

# The Effect of a Trithiol and Inorganic Fillers on the Photo-Induced Thermal Frontal Polymerization of a Triacrylate

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**ABSTRACT:** Thermal frontal polymerization is a process in which a localized reaction propagates through an unstirred system by the coupling of the thermal diffusion and the Arrhenius kinetics of an exothermic polymerization. A trithiol was found to affect the front velocity and the time for inducing a front upon exposure to UV light for trimethylolpropane triacrylate polymerization fronts with either kaolin or calcium carbonate filler present. The addition of trithiol and filler both decreased the front velocity. © 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 46: 8091–8096, 2008

**Keywords:** addition polymerization; frontal polymerization; kinetics (polym.); radical polymerization

## INTRODUCTION

Frontal polymerization is a process in which the reaction propagates directionally through the reaction vessel. To date three main types of frontal polymerizations have been reported: thermal frontal polymerization (TFP), which uses an external energy source to initiate the front<sup>1–4</sup>; photofrontal polymerization in which the localized reaction is driven by an external UV source applied continuously<sup>5–9</sup>; and isothermal frontal polymerization (IFP), which relies on the Norrish-Trommsdorff or gel effect,<sup>10,11</sup> that occurs when monomer and initiator diffuse into a polymer seed (small piece of polymer).<sup>12</sup>

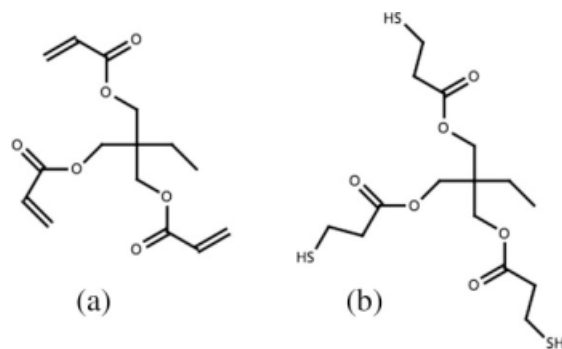
Herein, we focus attention on TFP that is initiated by light. Traditionally, TFP is initiated when a heat source contacts a solution of monomer and thermal initiator. Alternatively, a UV source can be used to initiate TFP if a photoinitiator is present as well as a thermal initiator.<sup>13</sup> The irradiation at the top air/liquid interface of a sample initiates a free-radical or cationic polymerization process, and the light is then terminated before the subsequent TFP begins. The energy from the exothermic photopolymerization diffuses into the adjacent region, raising the temperature and decomposing a thermal initiator. The result is a localized thermal reaction zone that then propagates through the reactants as a thermal wave.<sup>1–4</sup> The simplest example is a front propagating along the length of a glass tube.

An overwhelming majority of work with TFP has centered on free-radical homopolymerization of linear polymer systems, but other chemistries, such as anionic polymerization of  $\epsilon$ -caprolactam,<sup>14,15</sup> ring-opening metathesis polymerization,<sup>16</sup>

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**Figure 1.** Monomer structures: (a) trimethylol propane triacrylate (TMPTA) and (b) trimethylol propane tris(3-mercaptopropionate) (Trithiol).

polymerization of polyacrylate-poly(dicyclopentadiene) crosslinked networks,<sup>17</sup> dual cure epoxy-acrylate binary systems,<sup>18</sup> isocyanate-alcohol polymerization of polyurethanes,<sup>19–21</sup> atom-transfer radical polymerization,<sup>22</sup> thiol-ene polymerization,<sup>23</sup> hybrid free-radical-cationic systems, and photocurable cationic systems.<sup>24–28</sup> Several works have also been published recently on TFP of other systems.<sup>29–32</sup> A comprehensive bibliography of frontal polymerizations can be obtained at the website listed in reference.<sup>33</sup>

In work that sets the stage for the present investigation, Nason et al.<sup>13</sup> reported the UV-induced TFP of a series of acrylates and methacrylates. It was found that the delay time in igniting a front could be controlled by the photoinitiator and peroxide concentrations as well as the addition of a multifunctional thiol comonomer which simultaneously reduced oxygen inhibition while taking part in thiol-acrylate copolymerization that competed with the acrylate homopolymerization. The thiol lowered the time required to initiate the front as it reduced the oxygen inhibition at the surface where the frontal polymerization was initiated, but due to the slower rate of the thiol-acrylate copolymerization, the front velocity decreased with an increase of the thiol concentration.

In view of the success<sup>13</sup> in using multifunctional thiols to reduce the time required to initiate the frontal polymerization in nonfilled systems of the simultaneous acrylate and thiol-acrylate copolymerization in transparent mixtures, it is reasoned that multifunctional thiols may be effective in providing a conduit for initiating the frontal polymerization of highly filled acrylate systems, which are essentially impossible to initiate photolytically otherwise due to extensive oxygen inhibition at the surface resulting from competi-

tive light absorption/scattering resulting from the filler. Frontal polymerization of highly filled systems is very important, as fillers can enhance the mechanical properties of the final cured network while reducing cost. As well, the fillers can lower the front temperature, which can reach temperatures as high as 250 °C in unfilled systems. In our investigation we use kaolin, a typical hydrous aluminosilicate clay<sup>34</sup> typically used as a reinforcing agent in plastics and calcium carbonate<sup>34,35</sup> as representative fillers. We did not measure the front temperature but focused on front velocity and the effect of filler on the photoinitiation of the fronts and the resulting front velocities.

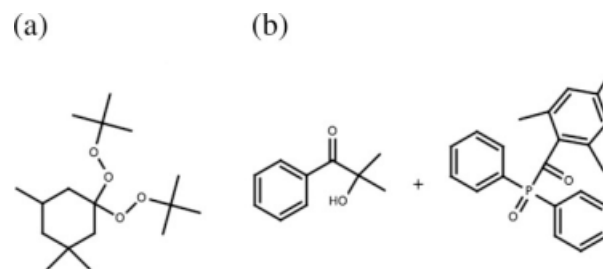
## EXPERIMENTAL

### Materials

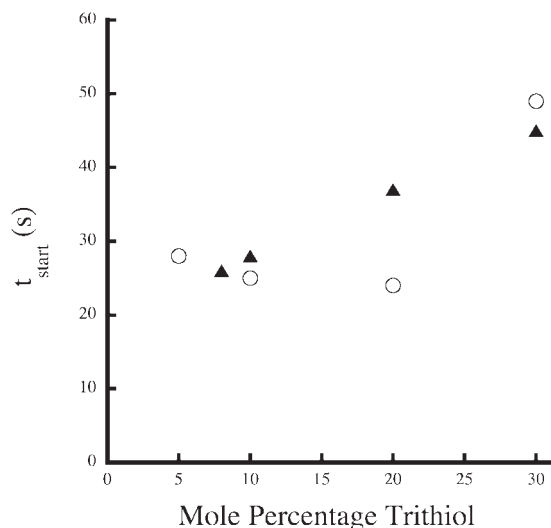
Figures 1 and 2 show the structures of the reactive monomers and initiators, respectively. The triacrylate was obtained from UCB. Trimethylol propane tris(3-mercaptopropionate) (Trithiol) was purchased from Hampshire Chemicals. Luperox 231 (1,1-di(*t*-butylperoxy)-3,3,5-trimethylcyclohexane) was obtained from Atofina, and benzoyl peroxide was purchased from Aldrich Chemical Company. The photoinitiators Darocur 4265 and Darocur 1173 were obtained from Ciba Specialty Chemical Company. The two fillers, Hubercarb FG-1 (calcium carbonate) and Huber 80 (kaolin), were obtained from J. M. Huber Corporation. All chemicals were used as received. Test tubes were purchased from VWR Scientific, and clear test tube labels were purchased from Wale Apparatus.

### Frontal Polymerization

The polymerizable systems were mixed with the photoinitiator and the thermal initiator and



**Figure 2.** Initiator structures: (a) Luperox 231 (1,1-di(*t*-butylperoxy)-3,3,5-trimethylcyclohexane); (b) 2-hydroxy-2-methyl-1-phenylpropanone; and 2,4,6-trimethylbenzoyldiphenylphosphine oxide (Darocur 4265).



**Figure 3.** (a)  $t_{\text{start}}$  as a function of mole percent Trithiol with calcium carbonate ( $\blacktriangle$ ); irradiance = 30 mW/cm<sup>2</sup>. (b)  $t_{\text{start}}$  as a function of mole percent Trithiol with kaolin (o); irradiance = 25 mW/cm<sup>2</sup>.

transferred to a 13 mm  $\times$  100 mm test tube with a clear ruler affixed to the side. The test tube was filled to within 1 cm of the top of the test tube and then clamped into place in a holder underneath the light source. Polymerizations were initiated in air-saturated samples. A high-intensity EFOS lamp system was used to induce the front photolytically with a light intensity of 25–40 mW/cm<sup>2</sup> measured by a radiometer from International Light Inc. Filler caused the system to be opaque, and hence, an infrared camera was used to observe the frontal velocity. The time for the front to travel 3 cm from the initial irradiation point is defined as  $t_{\text{start}}$ . The front velocity was measured after a steady-state velocity was attained, that is, after the front had traveled 3 cm. All samples, except in the case of Figure 7, had  $\sim$ 1 wt % Darocur 4265 [see Fig. 2(b) for component structure], and samples with calcium carbonate, except for Figure 8, had  $\sim$ 0.125 wt % Luperox 231 [see Fig. 2(b) for structure], whereas samples with kaolin had  $\sim$ 0.1 wt % Luperox 231.

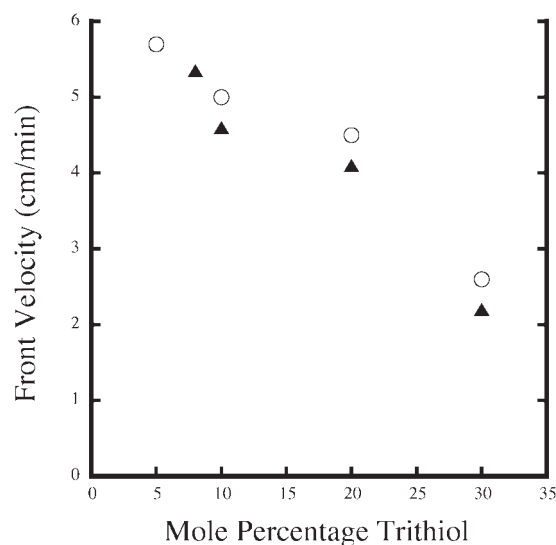
## RESULTS

### Frontal Polymerizations

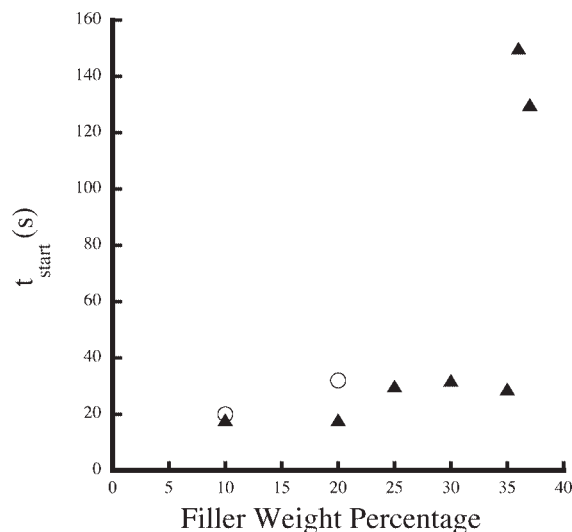
UV-induced frontal polymerizations were performed on a TMPTA-Trithiol system with peroxide, photoinitiator, and a filler (either kaolin or calcium carbonate). Figure 3(a), a plot of  $t_{\text{start}}$  versus mole percentage Trithiol with calcium carbon-

ate added, clearly shows that the presence of a critical concentration of Trithiol is needed to achieve frontal polymerization since at 0 and 5 mol % Trithiol, a front is not induced photolytically, but at 8 mol % Trithiol a front can be initiated. Thiols reduce oxygen inhibition in acrylate polymerization, as observed for unfilled frontal polymerization systems<sup>13,23</sup> and reported for coatings.<sup>36–38</sup> In an unfilled system, the front starts without the addition of thiol because the effective light intensity is greater due to the absence of filler and able to overcome oxygen inhibition. When filler is added, oxygen inhibition becomes a significant factor because the filler is competing with the photoinitiator for the absorption of light, and the rate of radical production is diminished. At high Trithiol concentration (35 mol %), frontal polymerization could not be induced photolytically. This is due to two reasons. First, the enthalpy of the thiol-acrylate copolymerization ( $-62$  kJ/mol of ene) is lower than for the acrylate homopolymerization ( $-80$  kJ/mol).<sup>13</sup> Second, the thiol-acrylate reaction is slower than the acrylate homopolymerization.<sup>13</sup> Figure 3(b) shows the same behavior with a different filler, kaolin. At very low (0.1 mol %) and high (40 mol %) concentrations of Trithiol, the frontal polymerization could not be induced photolytically.

Figure 4 shows the same trend for the front velocity when calcium carbonate or kaolin was

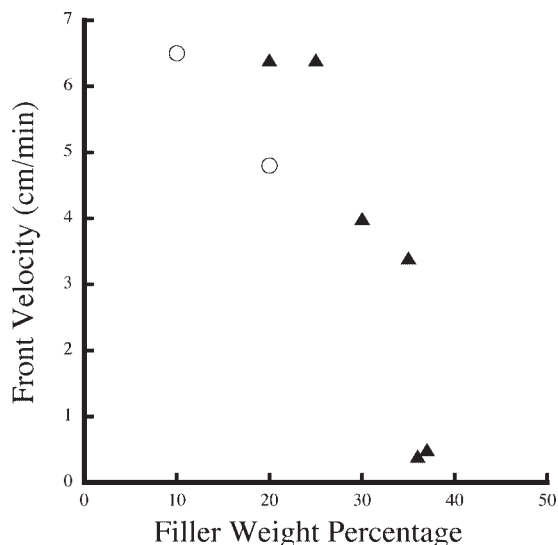


**Figure 4.** (a) Front velocity as a function of mole percentage Trithiol with calcium carbonate ( $\blacktriangle$ ); irradiance = 30 mW/cm<sup>2</sup>, (b) Front velocity as a function of mole percent Trithiol with kaolin (o); irradiance = 25 mW/cm<sup>2</sup>.



**Figure 5.** (a)  $t_{\text{start}}$  as a function of calcium carbonate concentration (▲); irradiance = 36 mW/cm<sup>2</sup>, (b)  $t_{\text{start}}$  as a function of kaolin concentration (○); irradiance = 25 mW/cm<sup>2</sup>.

present, that is, as the concentration of Trithiol was increased, the front velocity decreased. This was also observed for unfilled systems.<sup>13</sup> When the concentration of Trithiol reached ~35%, frontal polymerization could not be initiated/sustained. Again, this is due to the lower enthalpy of reaction and the slower rate of the thiol-acrylate polymerization process.

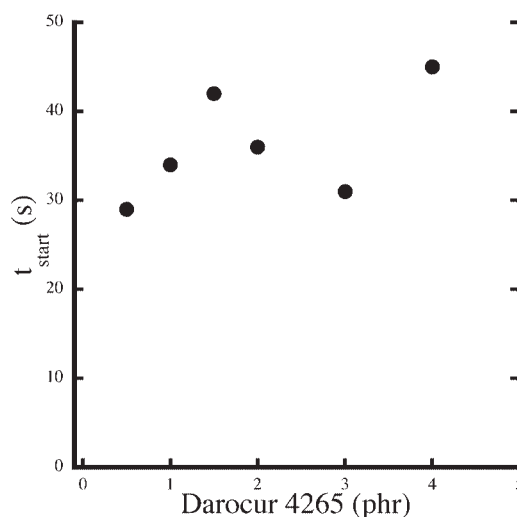


**Figure 6.** (a) Front velocity as a function of calcium carbonate concentration (▲); irradiance = 36 mW/cm<sup>2</sup>, (b) Front velocity as a function of kaolin concentration (○); irradiance = 25 mW/cm<sup>2</sup>.

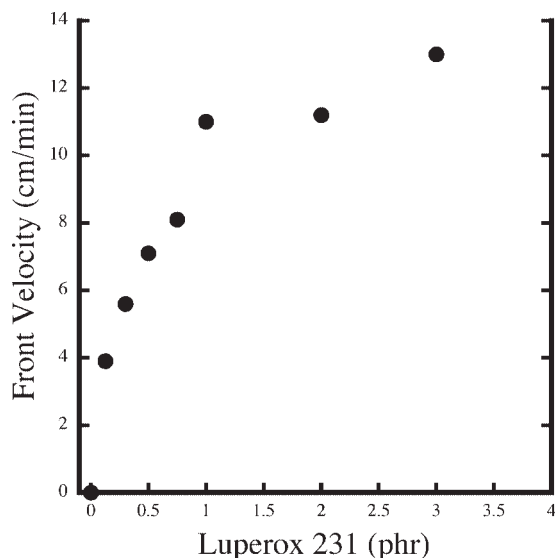
Figure 5 contains plots of  $t_{\text{start}}$  versus filler loading for calcium carbonate and kaolin. As either filler concentration was increased,  $t_{\text{start}}$  increased, with the value of  $t_{\text{start}}$  dependent on which filler was used. In the case of calcium carbonate [Fig. 5(a)], there was very little increase in  $t_{\text{start}}$  until the filler concentration reached 36 wt %, at which point there was a dramatic increase in  $t_{\text{start}}$  at higher loadings. Adding kaolin [Fig. 5(b)] exhibited a similar effect except that at 30 wt % of the filler the front could not be induced photolytically. As each filler absorbs and scatter light to different extents, it is not unexpected that variation in  $t_{\text{start}}$  should be observed.

Figure 6(a,b) shows plots of frontal velocity for each system in Figure 5 versus the filler concentration. Both fillers caused similar behavior. As the filler concentration increased, the front velocity became slower until a point was reached at which a front could not be initiated or sustained. As the amount of filler was increased, there was less of the polymerizable acrylate and thiol components present per unit volume, and therefore, less heat was released per unit volume to drive the frontal polymerization.

Next, the effect of the photoinitiator and thermal initiator on  $t_{\text{start}}$  and front velocity were assessed. In both of these cases, a sample comprised 90 mol % TMPTA and 10 mol % Trithiol was used. Figure 7 is a plot of  $t_{\text{start}}$  versus the photoinitiator concentration. There was very little change in  $t_{\text{start}}$  as the photoinitiator concentration was increased. Nason et al.<sup>13</sup> found that for



**Figure 7.**  $t_{\text{start}}$  as a function of photoinitiator concentration (Darocur 4265); irradiance = 30 mW/cm<sup>2</sup>.



**Figure 8.** Front velocity as a function of thermal initiator (Luperox 231) concentration; irradiance = 30 mW/cm<sup>2</sup>.

unfilled systems there was an optimal photoinitiator concentration and presumably if we had used high enough photoinitiator concentrations, a decrease in the  $t_{\text{start}}$  values would have been found. Figure 8 presents a plot of the front velocity versus the peroxide concentration. As expected, the front velocity increased substantially by over a factor of 3 as the peroxide concentration was increased by over an order of magnitude. This is a trend that is almost always observed for free-radical frontal polymerization,<sup>4</sup> and was observed for the UV-induced frontal polymerization of this same basic system without filler.<sup>13</sup>

## CONCLUSIONS

Two fillers, calcium carbonate and kaolin, were added to a TMPTA/thiol mixture. The presence of the filler reduces absorption of light by the photoinitiator, and hence, renders it impossible to initiate the frontal polymerization of TMPTA due to the oxygen inhibition at the surface. At low-thiol concentrations, the front could be initiated due to reduction in oxygen inhibition. However, as the thiol concentration increased, the time to start the front ( $t_{\text{start}}$ ) increased until a critical thiol concentration was attained and hence, the front could no longer be initiated. This resulted from the contribution of the slower, less exothermic

thiol-acrylate copolymerization process compared with the acrylate homopolymerization. It was also found that  $t_{\text{start}}$  increased and front velocity decreased as the filler concentration increased.

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