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The Effect of Acrylate Functionality on Frontal Polymerization Velocity and Temperature

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ABSTRACT

Frontal polymerization is a method of converting monomer(s) to polymer via a localized reaction zone that propagates from the coupling of thermal diffusion with the Arrhenius kinetics of an exothermic reaction. Several factors affect front velocity and temperature with the role of monomer functionality being of particular interest in this study. Polymerizing a di and triacrylate of equal molecular weight per acrylate revealed that as the proportion of triacrylate was increased the velocity and temperature increased. This is attributed to increased crosslinking and autoacceleration. Comparing several different acrylate monomers, both neat and diluted with DMSO so as to maintain constant acrylate group concentration, shows that velocity increases with increased functionality from mono to difunctional monomers. This trend breaks when applied to tri- and tetraacrylates, with fronts containing trifunctional monomer being the fastest. Acrylates containing hydroxyl functionality, as in the case of pentaerythritol based triacrylates, are slower than acrylates without. This is attributed to a chain transfer event and was tested using octanol and a hydroxyl-free acrylate. It has also been shown that small amounts of water cause a lowering of front velocity due to energy lost via vaporization, which lowers the front temperature.

KEYWORDS: frontal polymerization, acrylate, front velocity, front temperature, functionality

INTRODUCTION

Frontal polymerization is a method of converting monomer(s) to polymer via a localized reaction zone that propagates from the coupling of thermal diffusion with the

Arrhenius kinetics of an exothermic polymerization.

Frontal polymerization (FP) was first explored in the 1970s in Chernogolovka, Russia,^[1-6] with more work in the 1980s.^{[7-}

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^{11]} Pojman independently “rediscovered” frontal polymerization in the 1990s while researching methacrylate polymerizations.^[12-15] Since then, research on FP has expanded significantly to include cure-on-demand materials,^[16,17] synthesis of gels^[18-21] and gradient materials,^[22,23] epoxide polymerizations,^[24-27] composite materials,^[28-32] and self-stiffening materials^[33] and deep eutectic solvents.^[34,35] Most of the work on frontal polymerization has involved free-radical polymerization, although epoxy curing^[5,24,36-38] has been considered as well as ring-opening metathesis polymerization.^[39-42]

Here we will consider free-radical frontal polymerization. There are several factors that affect front velocity and front temperature with the relative reactivity of the monomer being paramount. For example, frontal acrylamide polymerization is very rapid,^[43] and fronts of acrylate polymerization are more rapid than methacrylates due to radical stability.^[44] Initiator concentration and stability are also important.^[45]

Although frontal polymerization is usually performed with neat monomers, it can be performed in high-boiling point solvents such as DMSO^[14,21,30,46], or glycerol.^[47]

Young et al.^[48] studied the effect of using a dimethacrylate or trimethacrylate on the polymerization rate of octylmethacrylate

photopolymerization. The trimethacrylate-containing solution polymerized faster than the dimethacrylate solution. Nason et al. studied 1,6-hexanediol diacrylate (HDDA) and trimethylolpropane triacrylate (TMPTA) polymerization by photo-DSC and found that TMPTA polymerized almost twice as fast as HDDA.^[44] Tryson and Schultz studied, by photo-DSC, the polymerization of lauryl acrylate, HDDA, and pentaerythritol tetraacrylate and found that lauryl acrylate polymerized more slowly than the multifunctional acrylates, but also found that the tetraacrylate polymerized slower than the diacrylate.^[49] Also, they found that conversion was significantly lower for the multifunctional acrylates. Lauryl acrylate polymerized almost to completion but HDDA achieved 46% and pentaerythritol tetraacrylate only 22% conversion.

We are particularly interested in the effect of functionality on the front velocity, because the front velocity determines how rapidly the curing can be achieved. Monoacrylates have been known to support slower fronts than multifunctional acrylates.^[44] However, front velocity is not only a function of the intrinsic reactivity of the monomer, but also the front temperature.^[50] In order to determine the effect of monomer functionality on the velocity of frontally polymerized systems, the monomers tested need to be chosen carefully. Typically, increasing the functionality of an acrylate

decreases the equivalent weight (g/mol of acrylate groups), which increases the acrylate group concentration. Since the front velocity of a system is dependent on the amount of heat released in the polymerization step of the reaction, a higher acrylate group concentration should give a higher front velocity.

To separate the effect of acrylate functionality from front temperature TMPTA (296.32 g/mol), a trifunctional acrylate, and 1,4-butanediol diacrylate (BDDA) (198.22 g/mol), a diacrylate, were selected for study since both have equivalent weights of 99 g/mol of acrylate groups. Comparing the front velocities obtained for each monomer, and using the same initiator concentration, allowed determination of the effect of monomer functionality on the front velocity and front temperature.

In order to study a variety of multifunctional acrylates, we first determined conditions that would support frontal polymerization in acrylates with functionalities ranging from mono to tetrafunctional. To compensate for the aforementioned differences in concentration of acrylate groups that arise from increased functionality, we dissolved the acrylates in DMSO such that the concentration of acrylate groups was constant. We also studied the effect of low concentrations of alcohol and water on the front velocity.

EXPERIMENTAL

1,4-butanediol diacrylate 90% (BDDA), 1,6-hexanediol diacrylate 85% (HDDA), and hexyl acrylate >96% (HA) were obtained from TCI. Di(ethylene glycol) diacrylate 75% (DEGDA), poly(ethyleneglycol) diacrylate (M_n 250) (PEGDA), di(trimethylolpropane) tetraacrylate (DTMPTA), and Luperox® 231 (1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane) 92%, were all obtained from Sigma-Aldrich. PETIA was obtained from Allnex. Trimethylolpropane triacrylate (TMPTA) was purchased from Sartomer, and 1-octanol 99% (OcOH) was obtained from Acros Organics. Fumed silica (Aerosil M5) was purchased from US Composites. DMSO (99%) and propylene carbonate were from Aldrich. Polygloss® 90 was purchased from KaMin performance minerals. All reagents were used as received. Figure 1 shows the structures of the monomers used.

Frontal polymerization samples were prepared by mixing the acrylate or acrylates together with Luperox® 231. Solvent and fumed silica were then incorporated, when appropriate, and the mixture was stirred thoroughly to ensure homogeneity. The reactant mixture was poured into 16 x 150 mm glass test tubes marked at 1 cm intervals, with a typical sample being roughly 20 mL. Frontal polymerization was induced via heat from a soldering iron or

butane torch. A butane soldering iron was heated and the tip was placed at the top of test tube against the glass. This heating element was held against the glass until the polymerization was initiated. For all intents and purposes any heat source can be used to initiate the polymerization as long as the sample amount is great enough to allow the reaction to equilibrate.

For the neat monomer polymerizations, the required polymerization conditions were 1 part per hundred resin (phr) Luperox® 231, meaning that for every 100 grams of monomer 1 gram of initiator was used. For the remainder of the experiments, a basis was needed in order to run all acrylates with the same concentration of acrylate groups. First, we determined the conditions to achieve frontal polymerization with neat hexyl acrylate (HA), which was 5 phr of fumed silica and 3 phr of Luperox® 231. The concentration of acrylate groups in pure hexyl acrylate is 5.68 M. In order to achieve the same for multifunctional acrylates, DMSO was used. All other components stayed the same.

For filled systems, a 1 phr Luperox® and monomer solution was mixed with 50 phr Polygloss® 90. The resulting putty-like material was then set into a wooden slab mold of dimensions 8 x 20 x 100 mm.

The propagation of the front was recorded using a video camera, and the front

temperature was tracked by capturing images periodically using a SeekThermal™ infrared camera on an iPhone. Figure S1 shows an example of an image taken with this camera. The values obtained were the temperature of the surface of the glass tube, but were proportional to the front temperature. The front velocity was calculated by plotting the position of the front versus time and determining the slope of the best fit line. All experiments were run in triplicate, the values averaged, and the standard deviation used for the error bars.

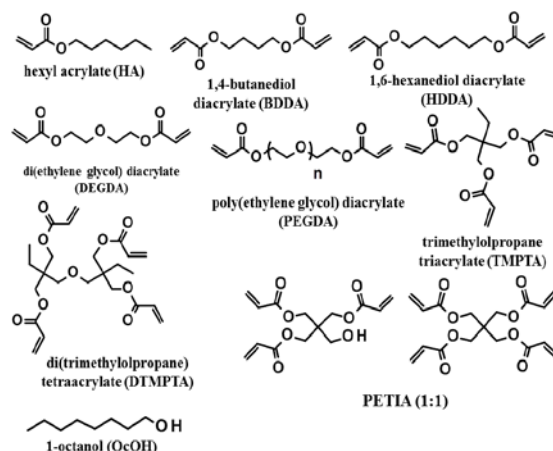


Figure 1. Reagents used.

RESULTS AND DISCUSSION

Increased monomer functionality effects on frontal polymerization

To first establish the front velocity and temperature behavior of acrylic monomers with different functionality, the relative molecular weight per acrylate group was not altered. All eight monomers chosen were

mixed with 1 phr initiator and polymerized using no diluent. These results are shown in Figure 2 (neat monomer). Hexyl acrylate, a mono functional acrylate, would not support a front under the chosen conditions. This could have likely been overcome with the use of and increased amount of initiator, but this was not done as it would likely have led to highly reactive and violent fronts that would not be able to be accurately monitored. There is no clear trend, but it should be noted that TMPTA, a triacrylate, produces the fastest fronts with difunctional acrylates (BDDA, HDDA, DEGDA, and PEGDA) being slightly slower. The difunctional acrylates propagate at similar velocities with DEGDA being slightly slower. Interestingly, the two tetrafunctional acrylates (DTMPTA and PETIA) produced the slowest fronts. PETIA is a 1:1 ratio of a triacrylate and a tetraacrylate based on pentaerythritol, which in the case of the triacrylate leaves a free hydroxyl group. The possible impact of this free hydroxyl group will be explored later.

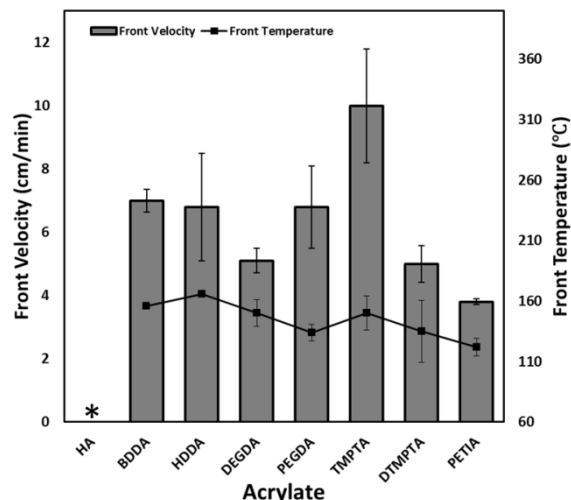


Figure 2. Front velocities and temperatures for acrylates of different functionality. The initiator (Luperox® 231) concentration was 1 phr, and no fumed silica or solvent was used. * Indicates that no front would propagate.

Figure 3 shows the comparison of TMPTA and HDDA and mixtures of the two. As the ratio of TMPTA is increased, the front velocity and temperature both increased. This trend continued with both temperature and velocity increasing as the amount of triacrylate increased. The velocity difference between pure HDDA and TMPTA was more than double, 2.19 times greater. This is in agreement with results reported by Nason et al.^[44] TMPTA produces faster fronts than HDDA due to its lower molecular weight per acrylate, 99 and 113 g/mol respectively, as well as the increased crosslinking due to higher functionality.

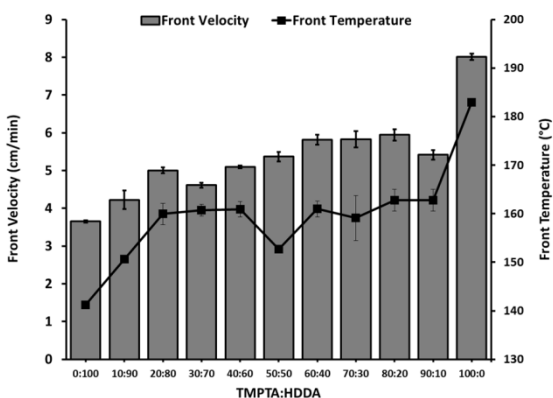


Figure 3. Front velocity and temperature as a function of the ratio of a triacrylate (TMPTA) to diacrylate (HDDA). No solvent was used. The concentration of Luperox® 231 was 0.1 phr.

Effects of functionality on frontal polymerization of acrylates with equal molecular weight per acrylate

In order to properly compare the intrinsic reactivity of acrylates of different functionality, it is necessary to control the concentration of acrylate groups. This is difficult given the few monomers that have different functionality, but equal acrylate concentration. One pair of monomers which allows this is 1,4-butanediol diacrylate (BDDA) and TMPTA, which have a molecular weight per acrylate of 99 g/mol. Figure 4 shows the comparison of the front velocities and temperatures as a function of the ratio of the two monomers. The data show a similar trend as was observed in the comparison of HDDA and TMPTA. As the

fraction of triacrylate was increased the velocity and temperature increased with pure TMPTA being approximately twice as fast as pure BDDA.

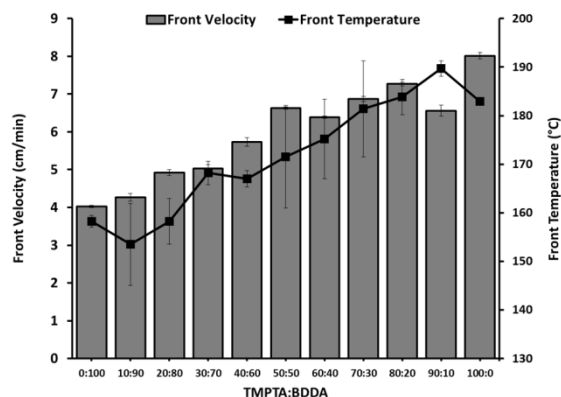


Figure 4. Front velocity and temperature as a function of the ratio of a triacrylate (TMPTA) to diacrylate (BDDA). No solvent was used. The concentration of Luperox® 231 was 0.1 phr.

Controlling equivalent weight for acrylates with different functionality

Monofunctional acrylates, or acrylates of higher functionality, are difficult to compare due to the lack of examples with the same equivalent weight; therefore, another method was employed to maintain a constant acrylate group concentration. First, conditions to run hexyl acrylate (HA) as a front were determined. This acrylate served as the standard to which all other acrylates could be compared, provided that they have an equivalent weight less than 156 g/mol per

acrylate groups. It was found that HA required 3 phr of Luperox® 231 and 5 phr of fumed silica to reliably run as a front in 16 x 150 mm cm glass test tubes. Fumed silica was added to increase the viscosity of the mixture in order to eliminate convection, which can quench fronts.^[51] Other acrylates were compared to HA by maintaining constant concentrations of acrylate groups (5.68 M). For acrylates with lower equivalent weights, such as TMPTA (99 g/mol acrylate groups), DMSO was used as an inert diluent to maintain constant acrylate group concentrations. DMSO was chosen because it has a high boiling point (~190 °C), was miscible with all the acrylates we tested, and has been used in fronts previously.^[14,21,30,46]

Figure 5 shows the results for HA, BDDA, and TMPTA using this method. HA, a monoacrylate, has a considerably lower front velocity than either multifunctional acrylate, as well as a correspondingly lower front temperature. The increase of front velocity with increasing acrylate functionality, especially from monofunctional to difunctional, is due to autoacceleration. Radical polymerization reactions are known to proceed at increased rates as the local viscosity of the reaction mixture increases.^[52,53] As monomer is converted into polymer, the mobility of large propagating radical chains becomes limited. While relatively small and mobile monomer units can easily diffuse and add to

the propagating centers, it becomes harder for two propagating radicals to come together and terminate. This decrease in the rate of termination causes an increase in the rate of polymerization, which is known as autoacceleration.^[54,55] Crosslinking of polymer chains causes this effect to occur at lower conversions, which means that monomers with higher functionality will autoaccelerate at lower conversion. Thoma et al. measured by EPR the concentration of the trapped radicals as high as 8.7×10^{-3} mol/kg.^[56] This explains the large difference in front velocity from monofunctional acrylate, in which there is no crosslinking, to diacrylate, in which there is extensive crosslinking as well as the smaller difference between difunctional and trifunctional acrylates.

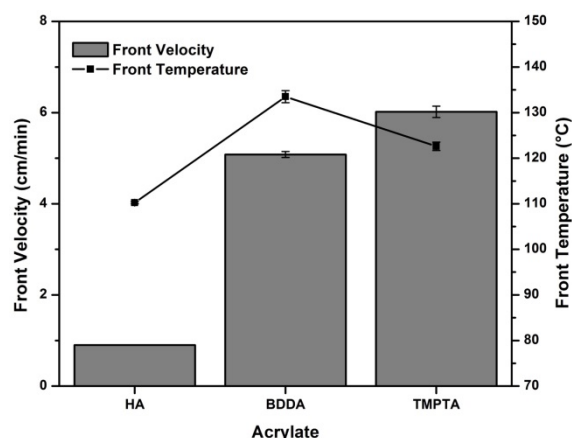


Figure 5. Frontal velocities and temperatures for HA, BDDA, and TMPTA. Experiments were performed in DMSO with 3 phr initiator, and 5 phr fumed silica.

Figure 6 presents the front velocities and front temperatures for four diacrylates in DMSO. It is curious that HDDA supports slower fronts than the other diacrylates, and a possible explanation for this could be the lower purity. If the impurity is some sort of monoacrylate, it could be the case that this copolymerization lowers the overall rate of reaction for the system. It has been shown in literature that during some photo-initiated copolymerization of acrylates of increasing side chain lengths, the systems with the highest amount of short chain methacrylate lowered the reaction rate in those systems.^[57,58]

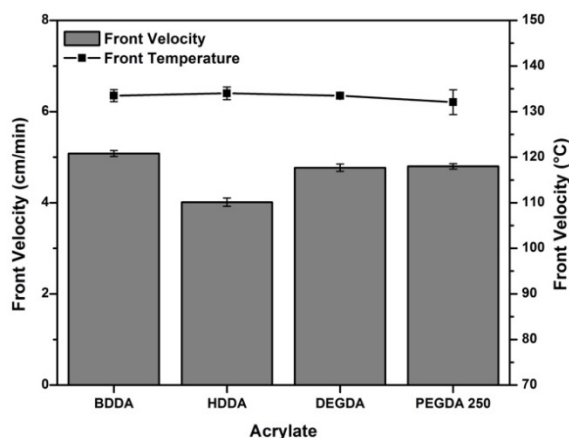


Figure 6. Front velocities and front temperatures of several difunctional monomers. Experiments were performed in DMSO with 3 phr initiator and 5 phr fumed silica.

The front velocities and front temperatures for several multifunctional acrylates are shown in Figure 7. The triacrylate TMPTA

produces the fastest fronts of this group, as well as for all acrylates tested. Although the dimer of TMPTA, DTMPTA is a tetraacrylate, this additional acrylate group does not increase the velocity of the front. PETIA is a 1:1 mixture of pentaerythritol triacrylate and pentaerythritol tetraacrylate. PETIA produces a slower front than both TMPTA and DTMPTA. As for the differences between the pentaerythritol-based and trimethylolpropane-based monomers, we suspected that the hydroxyl group on the pentaerythritol acted as a chain transfer agent, which reduced the crosslinking, and lowered the polymerization rate. We tested this hypothesis by adding an equimolar amount of 1-octanol to TMPTA; this indeed lowered the front velocity.

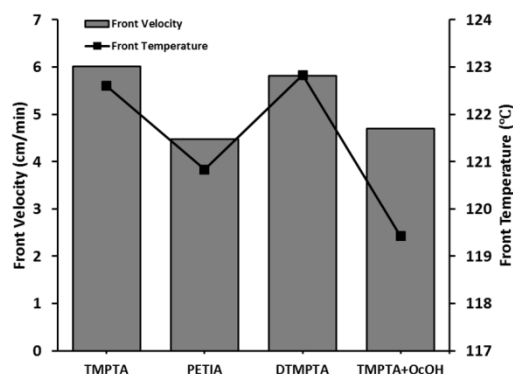


Figure 7. Front velocities and front temperatures of several difunctional monomers BDDA, HDDA, DEGDA, and PEGDA. Experiments were performed in

DMSO with 3 phr initiator and 5 phr fumed silica.

Effects of water and solvent

We observed in some experiments without solvent that if we dried the monomer, the fronts propagated faster than with the monomer straight from the container. We then tested the effect of water for the BDDA polymerization in DMSO. We added 1.5 % by weight water to the diacrylate in DMSO and observed an almost 20% decrease in velocity (Figure 8). To test if components in the DMSO could be acting as inhibitors, we switched to propylene carbonate (PC) as the solvent. The front velocity was decreased but within experimental uncertainty. We hypothesized that water could cause hydrolysis of the acrylates to produce acrylic acid, which was observed in the frontal polymerization of benzyl acrylate.^[59] If all the water hydrolyzed esters, then 13% of the acrylate groups would be converted to acrylic acid. We added 13 n/n% of acrylic acid to the formulation in propylene carbonate, which increased the front velocity. Although the system would be less crosslinked, the greater reactivity of acrylic acid overcame this effect.^[60] However, adding hexyl acrylate also increased the front velocity. In neither case was the front temperature affected.

We also considered whether water could act as a chain transfer agent but this was found not to be the case in previous studies.^[61,62]

We calculated the heat absorbed in vaporizing 1.5 g of water in a 100 g sample and using a heat capacity of the acrylate solutions of $2 \text{ J g}^{-1} \text{ K}^{-1}$, the result would be a decrease in front temperature of 17°C . The front temperature was lowered by 8°C in both DMSO and propylene carbonate. The front velocity is a strong function of temperature,^[63] which suggests that small amounts of water can reduce front velocity by absorbing heat through vaporization.

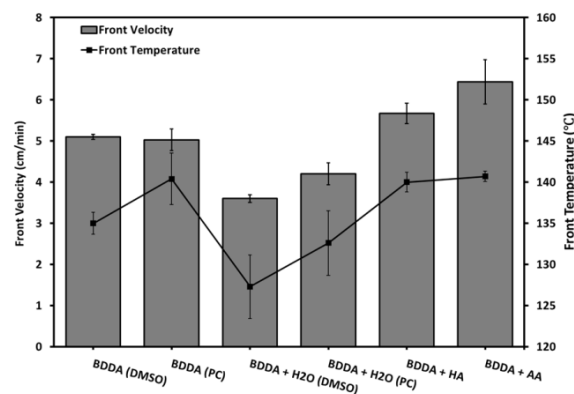


Figure 8. The effect of water or hexyl acrylate on acrylic acid on front velocities. BDDA was polymerized in DMSO or propylene carbonate. Compositions by mass: BDDA (59.23%), H_2O (1.52%), Luperox® 231 (2.80%), fumed silica (4.65%), propylene carbonate (31.80%). Hexyl acrylate (HA) and acrylic acid (AA) were used instead of water.

Filled Acrylate Systems

All of the experiments thus far have been conducted using systems that are of relatively low viscosity; they were all run in test tubes. For practical purposes, however, these monomer systems will often be incorporated with a filler in order to have a moldable material. To study if the same trend evident in unfilled systems was still present in filled systems, Polyglass®90, a kaolin clay, was added to make moldable putty. This was determined to be 47% by mass. Figure 9 shows that the overall trend in front velocity is the same as in the unfilled systems. There is a noticeable increase in velocity between di and triacrylate, with the PEGDA being lower than BDDA. This was the case in unfilled systems. As was the case for unfilled systems TMPTA produced the fastest fronts. Interestingly the filled systems showed overall higher velocities than in the systems with no filler. We proposed that this is due to heat loss and the surface area to volume ratio. Filled samples are run as slabs in wooden molds, of dimensions 3 cm x 2.5 cm x 10 cm because these putties cannot be added to a test tube. The wooden molds act to insulate the heat being produced by the propagating front on three of the four sides. The samples run in the test tube are able to lose heat from all sides through the test tube walls. This leads to higher front temperatures in the filled samples and thus higher front velocities.

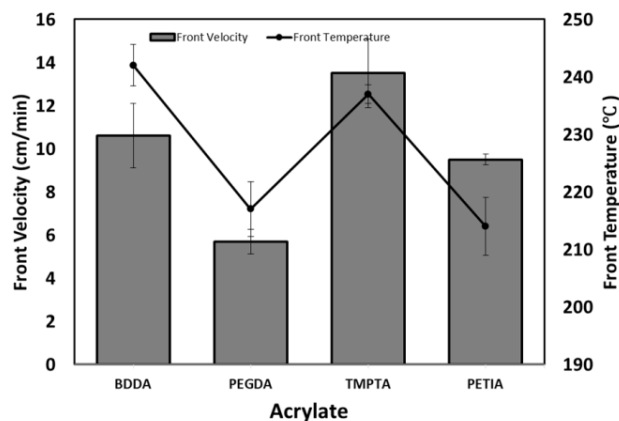


Figure 9. Filled acrylate systems. All samples contained 1 phr Luperox® 231 and 47% by mass Polyglass® 90. Front run in wooden slab molds of dimensions 3 cm x 2.5 cm x 10 cm.

CONCLUSIONS

We studied the effect of acrylate functionality on frontal polymerization velocity and temperature. BDDA and TMPTA have the same equivalent weight per acrylate. Frontally polymerizing them neat at different ratios revealed that the velocity increases as the ratio of TMPTA was increased with pure TMPTA polymerizing twice as fast as pure BDDA.

To set a baseline we polymerized several acrylates with different functionality and molecular weight per acrylate group. We then studied frontal polymerization of several acrylates in DMSO such that the concentration of acrylate groups was constant. Hexyl acrylate fronts were five times slower than BDDA fronts and six times slower than TMPTA fronts. Fronts with 1,6

hexanediol diacrylate propagated 20% slower than butanediol diacrylate or the two other diacrylates we studied, for which we have no explanation. We then compared a number of multifunctional acrylates. TMPTA fronts were the fastest. A 1:1 mixture of pentaerythritol triacrylate: tetraacrylate (PETIA) produced slower fronts than fronts of only tetraacrylate (DTMPTA). PETIA fronts were slower than ones with TMPTA because of chain transfer from the hydroxyl group, which we confirmed by adding octyl alcohol to TMPTA. Finally, we determined that small amounts of water slowed frontal polymerization, which we propose is caused by the reduction in front temperature from the heat of vaporization.

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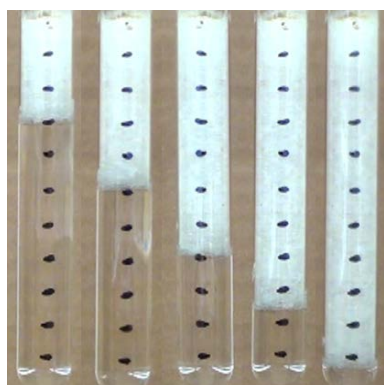
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GRAPHICAL ABSTRACT

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The effect of acrylate functionality on frontal polymerization velocity and temperature.

The velocity of a propagating front is studied as a function of monomer functionality for acrylate systems. Monomers of mono, di, tri, and tetra functionality were compared by modulating the molecular weight per double bond. This was accomplished through careful monomer selection, or using a high boiling nonreactive solvent.



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