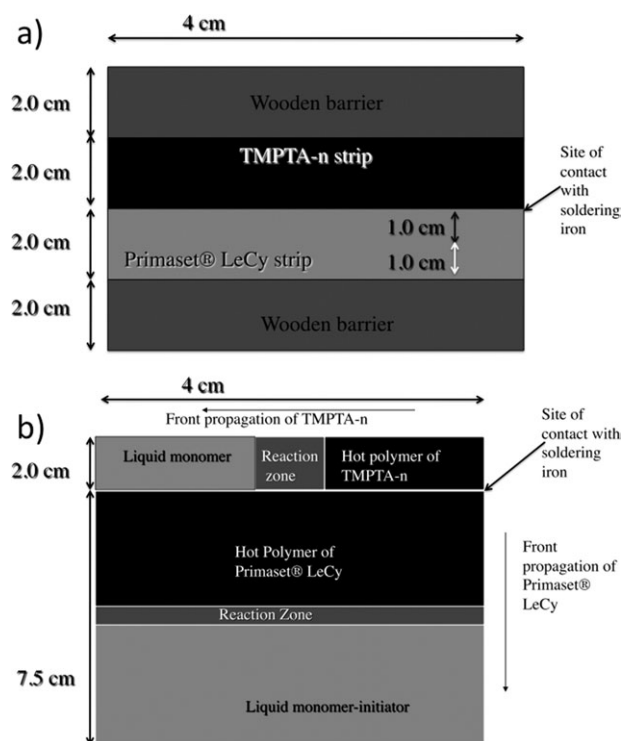


Figure 2. Dual-polymer system setup with the initial setup and propagating fronts.

measured with an Omega reader and type K thermocouple wire. The thermocouple wire was situated in the center of the cyanate ester system strip. Occasionally, the wire was situated in the center of the free-radical system strip to determine the temperature of the propagating front of the TMPTA-n system. Occasionally, the wire was also situated at middle of the border where the two strips touched or were adjacent to each other to determine the maximum temperature in this region. Movies of the propagating front were recorded with a camera before they were transferred to a computer. The front velocity for the acrylate strips was calculated by a plot of the distance versus time and with the slope of linear regression taken as the velocity. The initial front velocity for the cyanate ester resins was determined from a plot of distance versus time for the first centimeter that the cyanate ester propagated [the black arrow region in the Primaset LeCy strip in Figure 2(a)]. The steady-state front velocity for the same cyanate ester resin strip was determined by a plot of the distance versus time for the remaining portion of the cyanate ester that propagated [the white arrow region in the Primaset LeCy strip in Figure 2(a)].

RESULTS AND DISCUSSION

Frontal Polymerization of a Cyanate Ester

To achieve frontal polymerization, heat loss must be minimized. Heat loss can occur because of buoyancy-driven convection. The addition of enough filler to a liquid monomer-catalyst system to form a putty could be used to minimize heat loss from buoyancy-driven convection.¹⁷ Initial studies with the frontal

polymerization of cyanate esters tested different fillers, including kaolin clay and fumed silica, to determine the best filler to achieve a puttylike consistency. Three fumed silicas, Cab-O-Sil M-5 (untreated fumed silica), Cab-O-Sil EH-5 (a high-surface-area fumed silica), and Cab-O-Sil LM-150 (a low-surface-area fumed silica), and one ultrafine kaolin clay, Polygloss 90, were tested. Because of the different properties (different surface areas, bulk densities, particulate size, etc.) of the fillers, 10.0 g of the same Primaset LeCy-aniline system required different amounts of filler to achieve a puttylike consistency. Cab-O-Sil M-5 and Cab-O-Sil EH-5 required about 0.80 g of filler, whereas Cab-O-Sil LM-150 required about 0.90 g of filler to achieve a puttylike consistency. Although these fumed silicas had the same particle size (0.2–0.3 μm), differences in the surface area (200–380 m^2/g for Cab-O-Sil M-5 and EH-5 vs 130 m^2/g)^{18,19} required different loadings. The silica with the highest surface area, Cab-O-Sil EH-5, produced samples with the highest viscosity or consistency because of this highest surface area. Ultrafine kaolin clay required 4.50 g of filler to achieve a puttylike consistency. A much larger filler loading was required for the kaolin clay because of its much smaller surface area (22 m^2/g).^{19,20}

Once systems with puttylike consistencies were achieved, the initiator concentrations were varied between 1 and 8 phr aniline in the cyanate ester resin. Previous studies with other monomers established minimum initiator concentrations of 1 phr initiator in the monomer with maximum velocities achieved around 5–6 phr of initiator in the monomer.¹⁴ Because prior research with acrylates used initiator concentrations of 1 phr (1 g of initiator per 100 g of monomer or resin),¹⁴ the initial experiments tested Primaset LeCy systems with a minimum initiator concentration of 1 phr aniline in the cyanate ester with a maximum initiator concentration of 8 phr aniline in Primaset LeCy. Void formation and bubbling occurred in all of the tested systems, despite the various filler choices and initiator concentrations. An image of void formation is shown in Figure 3.

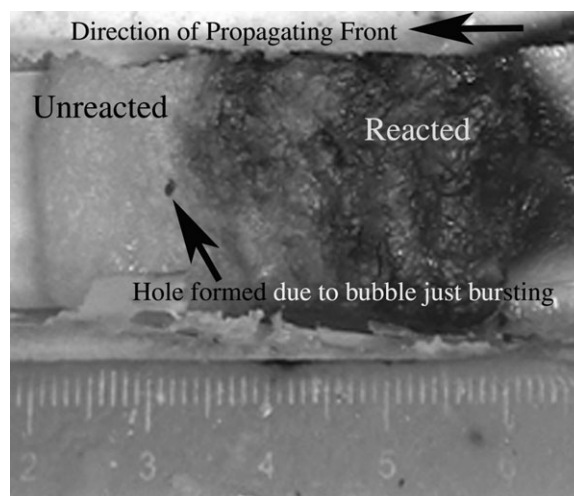


Figure 3. Example of the void formation in 3.6-phr aniline in the Primaset LeCy system with Cab-O-Sil M-5.

The dark spot or hole shown in Figure 3 was due to a burst bubble as amine evaporated off. This bubbling occurred because of the evaporation of the amine catalyst and generally occurred whenever a soldering iron was applied to one end of the strip. The length of time to ignite a front in a strip varied from less than 30 s to 5 min. With higher initiator concentrations, the time to ignite the front decreased from 5 min (for 1 phr aniline) to 30 s (for 5 phr aniline). In corresponding acrylate systems, frontal polymerization could be ignited in 30 s or less via the application of a soldering iron. Acrylates require less time to ignite a front for multiple reasons: they have lower molecular weights per reactive functional group and numbers of reactive functional groups required to form one polymer unit.²¹ Different acrylates require different times to ignite a front because of the differences in the molecular weight per ene.¹³

Although shorter ignition times occurred with higher aniline concentrations for the cyanate ester resin systems, more bubbling also occurred with higher initiator concentrations; this suggested that void formation was occurring because of the vaporization of the amine catalyst. The front temperatures of these systems with high initiator concentrations (5–8 phr aniline in Primast LeCy) had a maximum temperature of 304°C and a velocity of 1 cm/min. However, void formation and bubbling occurred and resulted in inconsistent results. As such, reproducibility was an issue because the same system could result in incomplete frontal polymerization, complete frontal polymerization, or no frontal polymerization at all with temperature ranges varying by as much as 100°C. Because of void formation, this range in front temperatures occurred despite the thermocouple wire situated in the center of the strip. Void formation resulted in the thermocouple wire registering a cooler temperature because of a lack of polymerization occurring at that spot where the thermocouple wire was situated. I made visual confirmation of the lower temperatures occurring because of void formation by slicing the strip open and observing a hole or gap in the region of the strip where the thermocouple wire was situated and with the thermocouple wire having little to no polymerized material on it. In instances where frontal polymerization rather than bubbling or void formation occurred, higher front temperatures were recorded, and the thermocouple wire was surrounded by yellow or brown polymerized material.

Despite void formation and bubbling, an increase in the initiator concentration resulted in both higher initial temperatures (the point before the soldering iron was applied) and maximum or front temperatures of the systems. For Cab-O-Sil M-5 systems, an increase in the amine concentration from 1 to 5 phr aniline resulted in shorter pot lives (the length of time it took for spontaneous polymerization to occur) and higher initial temperatures (28–70°C) before a soldering iron was applied. However, temperatures for the different initiator concentrations varied wildly, with temperatures as low as 120°C and as high as 306°C for 5 phr aniline. For the 5 phr aniline in the cyanate ester system with a maximum temperature of about 250°C or lower, the thermocouple wire had little polymerized material stuck to the tip of the thermocouple

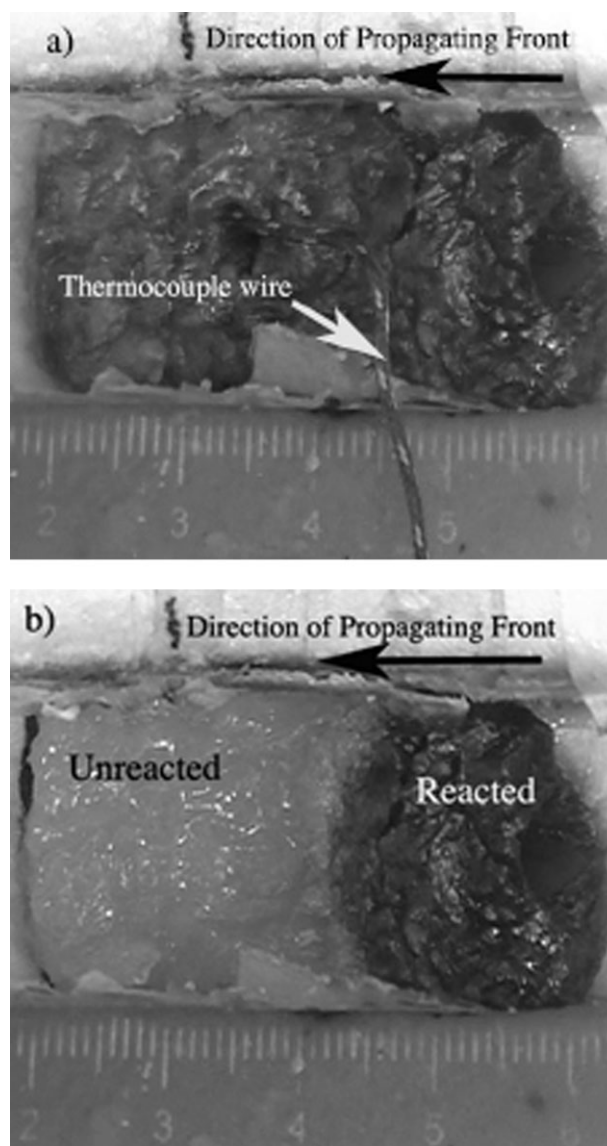


Figure 4. Images of the (a) complete polymerization of cyanate ester for 5-phr aniline in Primaset LeCy and (b) the propagating front for the same system.

wire and had a small hole or gap (<1–2 mm in area) between the thermocouple wire and the polymerized material. For another 5 phr aniline in the cyanate ester system with a maximum temperature of 306°C, the thermocouple wire was covered completely with brown polymerized material. The front velocities of these systems varied between 0.5 and 1 cm/min, with lower front velocities occurring for systems having lower maximum recorded temperatures.

Although the complete frontal polymerization of a cyanate ester with an amine catalyst was achieved for the first time, the results were inconsistent. The complete frontal polymerization for the Cab-O-Sil M-5 systems occurred for systems with an initiator concentration of 3.6–5 phr aniline in Primaset LeCy. An image of a propagating front for the cyanate ester system is shown in Figure 4.

For different fumed silica systems, such as that of Cab-O-Sil EH-5, the front temperatures ranged from 94 to 304°C, with higher initiator concentrations resulting in higher temperatures and shorter pot lives. The pot lives were shortened from 30 min for 4 phr aniline to 5 min for 6 phr aniline in Primaset LeCy so that spontaneous polymerization occurred before a front could be initiated. In marked contrast to the Cab-O-Sil systems, which had limited success in achieving frontal polymerization, the variation of the initiator concentration from 1 to 8 phr aniline in Primaset LeCy for kaolin clay-containing systems resulted in no frontal polymerization for any of these initiator concentrations; this was most likely due to the changing consistency of the systems (from puttylike to liquid/gel-like), which resulted in fluid flow quenching of any front at the site of the contact with the soldering iron. Also, more bubbling occurred with corresponding kaolin clay systems than with the fumed silica systems. Some bubbling could have been due to the presence of water. Although enough filler was added to kaolin clay systems to achieve a puttylike consistency, the kaolin clay systems lost their puttylike consistency within minutes of preparation and, instead, acquired a more fluidlike consistency. This was possibly due to the aluminum present in the kaolin clay. Aluminum is known to act as a catalyst for the curing of cyanate esters.²² The fumed silica systems retained their puttylike consistency.

Because bubbling and the formation of voids were issues for both the fumed silica and kaolin clay systems, Primaset LeCy and/or aniline were degassed from 2 to 24 h and for 2 h, respectively. Degassing the amine reduced the formation of bubbles a little but had little impact on the initiation of frontal polymerization. Degassing the cyanate ester 24 h before use resulted in less bubbling, but the formation of bubbles could still be seen with higher amine concentrations. Bubbling is known to occur because of the vaporization of a liquid, such as a phase-change material, and occurs at front temperatures above the boiling or melting point of the phase-change material and can result in quenched fronts.^{23,24} Because aniline boils at 184°C and the temperature of the soldering iron was known to be over 500°C, bubbling at the site of contact with the soldering iron was thought to be due to vaporization of the amine catalyst. The possibility of water causing bubble and void formation was eliminated by the drying or degassing of the monomer and aniline catalyst. Thus, an alternative means of igniting a front in the cyanate ester system with a liquid amine catalyst was examined.

Dual-Strip Frontal Polymerization

To verify that a cyanate ester resin with a liquid amine catalyst can be cured consistently via frontal polymerization and simply requires an external heat source at a lower temperature than a soldering iron to ignite, dual-strip frontal polymerization was used. Two strips composed of different systems were placed adjacent to each other in the setup depicted in Figure 2(a). After a soldering iron was applied briefly at the point between the two systems and as indicated in the setups in Figures 2(a) and 5(a), the free-radical polymerization system (TMPTA-n with Luperox 231 as the thermal initiator) polymerized completely with a front temperature of about 250°C (at the center of the strip). The heat from this strip helped to

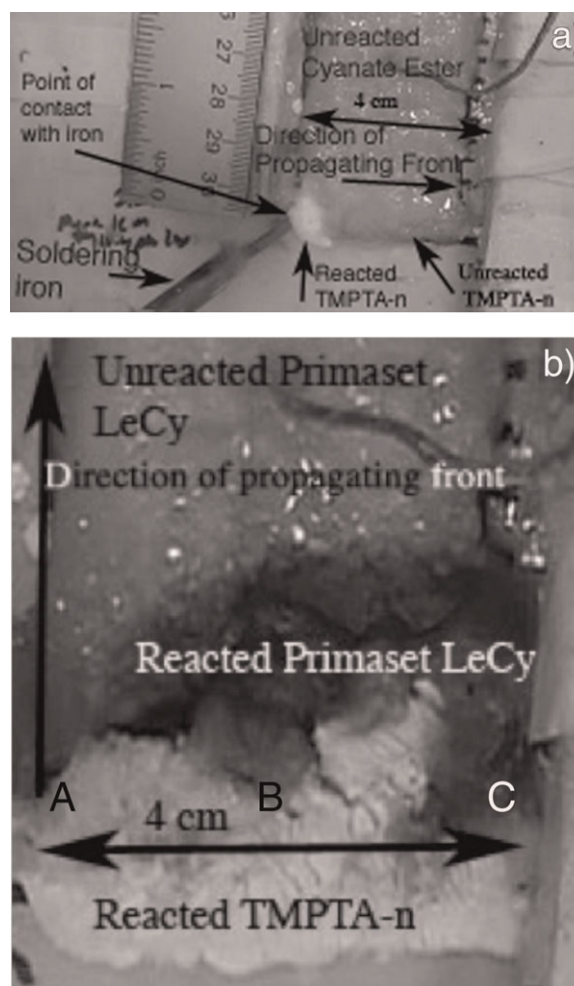


Figure 5. Images of the (a) propagating TMPTA-n front and (b) propagating cyanate ester front.

ignite the Primaset LeCy propagation perpendicular to the propagating front of the TMPTA-n strip, as shown in Figure 2(b). Within 20 s of the TMPTA-n strip completely polymerizing, a cyanate ester system's front perpendicular to the TMPTA-n system's front began to propagate and achieved a maximum front temperature of 400°C. An image of the cyanate ester front is shown in Figure 5(b).

Complete polymerization of the cyanate ester occurred within minutes; this proved that a cyanate ester could propagate via thermal frontal polymerization. It simply required a lower temperature heat source than a soldering iron.

The soldering iron was applied at the point between the cyanate ester strip and the acrylate strip, as shown in Figure 5(a), with the frontal polymerization of the TMPTA-n strip occurring at the site of contact with the soldering iron. In contrast, the frontal polymerization of the cyanate ester resins started simultaneously at center of the strip where the TMPTA-n and Primaset LeCy systems pointed [the point labeled B in Figure 5(b)] and at the point furthest away from the site of contact with the soldering iron and the point where the TMPTA-n and cyanate ester resins touched [the point labeled

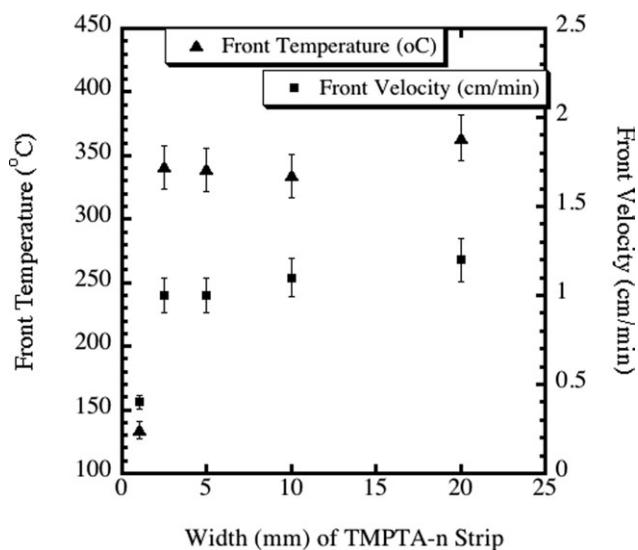


Figure 6. Plot of the front temperature and steady-state velocity for Primaset LeCy strips as a function of width of the TMPTA-n strip.

C in Figure 5(b)]. The initial site of contact with the soldering iron and the two different strips is labeled A in Figure 5(b) and is labeled and shown in Figure 5(a). Because the frontal polymerization of the cyanate ester started as far away as possible from this site of contact with the soldering iron but still close to the edges where the TMPTA-n and Primaset Le Cy regions touched, the frontal polymerization of the cyanate ester resin must have been ignited from the heat of the polymerized TMPTA-n strip rather than from the initially hotter region where the soldering iron was applied. Thus, the lower temperature of the TMPTA-n strip was hot enough to ignite the frontal polymerization of the cyanate ester without boiling off the amine catalyst.

This process worked for this system because aniline has a boiling point of 184°C, and the front temperature of the TMPTA-n strip in the center of the strip was about 250°C, which was much lower than the temperature of the soldering iron. The temperature at the point between the two strips was about 150–200°C. Because of heat loss to the surrounding air, the front temperature of the TMPTA-n strip varied, with the edges and surface of the TMPTA-n strip at lower temperatures than the recorded maximum temperature. Having the Primaset LeCy system's front propagate perpendicular to the edge of the hot TMPTA-n polymerized strip rather than at the site of the contact with the soldering iron demonstrated that the cyanate ester strip was initiated from the heat of the acrylate strip rather than from that of the soldering iron.

The cyanate ester strip, which was not mixed with the free-radical system, used heat from the exothermic propagation reaction as an external heat source to initiate its own frontal polymerization reaction and only started to propagate after the free-radical system was completely polymerized. The frontal polymerization of the cyanate ester was not continuously heated by the polymerization of the free-radical system and propagated perpendicularly to the free-radical system's strip. Thus, the cyanate ester system used heat from the exothermic propagation reaction as an external heat source to initiate its own frontal polymerization reaction; this demonstrated a unique method of initiation.

Because thermal diffusion is a controlling facet of frontal polymerization, systems with different dimensions for strips will produce different front temperatures and velocities. To determine how heat from one frontally propagating system could affect another system adjacent to it, different widths of acrylate strips were tested.

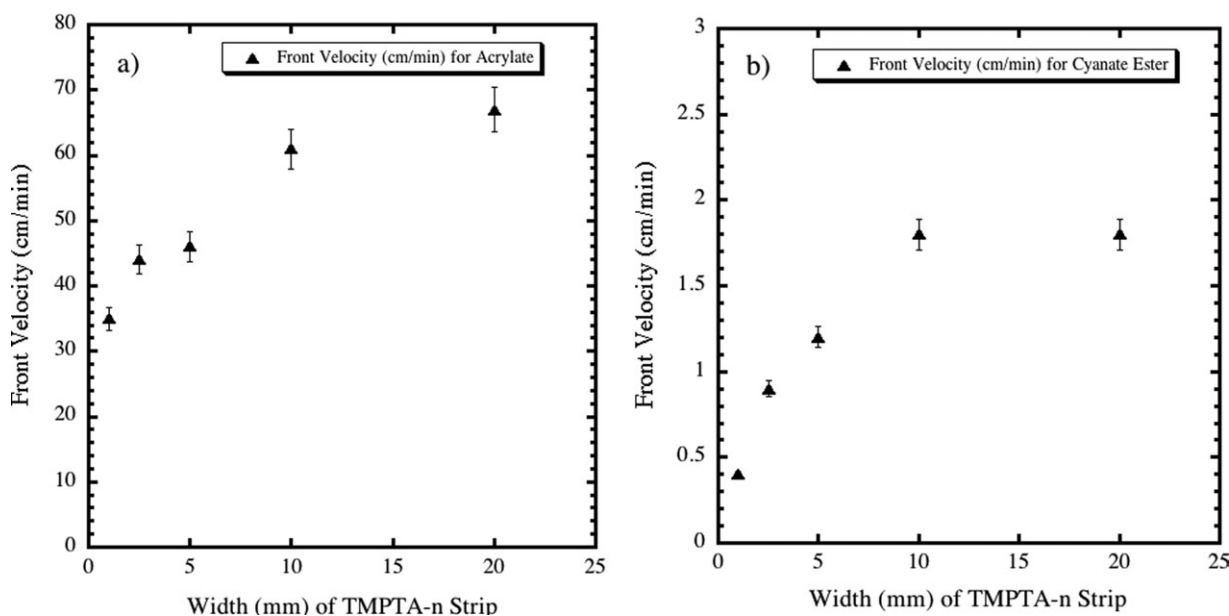


Figure 7. Plot of the front velocity of the (a) TMPTA-n strip and (b) initial front velocity of the Primaset LeCy strip as a function of the width of the TMPTA-n strip.

With increasing strip width of the acrylate system, the front velocity initially increased for the cyanate ester system, as shown in Figure 6, but, thereafter, did not change or changed very little. The front temperature of the cyanate ester systems normally was not affected. For 1.0 mm strips, the front temperature and velocity of the Primaset LeCy system were much lower than those of any of the other cyanate ester systems because the acrylate system lost a large amount of heat to the surrounding air and had a great deal of its strip exposed to and surrounded by air. With increasing width, less acrylate was exposed to air so that less heat was lost to the surrounding air. For acrylate strips with widths of 2.5 mm and greater, the changing dimensions of the acrylate strip did not affect the front temperature or velocity of the cyanate ester strip once a steady state was achieved. A steady state in front velocity was achieved once 1 cm of the cyanate ester strip had propagated.

In contrast, the width of the acrylate strip affected the initial front velocity of the cyanate ester strip before a steady state was achieved [Figure 7(b)]. The front velocity was measured at periodic intervals, including those close to the point where the two systems were adjacent. The front velocity eventually reached a steady state. However, the initial velocity close to the site of contact with the soldering iron reached higher front temperatures and velocities because of the larger amount of heat available from the applied heat source. Reducing the width of the acrylate strip reduced the amount of heat available for diffusion from the polymerized acrylate strip to the adjacent cyanate ester strip. As a result, the initial amount of heat applied to initiate frontal polymerization in the Primaset LeCy system was reduced; this resulted in lower front velocities for the cyanate ester strips adjacent to acrylate strips with lower widths.

To further highlight how the front velocity was affected by the dimensions of the strip and the amount of reactive material present and how thermal diffusion is a controlling factor in frontal polymerization, the front velocities for the TMPTA-n and Primaset LeCy strips were plotted as a function of the width of the TMPTA-n strip, as shown in Figure 7.

As the plot in Figure 7(a) demonstrates, increasing the width of the TMPTA-n strip resulted in higher front velocities for the acrylate strip. This increase was due to an increasing amount of reactive material present so that more heat was released. Furthermore, increasing the TMPTA-n strip width resulted in higher initial front velocities for the Primaset LeCy strips [Figure 7(b)] because of the higher initial amount of heat from the TMPTA-n strip diffusing into the cyanate ester strip. Eventually, a steady state in front velocity was achieved, and the front velocity was not affected by the width of the acrylate strip (as shown in Figure 6) because heat from the strip was no longer providing the means to ignite the front. Instead, the cyanate ester resin was self-propagating and used heat from its own polymerization reaction to drive its cyclotrimerization reaction or polymerization. Results with this dual-strip system were reproducible, and we repeated the experiment multiple times to ensure reproducibility. As a result, the graphs in Figures 6–7 show an experimental uncertainty of 10%.

CONCLUSIONS

For the first time, the thermal frontal polymerization of a cyanate ester was achieved, albeit sometimes with inconsistent results. Fumed silica was the optimal filler because the systems retained their puttylike consistency. Lower initiator concentrations of 1 phr initiator in the monomer may work for acrylate systems, but higher initiator concentrations were required for the cyanate ester systems. Although the results were inconsistent for complete frontal polymerization with a soldering iron, a dual-polymerization system rather than the more traditional route with a soldering iron resulted in consistent results and complete frontal polymerization. The higher temperature of a soldering iron initially resulted in so much aniline being evaporated off that bubbles and voids hindered the frontal polymerization so that lower initiator concentrations occurred. As a result of void formation and bubbling, heat could not diffuse effectively into the surrounding region and initiated polymerization well enough to produce consistent results. Thus, thermal diffusion was an important factor and controlled the frontal polymerization.

The initial amount of heat applied via an external heat source affected the initial front velocity of the cyanate resin system as it started to reach a steady state, but once a steady state was reached, the steady-state front velocity was not affected by the initial amount of heat applied via an external heat source, for example, the width of the acrylate strip. Additionally, the input of heat from the external heat source did not affect the front temperature of the cyanate ester strip because the front temperature was measured in the center of the cyanate ester strip rather than at one end of the strip or at the edge where the two strips touched or were adjacent to each other. As expected, increasing the amount of reactive material for the acrylate present resulted in higher front velocities and temperatures for the acrylate system strips (but not for the cyanate ester system strips) because more heat was released/produced from the homopolymerization of the acrylate. For the acrylate strip, more heat was released because more acrylate was present or available, and it underwent exothermic polymerization. Thus, although the frontal polymerization of the cyanate ester with the liquid amine catalyst was achieved through the traditional use of a soldering iron, the results were inconsistent. However, the use of a less exothermic heat source resulted in few voids and bubbles and a higher initiator concentration so that frontal polymerization could be achieved consistently and with reproducible results.

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