UV-Induced Frontal Polymerization of Multifunctional (Meth)acrylates

Charles Nason,[†] Todd Roper,[†] Charles Hoyle,*[,†] and John A. Pojman[‡]

Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi 39406, and Department of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, Mississippi 39406

Received July 14, 2004; Revised Manuscript Received February 28, 2005

ABSTRACT: Photoinduced frontal polymerization was performed on a variety of multifunctional (meth)-acrylates, and evaluation of the effect of monomer structure on the ability to sustain a traveling front was made. Photo-DSC was used to measure the photopolymerization rate of each monomer at 25 °C. The results were correlated with their ability to initiate and sustain a traveling front polymerization. The start time and the front velocity of each (meth)acrylate that could initiate/sustain a front photolytically were measured. The results clearly demonstrate that the molecular weight per double bond is directly related to the front velocity. Trimethylolpropane triacrylate (TMPTA), which exhibited the fastest front velocity, was evaluated in depth to determine the effect of varying the photoinitiator and thermal initiator on the frontal polymerization rate. When a multifunctional thiol was added to TMPTA, the start time was dramatically reduced and the velocity increased for low thiol concentrations. However, the velocity decreased when higher concentrations of thiol were added.

Introduction

In 1967, Merzhanov and Borovinskaya reported the first self-propagating high-temperature synthesis.[1] This process, in which a pellet of reactant was ignited at one end, resulted in a self-propagating combustion wave. The advantage of this self-propagating system was that the initial stimulus was the only energy required to induce and sustain the reaction. In 1972, Chechilo and Enikolopyan used the same approach to cure vinyl monomers via free-radical polymerization initiated by peroxides.[2,3] Basically, a method was developed to convert monomer into polymer by means of a localized reaction zone that propagates due to the heat released from the polymerization reaction. They polymerized methyl methacrylate under high pressure to eliminate convective instabilities that are detrimental to traveling fronts. About two decades later, Pojman et al. reported the thermally induced frontal polymerization of methacrylic acid at ambient pressure in standard test tubes.[4] A large number of subsequent papers on thermally induced frontal polymerization have been published during the past decade.[5−35]

For a traveling front based upon free-radical polymerization to exist there are some important factors to consider. First, there must not be any reaction of the monomer(s) at ambient temperature. Second, an initial energy input, either heat or light, should produce radicals that initiate polymerization. The conversion of monomer to polymer is highly exothermic, inducing a self-propagating thermal wave or reaction, as shown in Figure 1, which results in a boundary separating polymer and liquid monomer. Highly exothermic reactions are more likely to sustain a traveling front because the heat produced must exceed the heat that is lost through the reaction vessel or mold. It is essential that the monomer should have a high boiling point to prevent bubble formation induced by the high temperature at the epicenter of the traveling front.

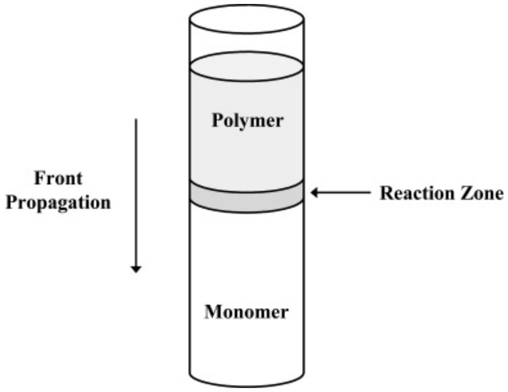


Figure 1. Schematic of frontal polymerization.

Photopolymerization is an efficient process in which liquid monomer is converted to polymer via a photoinitiated process. To date, photopolymerization has been limited primarily to induce curing of thin coatings and adhesives. The problem in photopolymerizing thick samples arises from the light not being able to penetrate deep enough to cure the resin. Even with this limitation, there have been some reported examples of photocuring thick samples using a bleachable photoinitiator.[36,37] In these systems, the photoinitiator bleached allowing light to penetrate deep into the sample in what can be classified as a type of frontal polymerization.

UV-induced cationic frontal polymerization of cationic polymerization has been reported by several groups.[38−41] In these systems, a cationic photoinitiator was irradiated to induce a traveling front. Pojman and co-workers used UV light to induce a free-radical frontal polymerization of a 1,6-hexanediol diacrylate in DMSO with silica gel present.[42] In this system, a small amount of photoinitiator was injected into the center of the resin, which was then exposed to UV light. To our knowledge, this is the only documented UV-induced polymerization of a multifunctional acrylate.

[†] Department of Polymer Science.

[‡] Department of Chemistry and Biochemistry.

* To whom correspondence is to be addressed: e-mail Charles.Hoyle@usm.edu; Ph 601-266-4873; Fax 601-266-5504.

10.1021/ma048569y CCC: $30.25

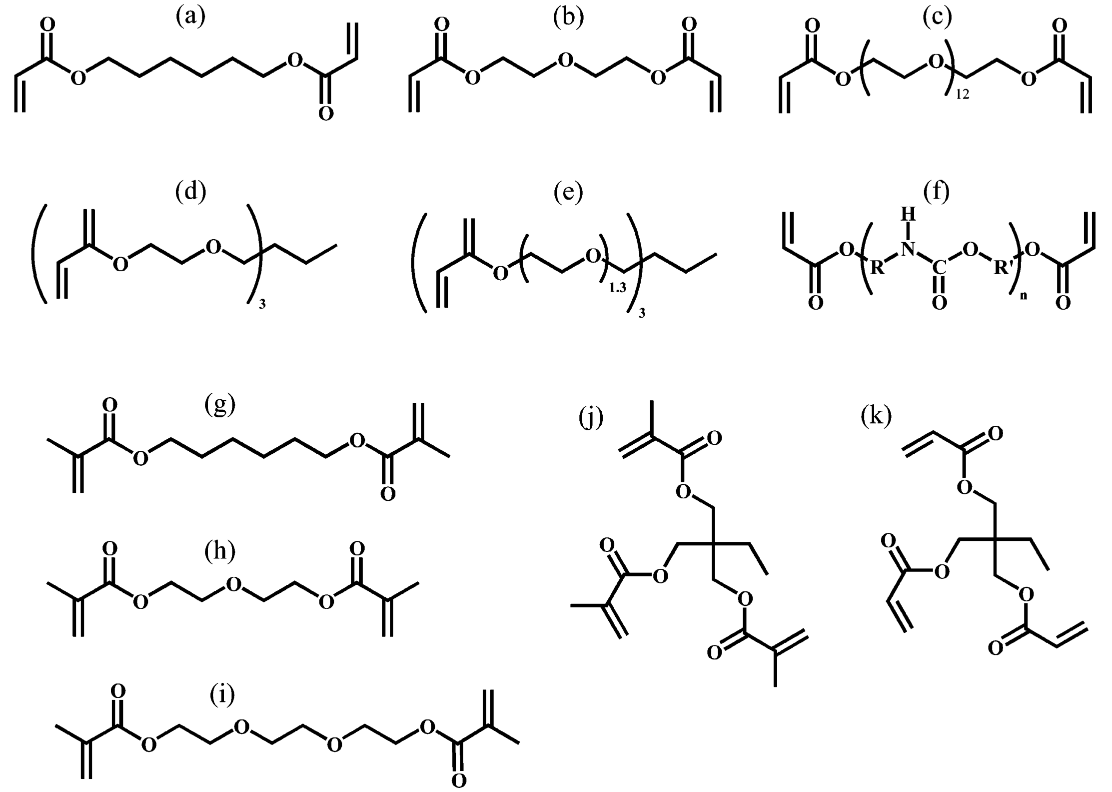


Figure 2. Chemical structures of the acrylate and methacrylate monomers: (a) hexanediol diacrylate (HDDA), (b) diethylene glycol diacrylate (DEGDA), (c) poly(ethylene glycol) diacrylate (PEGDA), (d) trimethylolpropane ethoxy triacrylate (TMPEOTA-I), (e) trimethylolpropane ethoxy triacrylate (TMPEOTA-II), (f) difunctional urethane acrylate (Ebecryl 8402), (g) hexanediol dimethacrylate (HDDMA), (h) diethylene glycol dimethacrylate (DEGDMA), (i) triethylene glycol dimethacrylate (TREGDMA), (j) trimethylolpropane trimethacrylate (TMPTMA), (k) trimethylolpropane triacrylate (TMPTA).

A comprehensive study of frontal polymerization of UV-induced multifunctional (meth)acrylates has not been performed. Herein, we report the effect of monomer structure and functionality on traveling frontal polymerization. Correlations between polymerization exotherms recorded by photo-DSC, monomer structure, and frontal propagation are made. A fundamental relationship between front velocity and reactant molecular weight per acrylate unit was established.

Experimental Section

Materials. Standard acrylate and methacrylate monomers were obtained from UCB Chemicals and Aldrich Chemical Co. Ebercryl 8402 from UCB is a low-viscosity (15 000 cP at 25 °C) acrylated aliphatic urethane oligomer with a density of 1.12 g/mL at 25 °C, a molecular weight of 1000 g/mol, and a functionality of two. Trimethylolpropane tris(3-ethylmercaptopropionate) was purchased from Aldrich Chemical Co. The thermal initiator, Luperox 231 (1,1-di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane), was obtained from Atofina. The photoinitiators, Darocur 4265 and 1173, were obtained from Ciba. All chemicals were used as received. The chemical structures of the (meth)acrylate monomers are shown in Figure 2, while the chemical structures of the initiators and trifunctional thiol are depicted in Figure 3.

Photo-DSC. Photo-DSC exotherms were measured on a Perkin-Elmer differential scanning calorimeter 7 modified to accommodate a Canrad-Hanovia medium-pressure mercury lamp source from Ace Glass. Light intensities were measured via a blackbody absorber. A mechanical shutter was placed between the light source and the sample chamber to provide control of exposure time. Sample pans were crimped and injected with 2 μL samples, giving a film thickness on the order of 200 μm (approximately 8 mils).

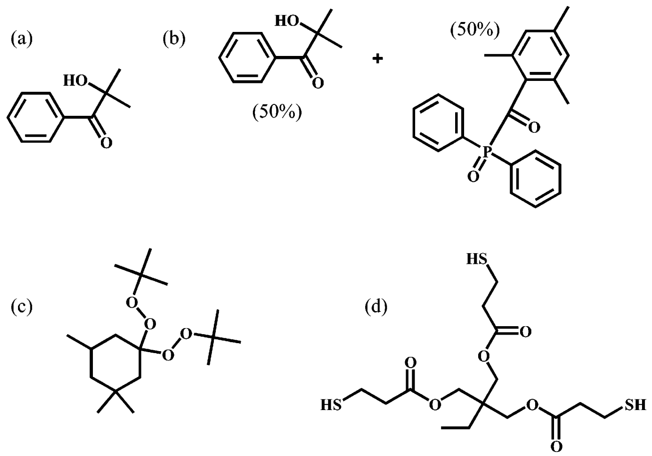


Figure 3. Chemical structures of (a) 2-hydroxy-2-methyl-1-phenylpropanone (Daracur 1173), (b) 2-hydroxy-2-methyl-1-phenylpropanone, and 2,4,6-trimethylbenzoyldiphenylphosphine oxide (Daracur 4265), (c) 1,1-di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane (Luperox 231), and (d) trimethylolpropane tris(3-ethylmercaptopropionate).

Enthalpy of Polymerization. The enthalpy of polymerization for a thiol−acrylate system was determined in a two-step process: real-time infrared analysis of the acrylate and thiol conversion as a function of time followed by photo-DSC measurement of the heat released during the thiol−ene photoreaction. Monofunctional reagents, ethyl 3-mercaptopropionate and hexyl acrylate, were used to increase the accuracy by ensuring that the reactions all proceeded to completion. Multiple samples were run. The average enthalpy of polymerization for thiol−acrylate was 14.8 kcal/mol with a standard deviation of 1.0 kcal/mol.

Frontal Polymerization. For frontal polymerization, the resin, photoinitiators, and peroxides were mixed together and transferred to a 16 × 125 mm borosilicate test tube with clear ruler tape affixed to the side of the test tube. The filled test

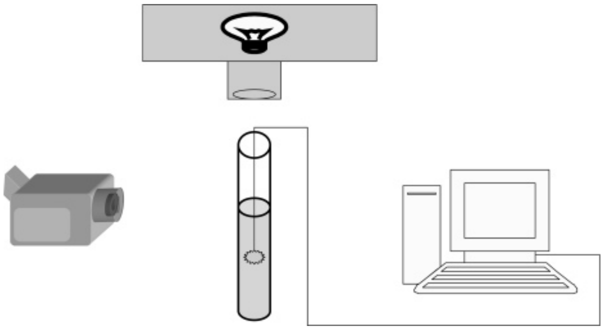


Figure 4. Experimental setup for frontal polymerization.

tube was clamped into a holder approximately 7 in. underneath the light source, which was a medium-pressure mercury lamp from Ace Glass (Figure 4). The output of the medium-pressure mercury lamp was filtered with a neutral density filter to give a light intensity of approximately 5.9 mW/cm^2 at the monomer surface (Figures 7−12) or approximately 5.1 mW/cm^2 at the top of the glass cover in contact with the monomer (Table 1 and Figure 6). For the results in Table 1 and Figure 6, nitrogen was passed over the top surface of the monomer for 2.5 min prior to covering with a glass plate. This allowed measurement of the time required to initiate the front unencumbered by the effect of oxygen at the surface which delays the time to initiate the front. Once the time required to initiate the front in the absence of oxygen at the surface was measured for the results in Table 1 and Figure 6, all other fronts (Figures 7−12 for TMPTA) were initiated in an open test tube at ambient conditions. A Sony video camera was set up on one side of the test tube to record the initiation of the front and its velocity in cm/min. The camera recorded the start time (T_{start}), which is defined as the time it takes to induce the frontal polymerization with UV light. In some cases, if the front could not be started photolytically, a thermal heat source was used to decompose the thermal initiator directly, i.e., since samples could not be initiated effectively photolytically under the conditions employed, thermal initiation was induced by touching a thermal heat source to the outside of the test tube, corresponding to the position of the air/monomer interface for PEGDA (350 g/mol per functional group) and TMPEOTA-II (201 g/mol per functional group). Whether initiated photolytically or thermally, the frontal velocity (V_{front}) was found by measuring the time it takes for the front to travel a specified distance and is given in terms of cm/min. All values for V_{front} are accurate to within 10% as determined from running select samples twice. The possibility that heat from the light source could have been responsible for initiating frontal polymerization was eliminated by exposing one of the reactive samples without any added photoinitiator to the medium-pressure lamp source. Without photoinitiator, no front was observed for the same exposure conditions used to initiate frontal polymerization of samples with photoinitiator present. Finally, it is noted that no samples were purged with nitrogen since any frontal application will be conducted in air-saturated systems. The results in nitrogen-purged systems would follow similar trends to those reported herein, although the magnitude of values reported would vary.

Results and Discussion

To obtain a clear relationship between the traveling front velocity and monomer structure, several (meth)acrylates with varying structure were evaluated. In each case, information concerning the basic reactivity of the monomer was evaluated by photo-DSC. Corresponding polymerization front parameters were measured for comparison with the polymerization exotherms obtained by photo-DSC. The monomers varied in type (acrylate vs methacrylate) and molecular weight per double bond (99−500 g/mol per double bond). Structures and acronyms for each monomer are shown in Figure 2. The structures and corresponding acronyms of the peroxide, the two photoinitiators, and the trithiol are given in Figure 3.

Photo-DSC of Monomers. Prior to evaluating each monomer in actual frontal polymerization reactions, polymerization exotherms were recorded since the ability to initiate and sustain a rapid frontal polymerization should be dependent to an extent on the rate of heat generated. To evaluate the inherent polymerization reactivity of each monomer, photo-DSC exotherms for samples with 1 wt % Darocur 4265 photoinitiator were recorded. Examples of photo-DSCs of three of the monomers are shown in Figure 5. Parameters obtained from the photo-DSC exotherms of the monomers in Figure 5 and several other monomers listed in Table 1 include the peak exotherm maximum ($H_{\max}$) and the time to attain the peak maximum ($T_{\max}$). We note that the photo-DSC results were obtained at 25 °C and therefore the $H_{\max}$ and short $T_{\max}$ values will certainly be different at the polymerization front where temperatures in excess of 200 °C occur. Nonetheless, the values obtained from the photo-DSC results at 25 °C should serve as a relative guideline for indicating acrylate reactivity during frontal polymerization. The photo-DSC results for all of the acrylates in Table 1, except Ebecryl 8402, have large $H_{\max}$ and short $T_{\max}$ values, suggesting that they should be likely candidates to initiate and sustain a frontal polymerization. Ebecryl 8402, a difunctional acrylated urethane oligomer with a high molecular weight between functional groups, has a very low $H_{\max}$ value and, combined with its high molecular weight per acrylate functional group, would not be expected to initiate and sustain frontal polymerization. The methacrylates all exhibit low exotherms and also might not be expected to sustain a rapid frontal polymerization, even though their equivalent weights (molecular weight per methacrylate group) are all fairly low. As for the other acrylates other than Ebercryl 8402, it cannot be assumed simply on the basis of the photo-DSC exotherm data at 25 °C that all will be able to sustain a front or that the front can be initiated photolytically. As we will show, it is essential that the molecular weight per acrylate double bond also be taken into account since it will directly impact the total heat evolved per unit volume during the polymerization. Finally, we note that at the high temperature of the frontal polymerizations (in excess of 200 °C) the polymerization rates and conversions will be different than measured at 25 °C.

UV-Induced Frontal Polymerization. The ability to predict how a given monomer structural feature impacts frontal polymerization is critical in designing efficient UV-induced frontal polymerizations. In light of this, all of the acrylate monomers in Table 1 were evaluated for their propensity to initiate and sustain frontal polymerization upon exposure to light. A thermal initiator, peroxide or nitrile, is necessary for frontal polymerization. The peroxide affects the front velocity as would be expected; the lower the stability of the peroxide, the faster the front.[8] We chose to use Luperox 231 because it is stable at room temperature, it is a liquid and easy to dissolve in the resins, and it produces half as much gas per radical upon decomposition as most peroxides and nitriles.[23,25,27] The parameters recorded in Table 1 deal with whether the front could be induced photolytically, the lamp exposure time to initiate the frontal polymerization (T_{start}), and the

Table 1. Photo-DSC and Frontal Polymerization Characteristics for Meth(acrylate) Monomers[a]

	MW/bond (g/mol)	photo	$H_{\max}$ (mW)	$T_{\max}$ (s)	V_{front} (cm/min)	T_{start} (s)
acrylate						
TMPTA	99	yes	43	6	15.0	17
DEGDA	107	yes	87	8	10.0	5
HDDA	113	yes	71	9	8.0	8
TMPEOTA-I	143	yes	67	6	6.3	9
TMPEOTA-II	201	no	56	7	1.43	
PEGDA	350	no	36	9	0.68	
Ebecryl 8402	500	no	6.6	12	no front	no front
methacrylate						
DEGDMA	121	no	6	50	0.7	
HDDMA	126	no	2	63	0.5	
TMPTMA	129	no	5	11	0.7	
TREGDMA	143	no	7	45	0.7	

[a] Exotherm data were recorded for exposure to the output of a medium-pressure mercury lamp with 0.44 mW/cm^2. Frontal results for acrylates with molecular weight per acrylate double bond of 143 g/mol or less were obtained for exposure of a sample prepared with a nitrogen blanket/glass plate combination as described in the Experimental Section for exposure to the output of a medium-pressure mercury lamp with 5.9 mW/cm^2. Thermal fronts for acrylates with molecular weight per acrylate double bond of 201 or 350 g/mol as well as all methacrylates were initiated by touching a soldering iron to the edge of the glass test tube. The frontal polymerization of the Ebercryl 8402 sample could not be initated thermally or with light. In all cases 1 wt % Luperox 231 and 2 wt % Darocur were added.

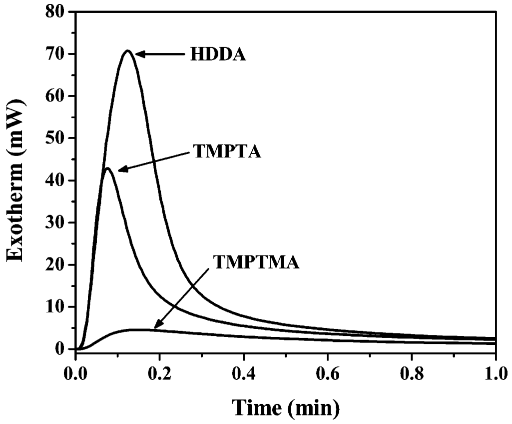


Figure 5. Photo-DSC exotherms of HDDA, TMPTA, and TMPTMA with 1 wt % Darocur 4265; nitrogen purge, using the full arc of a medium-pressure mercury lamp with irradiance of 0.4 mW/cm^2.

velocity of the front (V_{front}). Frontal polymerization could only be initiated photolytically for acrylates with molecular weight per acrylate double bond of 143 g/mol or less. This illustrates the importance of a high double bond concentration per unit volume in initiating/sustaining a front upon exposure to light. Of course, it is important that monomers also exhibit rapid polymerization, as we have already discussed in terms of the exotherm results. The combination of a high $H_{\max}$ value with a low molecular weight per acrylate double bond is essential for initiation of a front by light. In the cases for the acrylate with higher molecular weight per double bond, i.e., TMPEOTA-II (MW per acrylate functional group is 201 g/mol), PEGDA (MW per acrylate functional group is 350 g/mol), Ebecryl 8402 (MW per acrylate functional group is 500 g/mol), and all of the methacrylates, attempts were made to initiate the front thermally since under the conditions employed fronts could not be initiated for any of these monomers with light.

Closer analysis of the data in Table 1 indicates that acrylate monomers with the lowest MW per double bond resulted in frontal polymerization with the fastest velocity; i.e., TMPTA with the lowest MW per double bond (99 g/mol) has the fastest frontal velocity (15 cm/min). As we mentioned before, the monomer with the highest MW per acrylate double bond, Ebecryl 8402 (500 g/mol), did not sustain a traveling front even with attempts to initiate it thermally. This is consistent with both the low photo-DSC exotherm and the low molecular weight per acrylate double bond. To better illustrate the effect of the monomer molecular weight, the frontal velocities of all the acrylate monomers in Table 1, whether initiated photolytically or thermally, are plotted as a function of MW per acrylate double bond in Figure 6. As seen in Figure 6, when the monomer has a MW per acrylate double bond of 150−200 g/mol or greater, the frontal velocity becomes very slow. When the MW per acrylate double bond is 350 or 500 g/mol, a stationery front (note that a thermal heat source was applied to the top of these samples) is no longer either sustained or initiated. The sample of PEGDA (MW per acrylate double bond of 350 g/mol) did experience a front when initiated thermally, but it was not sustained. For Ebecryl 8402 (MW per acrylate double bond of 500 g/mol) no frontal activity was noted. The plot in Figure 6 is particularly important since it can be used to predict the frontal velocity of various acrylate monomers by simply knowing the molecular weight per acrylate group.

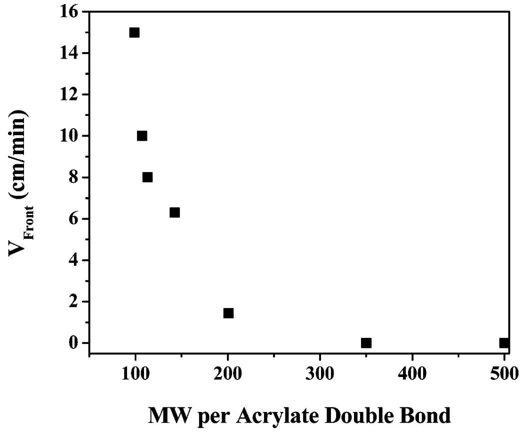


Figure 6. Front velocity (V_{front}) vs MW per acrylate double bond; 1 wt % Luperox 231, 2 wt % 4265; glass cover. Monomers (MW per acrylate double bond) for photoinitiated fronts are TMPTA (99), DEGDA (107), HDDA (113), and TMPEOTA-I (143): Irradiance of 5.1 mW/cm^2. Monomers (MW per acrylate double bond) for thermal fronts are TMPEOTA-II (201), PEGDA (350), and Ebecryl 8402 (500). Thermal source applied to samples.

As expected from the photo-DSC exotherm data in Table 1, the methacrylates are not capable of initiating

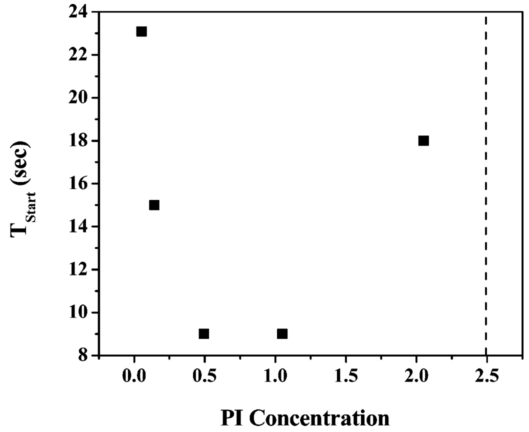


Figure 7. T_{start} for TMPTA as a function of Darocur 4265 photoinitiator concentration; 0.4 wt % Luperox 231; in air; irradiance of 5.9 mW/cm^2.

frontal polymerization photochemically under the conditions employed. However, frontal polymerization of all of the methacrylates could be induced thermally. The resultant frontal velocities of the methacrylates are extremely slow in comparison to the acrylates. There is little question from the data in Table 1 that for methacrylates, which polymerize slower than acrylates because of the steric hindrance of the methyl group and the higher radical stability, the rate of heat evolution is insufficient to induce a rapid frontal polymerization.

Since TMPTA displayed the fastest frontal velocity of any of the monomers in Table 1, it was chosen for more in-depth study. Additional results are obtained for TMPTA samples without the glass slips placed on the monomer. Figure 7 is a plot of T_{start} for TMPTA as a function of the photoinitiator (Darocur 4265) concentration. As can be seen in Figure 7, for an increase of photoinitiator concentration from 0.1 to 0.5 wt %, T_{start} dramatically decreases and remains low up to 1 wt % photoinitiator. The decrease in T_{start} with photoinitiator concentration results from the higher initiation rate typically observed for conventional photopolymerization processes. An additional increase in photoinitiator concentration leads to an increase in T_{start} due to an inner filter effect. This occurs in the case of Darocur 4265 at concentrations of greater than 1 wt % because of the high extinction coefficient in the range of the output of the mercury lamp source. The inner filter effect when Darocur 4265 is used is such that for concentrations of 2.5 wt % photoinitiator or greater, a frontal polymerization cannot be induced. When a photoinitiator with lower extinction coefficients is used, the values for T_{start} remain low even for higher concentrations of photoinitiator as shown in Figure 8 for Darocur 1173 as the photoinitiator.

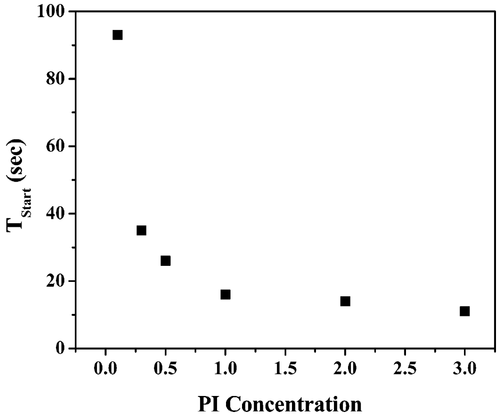


Figure 8. T_{start} for TMPTA as a function of Darocur 1173 photoinitiator concentration; 1 wt % Luperox 231; in air; irradiance of 5.9 mW/cm^2.

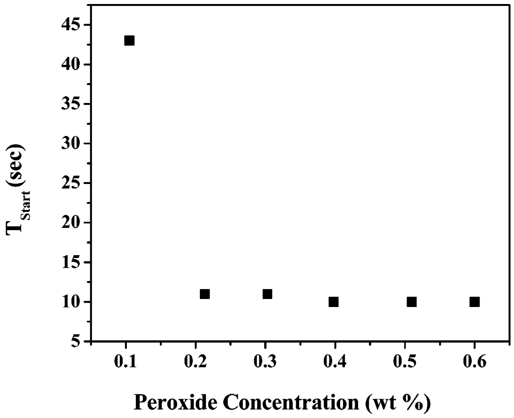


Figure 9. T_{start} for TMPTA as a function of Luperox 231 concentration; 1 wt % Darocur 4265; in air; irradiance of 5.9 mW/cm^2.

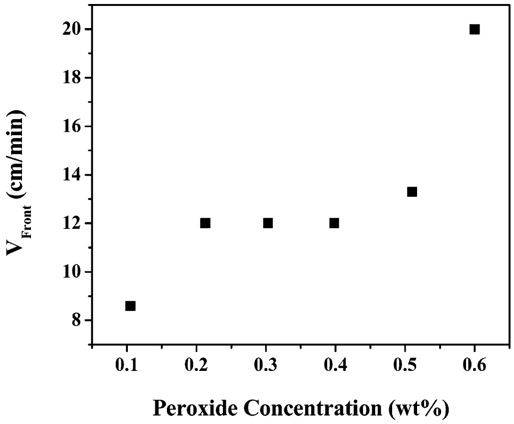
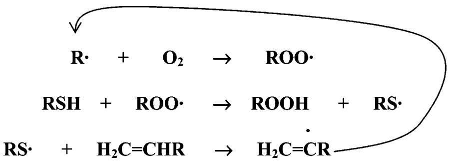


Figure 10. V_{front} for TMPTA as a function of Luperox 231 concentration; 1 wt % Darocur 4265; in air; irradiance of 5.9 mW/cm^2.

Figure 9 shows a plot of T_{start} for TMPTA as a function of the thermal initiator concentration (Luperox 231). Once a critical concentration of 0.2 wt % of thermal initiator is present, T_{start} is independent of peroxide concentration; i.e., there is a critical peroxide concentration required to induce a frontal polymerization. If the concentration of peroxides is too low, then the front cannot be sustained since the rate of radical production will be too low to induce a traveling front. As the peroxide concentration is increased, there is an increase in V_{front} (Figure 10) due to an increasing rate in radical production with peroxide concentration. Of course, although not shown explicitly here, if the concentration of peroxide is too large, the frontal polymerization may reach a stage where the reaction becomes unstable or even explosive. Thus, it is imperative to select a peroxide concentration large enough to maximize V_{front}, but not so large that a stable front cannot be maintained.

Addition of a Multifunctional Thiol. It is well-known that the free-radical polymerization of acrylates is severely inhibited by oxygen;[43−45] oxygen is a triplet diradical that reacts with the carbon-centered radicals involved in the polymerization process. Since radicals are terminated by reaction with oxygen, the rate of reaction is severely reduced and can even cease when

Scheme 1. Mechanism for Scavenging of Oxygen in Presence of Thiol



$$R\cdot + O_2 \rightarrow ROO\cdot$$

$$RSH + ROO\cdot \rightarrow ROOH + RS\cdot$$

$$RS\cdot + H_2C{=}CHR \rightarrow H_2C{=}\dot{C}R$$

free-radical polymerization is initiated in the presence of air. In the frontal polymerizations of acrylates described herein in Figures 7−10, the concentration of oxygen at the air/monomer interface is particularly large due to direct contact with atmospheric oxygen. Hence, because of a continual rapid diffusion of oxygen into the monomer surface boundary layer, the concentration of oxygen dissolved in the initiation zone of the frontal polymerization is large enough to affect the onset of free-radical polymerization and hence the initiation of the front. The oxygen inhibition at the surface results in the need for producing a high concentration of initiating radicals to effectively eliminate the oxygen inhibition effect. The result is a significant increase in the time required to initiate the front; i.e., T_{start} values are large. Oxygen inhibition can be overcome by using a higher light intensity source, but since applications for frontal polymerization demand that a low-intensity lamp source be used, this is not a viable option. Also, as for the data generated in Table 1 and Figure 6, it is possible to place a glass plate over the sample to be cured by a frontal polymerization process. However, this is not a viable for most applications. It would be highly desirable to simply modify the monomer system and reduce T_{start} by a chemical oxygen scavenging process. It has been shown that thiols decrease oxygen inhibition[43,46] by the chain transfer process in Scheme 1. In the first step a carbon-centered propagating radical reacts with oxygen forming a peroxy radical. Normally the peroxy radical would couple with the radical on the end of the growing chain, terminating the chain, or hydrogen abstract from a C−H bond. If thiol is present in the system, the peroxy radical abstracts a hydrogen from the thiol forming a thiyl radical. The newly formed thiyl radical then adds to a vinyl double bond, producing a new carbon-centered radical. The chain process will continue until oxygen is depleted, and the acrylate polymerization will then begin unencumbered by dissolved oxygen. As depicted in Figure 11, if the thiol in Figure 3 is added to TMPTA, then oxygen inhibition is reduced and T_{start} is decreased significantly. This is consistent with literature reports that addition of thiols to acrylate coatings significantly reduces.[43,46] In a more careful analysis of the results in Figure 11, it is obvious that thiol concentrations of greater than 10 wt % have no effect on reducing T_{start} further. High thiol concentration can, however, have an adverse effect on V_{front}. As shown in Figure 12, the front velocity decreases with an increase of thiol over 1 mol % since acrylate homopolymerization is faster than the thiol−ene copolymerization, thus lowering V_{front}. For samples with 50 mol % thiol functional groups the front cannot be initiated/sustained. The reason for the lower V_{front} values in Figure 12 with increasing trithiol content is twofold. First, V_{front} is no doubt reduced by the lower enthalpy of thiol−acrylate copolymerization (ΔH is 14.8 kcal/mol of ene as determined by a procedure described in the Experimental Section) compared to acrylate homopolymerization (19.2 kcal/mol acrylate).[47] We estimate that the heat release for complete conversion would decrease from about 0.12 kcal/g of sample to about 0.081 kcal/g (i.e., about 34%) as 30 mol % thiol is added to TMPTA. Of course, complete conversion may well not be obtained; our estimate then reflects an upper estimate for the heat release effect on V_{front} as thiol is added. This estimate assumes that the reaction enthalpies for the two reactions have equal dependence upon temperature so that the enthalpy values obtained at 25 °C reflect the relative enthalpies of reaction at the front temperature. The other effect that occurs when thiol is added is the reduction in conversion rate expected for the slower thiol−acrylate reaction. In summary, both effects, the reduction in total heat release and the slower rate for the thiol−acrylate reaction, account for the lower V_{front} values with increasing thiol content.

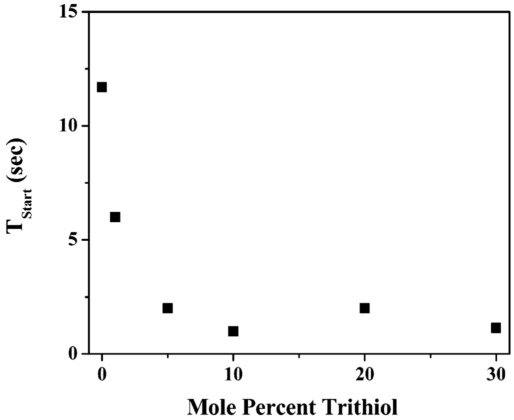


Figure 11. T_{start} for TMPTA as a function of mol % thiol; 0.3 wt % Darocur 4265; 0.3 wt % Luperox 231; in air; irradiance of 5.9 mW/cm^2.

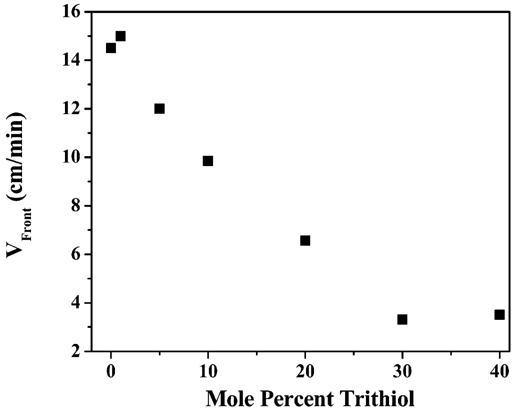


Figure 12. V_{front} for TMPTA as a function of mol % thiol; 0.3 wt % Darocur 4265; 0.3 wt % Luperox 231; in air; irradiance of 5.9 mW/cm^2.

Conclusions

Herein, we have shown that thick materials can be produced by UV-induced frontal polymerization of multifunctional acrylate monomers. Photo-DSC was used to record exotherms of the photopolymerization of several (meth)acrylates. The exotherm results, along with monomer molecular weight considerations, were correlated with frontal polymerization rate parameters of each monomer. Because of steric effects and stability of the radical, methacrylates polymerize slowly and exhibited a very slow frontal velocity. In the case of acrylates, the front velocity was found to be directly related to the molecular weight per double bond of the monomer. TMPTA, which had the fastest frontal velocity, was evaluated in detail. The exposure time required to begin the TMPTA front was measured as a function of both the thermal and photoinitiator concentration. Once a critical concentration of initiator was attained, the time to start the frontal polymerization was invariant with further increases in concentration of either photoinitiator or thermal initiator. Also, the frontal velocity increased as the thermal initiator concentration increased. At low concentrations of thiol, T_{start} was reduced and V_{front} increased modestly. At higher concentrations of thiol, V_{front} decreased as the polymerization process changed from homopolymerization to a combination of acrylate homopolymerization and thiol−acrylate copolymerization.

Acknowledgment. We gratefully acknowledge Fusion UV Systems Inc. and Lockheed Martin for funding.

References and Notes

(1) Merzhanov, A. G.; Borovinskaya, I. P. *Dokl. Akad. Nauk SSSR* **1972**, *204*, 336.
(2) Chechilo, N. M.; Enikolopyan, N. S. Effect of the Concentration and Nature of Initiators on the Propagation Process in Polymerization. *Dokl. Phys. Chem.* **1975**, *221,* 392.
(3) Chechilo, N. M.; Enikolopyan, N. S. Effect of Pressure and Initial Temperature of the Reaction Mixture during Propagation of a Polymerization Reaction. *Dokl. Phys. Chem.* **1976**, *230,* 840−843.
(4) Pojman, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 6284.
(5) Volpert, Vit. A.; Volpert, Vl. A.; Pojman, J. A. *Chem. Eng. Sci.* **1994**, *14*, 2385.
(6) Volpert, V.; Volpert, V. *Eur. J. Appl. Math.* **1994**, *5,* 201.
(7) Savostyanov, V. S.; Kritskaya, D. A.; Ponomarev, A. N.; Pomogailo, A. D. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32,* 1201.
(8) Pojman, J. A.; Willis, J.; Fortenberry, D.; Ilyashenko, V.; Khan, A. *J. Polym. Sci., Part A: Polym Chem.* **1995**, *33,* 643.
(9) Pojman, J. A.; Ilyashenko, V. M.; Khan, A. M. *Physica D* **1995**, *84*, 260.
(10) Kim, C.; Teng, H.; Tucker, C. L.; White, S. R. *J. Comput. Mater.* **1995**, *29,* 1222.
(11) Nagy, I. P.; Sike, L.; Pojman, J. A. *Adv. Mater.* **1995**, *7*, 1038.
(12) Szalay, J.; Nagy, I. P.; Barkai, I.; Zsuga, M. *Angew. Makromol. Chem.* **1996**, *236*, 97.
(13) Volpert, V.; Volpert, V. A.; Pojman, J. A.; Solovyov, S. E. *Eur. J. Appl. Math.* **1996**, *7,* 303.
(14) Garbey, M.; Taik, A.; Volpert, V. *Q. Appl. Math.* **1996**, *54,* 225.
(15) Pojman, J. A.; Willis, J. R.; Khan, A. M.; West, W. W. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 991.
(16) Pojman, J. A.; Ilyashenko, V. M.; Khan, A. M. *J. Chem. Soc., Faraday Trans.* **1996**, *92,* 2824.
(17) Pojman, J. A.; Curtis, G.; Ilyashenko, V. M. *J. Am. Chem. Soc.* **1996**, *115*, 3783.
(18) Pojman, J. A.; Elcan, W.; Khan, A. M.; Mathias, L. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35,* 227.
(19) Chekanov, Y.; Arrington, D.; Brust, G.; Pojman, J. A. *J. Appl. Polym. Sci.* **1997**, *66,* 1209.
(20) Tredici, A.; Pechhini, R.; Sliepcevich, A.; Morbidelli, M. *J. Appl. Polym. Sci.* **1998**, *70,* 2695.
(21) Tredici, A.; Pecchini, R.; Morbidelli, M. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36,* 1117.
(22) Volpert, V. A.; Volpert, V. A.; Ilyashenko, V. M.; Pojman, J. A. *Chem. Eng. Sci.* **1998**, *53,* 1655.
(23) McCaughey, B.; Pojman, J. A.; Simmons, C.; Volpert, V. A. *Chaos* **1998**, *8*, 520.
(24) Pojman, J. A.; Gunn, G.; Patterson, C.; Owens, J.; Simmons, C. *J. Phys. Chem. B* **1998**, *102*, 3927.
(25) Masere, J.; Stewart, F.; Meehan, T.; Pojman, J. A. *Chaos* **1999**, *9*, 315.
(26) Chekanov, Y. A.; Pojman, J. A. *J. Appl. Polym. Sci.* **2000**, *78,* 2398.
(27) Bazile Jr., M.; Nichols, H. A.; Pojman, J. A.; Volpert, V. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 3504.
(28) Fiori, S.; Mariani, A.; Ricco, L.; Russo, S. *e-Polym.* **2002**, *29*, 1.
(29) Fiori, S.; Malucelli, G.; Mariani, A.; Ricco, L.; Casazza, E. *e-Polym.* **2002**, *57*, 1.
(30) Gill, N.; Pojman, J. A.; Willis, J.; Whitehead, J. B. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 204.
(31) Washington, R. P.; Steinbock, O. *Polym. News* **2003**, *28*, 303.
(32) Pojman, J. A.; Varisli, B.; Perryman, A.; Edwards, C.; Hoyle, C. *Macromolecules* **2004**, *37,* 691.
(33) Pojman, J. A.; Griffith, J.; Nichols, H. A. *e-Polym.* **2004**, *13*, 1.
(34) Mariani, A.; Bidali, S.; Fiori, S.; Sangermano, M.; Malucelli, G.; Bongiovanni, R.; Priola, A. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 2066.
(35) Crivello, J. V.; Falk, B.; Zonca., M. R. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 1630.
(36) Decker, C.; Bendaikha, T.; Decker, D.; Zahouily, K. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1997**, *38* (1), 487.
(37) Ivanov, V.; Decker, C. *Polym. Int.* **2001**, *50*, 113.
(38) Coons, L. S.; Rangarajan, B.; Godshall, D.; Scranton, A. B. Photopolymerization of Vinyl Ester: Glass Fiber Composites. In *Photopolymerization: Fundamentals and Applications;* ACS Symposium Series 673; Scranton, A. B., Bowman, C. N., Peiffer, R. W., Eds.; American Chemical Society: Washington, DC, 1997; pp 203−218.
(39) Scott, G. Ultraviolet curable resin compositions having enhanced shadow cure properties. U.S. Patent 6,245,827, 2001.
(40) Crivello, J. V.; Falk, B.; Zonca, M. R. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 1630.
(41) Mariani, A.; Bidali, S.; Fiori, S.; Sangermano, M.; Malucelli, G.; Bongiovanni, R.; Priola, A. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42,* 2066.
(42) Pojman, J. A.; Popwell, S.; Fortenberry, D. I.; Volpert, V. A. Nonlinear dynamics in frontal polymerization. *ACS Symp. Ser.* **2004**, *869*, 106−120.
(43) Gush, D. P.; Ketley, A. D. *Mod. Paint Coat.* **1978**, *68*, 58.
(44) Roffey, C. G. *Photogeneration of Reactive Species for UV Curing*; John Wiley and Sons New York, 1997; p 233.
(45) Jacobine, A. F. In *Radiation Curing in Polymer Science and Technology*; Fouassier, J. P., Ed.; Elsevier: New York, 1993; pp 219−268.
(46) Morgan, C. R. *J. Radiat. Curing* **1980**, *7*, 10.
(47) Tryson, G. R.; Shultz, A. R. *J. Polym. Sci., Polym. Phys.* **1979**, *17*, 2059.

MA048569Y