

UV Induced Frontal Polymerization of (Meth)Acrylates

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Abstract

A novel technique, photo-induced frontal polymerization, has been evaluated for a wide variety of monomers. Photo-DSC and frontal polymerization were carried out on each monomer. The Photo-DSC data was used to predict whether frontal polymerization would be initiated and sustained by a particular monomer. TMPTA was found to have the fastest frontal velocity, so detailed studies were performed by varying both the photoinitiator and the peroxide concentrations to determine their effects on the frontal velocity and the time required for the reaction to begin after exposure to light.

Introduction

Although UV curing was introduced in the U.S. in the early 1970's, uses are still limited primarily to coatings and adhesives applications. In this paper we demonstrate that UV light can be used to cure very thick samples. A novel technique, photo-induced frontal polymerization, will be presented in which there is no limitation on thickness.

Frontal polymerization is a method used to convert monomer into polymer by means of a localized reaction zone that propagates due to the heat released from the polymerization reaction. In 1967, Chernogolovka, Merzhanov, and Borovinskaya reported on self-propagating high-temperature synthesis.¹ This process, in which a pellet of reactant is ignited at one end, results in a self-propagating combustion wave. The advantages of this self-propagating system are that the initial stimulus is the only energy needed and that superior products result.

In 1972, Chechilo and Enikolopyan used the same approach to cure vinyl monomers via free-radical polymerization initiated by peroxides.^{2,3} They polymerized methyl methacrylate under high pressure to eliminate convective instabilities that are detrimental to traveling fronts. In 1991, Pojman reported on the frontal polymerization of methacrylic acid at ambient pressure in standard test tubes.⁴ Numerous other papers on the subject of frontal polymerization have been published during the past decade.⁵⁻¹⁶

For a traveling front to exist there are some important factors to consider. First, there must not be any reaction at ambient temperature. Second, an initial energy input, either heat or light, must produce radicals that initiate the polymerization of monomer. As the monomer is converted into polymer heat is given off causing a self-propagating thermal wave or reaction, as shown in Figure 1, that separates cured 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. The monomer should also have a higher boiling point than the front temperature to prevent bubble formation.

Herein, we report on the effect of monomer structure and functionality on parameters associated with frontal polymerization. Correlation between polymerization exotherms recorded by photo-DSC and frontal propagation will be made.

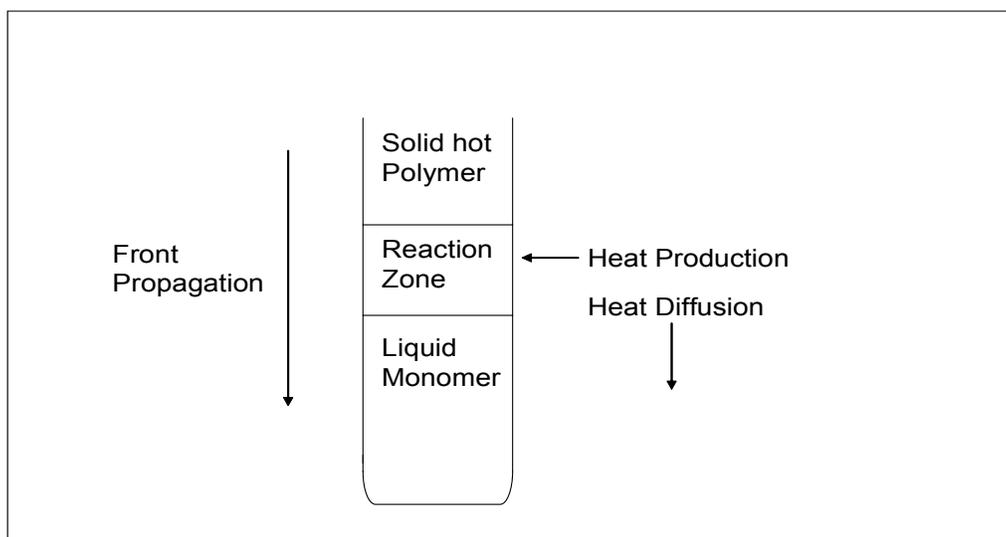


Figure 1. Schematic of Frontal Polymerization

Experimental

Monomers were obtained from UCB Chemicals and Aldrich Chemical Company. Luperox 231 (1,1-di(t-butylperoxy)-3,3,5-trimethylcyclohexane) was obtained from Atofina. Darocur 4265 and 1173 were obtained from Ciba. All chemicals were used as received.

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 at the sample pans via a black body 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 (about 8 mils).

For frontal polymerization, the resin, photoinitiators, and peroxides were mixed together and transferred to a 16x125 mm test tube with clear ruler tape affixed to the side of the test tube. A filled test tube was clamped into place in a holder underneath the light source. Nitrogen was then blown over the top of the test tube for 2.5 minutes. Subsequently, a glass cover was placed on top of the test tube. The video camera was setup on one side of the test tube. The velocity and the start time were recorded on a Sony Handycam. The camera recorded the start time (T_{start}), which is defined as the time it takes to induce the frontal polymerization with UV light. If the front did not start photolytically then a thermal heat source was used to initiate the thermal initiator directly. The frontal velocity (V_{front}) was found by measuring the time it takes for the front to travel a given distance.

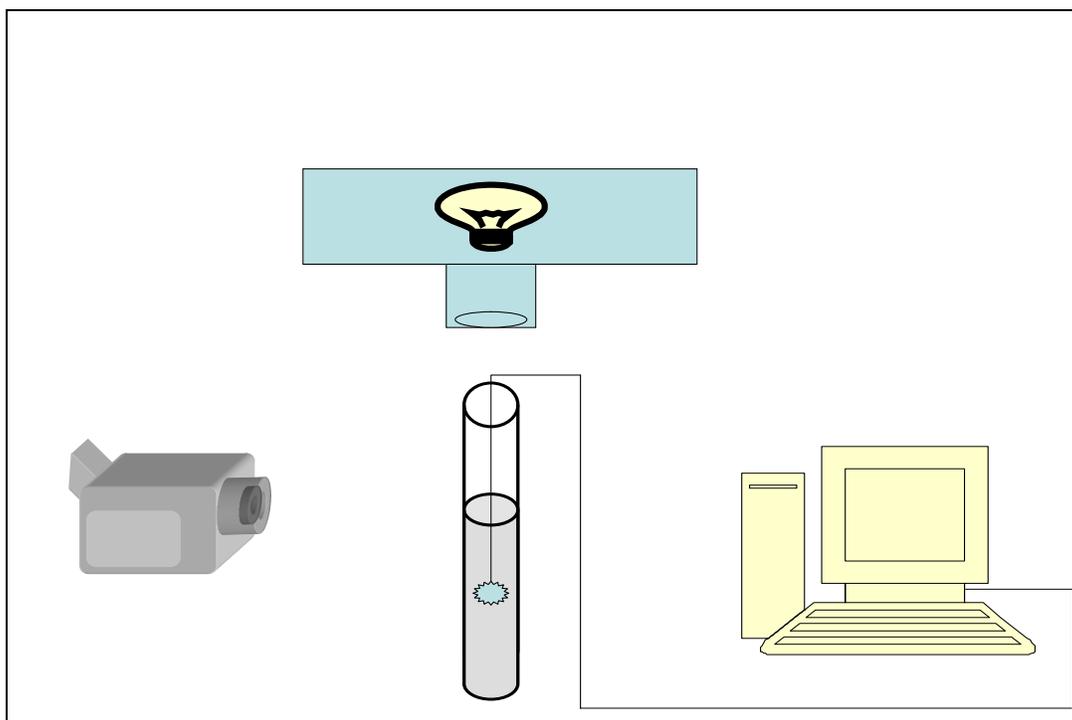


Figure 2. Set-up of Frontal Polymerization Apparatus

Results and Discussion

A total of 9 (meth)acrylates were chosen for evaluation. The monomers varied in type (acrylate versus methacrylate), functionality (2 or 3), and molecular weight per double bond (99 to 500 g/mole per double bond). The following monomers/acronyms were used; TMPTA, trimethylolpropane triacrylate; DEGDA, diethylene glycol diacrylate; HDDA, 1,6-hexanediol diacrylate; TMPEOTA, trimethylolpropane ethoxy triacrylate; Ebecryl 8402 (difunctional urethane acrylate); DEGDMA, diethylene glycol dimethacrylate; HDDMA, 1,6-hexanediol dimethacrylate; TMPTMA, trimethylolpropane trimethacrylate; TREGDMA, triethylene glycol dimethacrylate; Luperox 231, 1,1-Bis-(t-Butylperoxy)-3,3,5-trimethylcyclohexane (thermal initiator); Darocur 1173 (photoinitiator); Darocur 4265 (visible photoinitiator). Information about each monomer is shown in Table 1. In order to evaluate the inherent polymerization rate of each monomer, photo-DSC exotherms for samples with 1 wt% Darocur 4265 were recorded. An example of a photo-DSC of three of the monomers is shown in Figure 3. Parameters obtained from the photo-DSC exotherms of each monomer listed in Table 1 include the peak exotherm maximum (H_{max}) and the time to attain the peak maximum (T_{max}). The photo-DSC results for all of the acrylates, except Ebecryl 8402, have large H_{max} and short T_{max} values which means that they produce enough heat in a short amount of time to induce frontal polymerization. Ebecryl 8402 acrylate monomer with a high molecular weight between functional groups has a low H_{max} and would not be expected to initiate and sustain frontal polymerization. The methacrylates all exhibit low exotherms and also should not sustain a frontal polymerization.

Next each monomer was evaluated for its propensity to initiate and sustain frontal polymerization. The parameters recorded in Table 1 deal with whether the front started photolytically (Photo), the time it took to start the frontal polymerization (T_{start}), and the velocity of the front (V_{front}). In Table 1 the monomers are divided into two groups, acrylates and methacrylates. Each group is then arranged in ascending order of increasing molecular weight (MW) per double bond. Monomers with the lowest MW per double bond should give off the highest amount of heat and have the fastest velocity. This is indeed true, since TMPTA with the lowest MW per double bond (98.6 g/mol) has the fastest frontal velocity (15 cm/min). The monomer with the highest MW per double bond, Ebecryl 8402 (500 g/mol), did not sustain a traveling front as predicted by the exotherm data. As can be seen in Table 1 as the MW per double bond increased the velocity decreased.

As expected from the exotherm data, the methacrylates are not capable of initiating frontal polymerization photochemically under the conditions employed. Although it is possible to initiate the methacrylate frontal polymerization thermally, the resultant frontal velocities are also extremely slow in comparison to the acrylates. It is known that methacrylates polymerize slower than acrylates because of the steric hinderance of the methyl group and the higher radical stability.

Table 1. Characteristics and Results of Resins Run on a Photo-DSC and Frontally

	Functionality	MW per Double Bond	Photo (Y/N)	H_{max} (mW)	T_{max} (sec)	V_{front} (cm/min)	T_{start} (sec)
Acrylates							
TMPTA	3	98.6	Yes	43	36	15	17
DEGDA	2	107	Yes	86.5	38	10	5
HDDA	2	113	Yes	71	39	8	8
TMPEOTA	3	142.6	Yes	67	36	6.3	9
Ebecryl 8402	2	500	No	6.6	42	NA	NA
Methacrylates							
DEGDMA	2	121	No	6	80	0.71	NA
HDDMA	2	126	No	1.6	93	0.45	NA
TMPTMA	3	128.6	No	4.6	41	0.73	NA
TREGDMA	2	143	No	7	75	0.67	NA

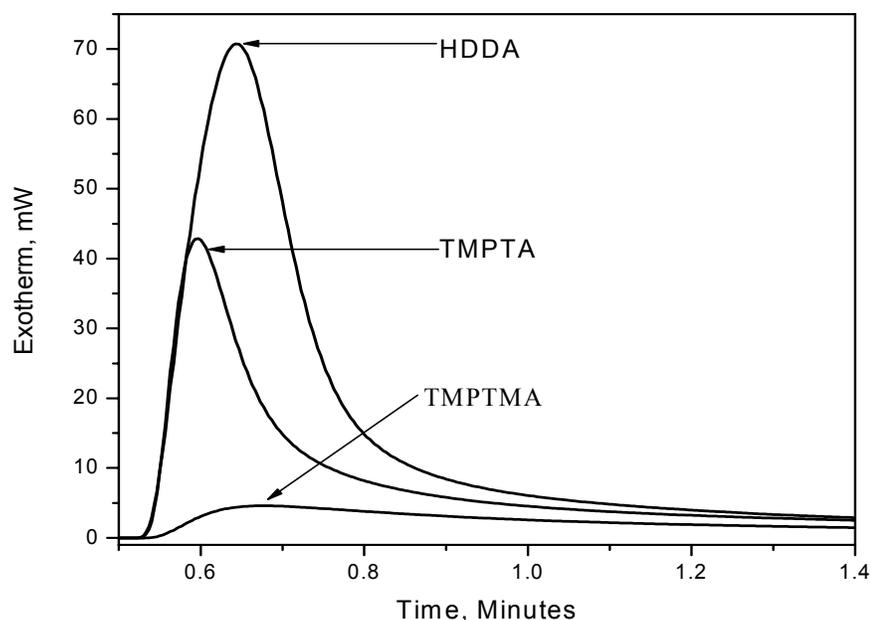


Figure 3. Photo-DSC exotherms of HDDA, TMPTA, and TMPTMA with 1wt% Darocur 4265 using the full arc of a medium pressure mercury lamp with irradiance of 0.44 mW/cm^2 .

Since TMPTA had the fastest frontal velocity it was chosen for more in-depth study. Figure 4 is a frontal polymerization plot of T_{start} of TMPTA as a function of the photoinitiator concentration. As can be seen in Figure 4, for an increase of 0.1 wt% to 0.3 wt%, T_{start} dramatically decreases. This decrease continues to 1 wt% photoinitiator at which point T_{start} is not affected by an additional increase in photoinitiator concentration. With an increase in photoinitiator concentration more radicals are formed to react with the monomer, producing enough heat to decompose the thermal initiator. Both a small amount and a large amount of photoinitiator can have adverse effects on inducing frontal polymerization. In the case of a small amount of photoinitiator, there are not enough radicals produced to react with the monomer and generate heat to induce the frontal polymerization. If oxygen is present, then the radicals will react with oxygen. If there are not enough radicals to overcome oxygen inhibition, then enough heat will not be produced to induce a frontal reaction. Too much photoinitiator can cause an inner filter effect. Although not included in this paper, we have shown that addition of a thiol leads to substantial decreases in the start time of frontal polymerization in air.¹⁷

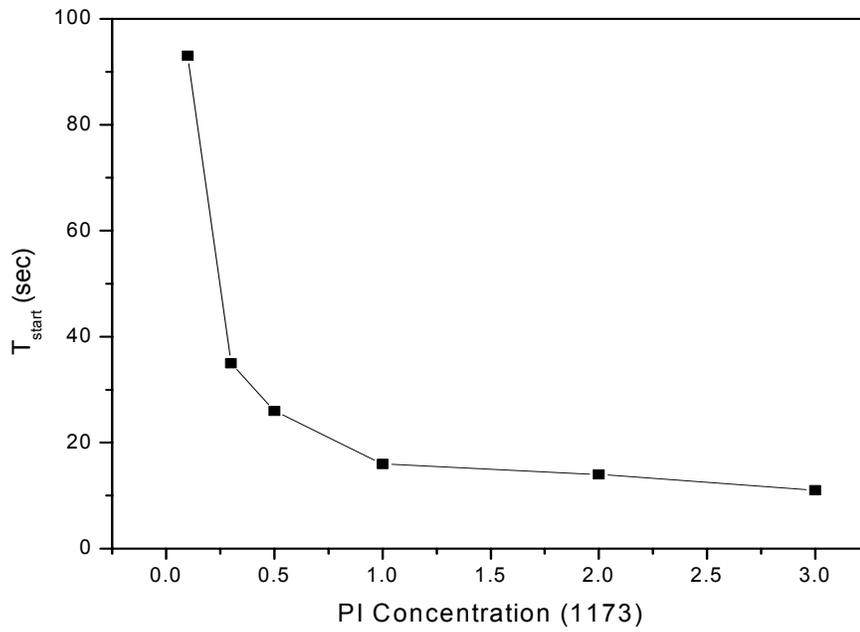


Figure 4. T_{start} as a function of photoinitiator concentration; TMPTA; 0.4 wt% Luperox 231; In air; irradiance of 5 mW/cm².

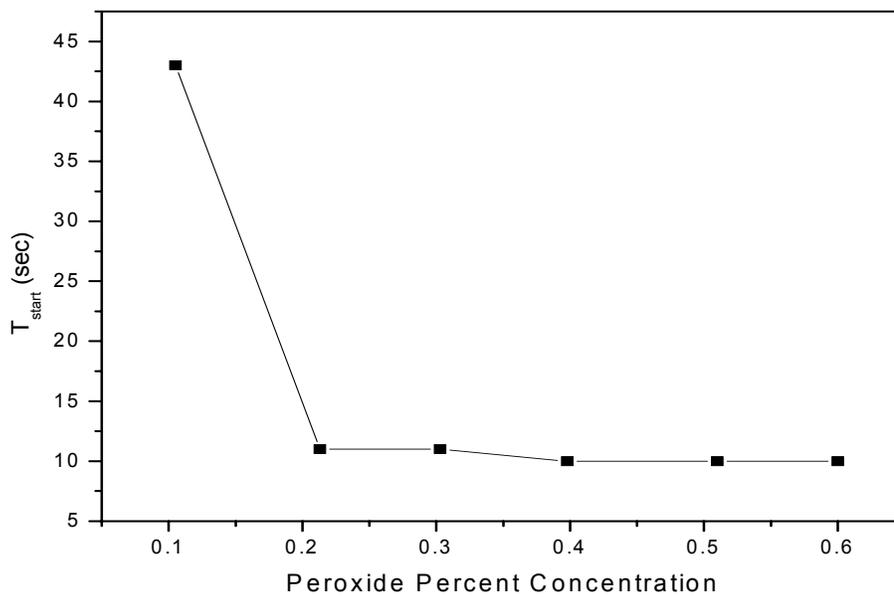


Figure 5. T_{start} as a function of peroxide concentration; TMPTA; 1 wt% Darocur 4265; In air; irradiance of 5 mW/cm².

Figure 5 is a frontal polymerization plot of T_{start} for TMPTA as a function of the thermal initiator concentration (Luperox 231). Once a critical amount of thermal initiator is added, 0.2 wt% in this case, T_{start} is independent of peroxide concentration. The only benefit to adding more peroxide is that there will be an increase in V_{front} as shown in Figure 6.

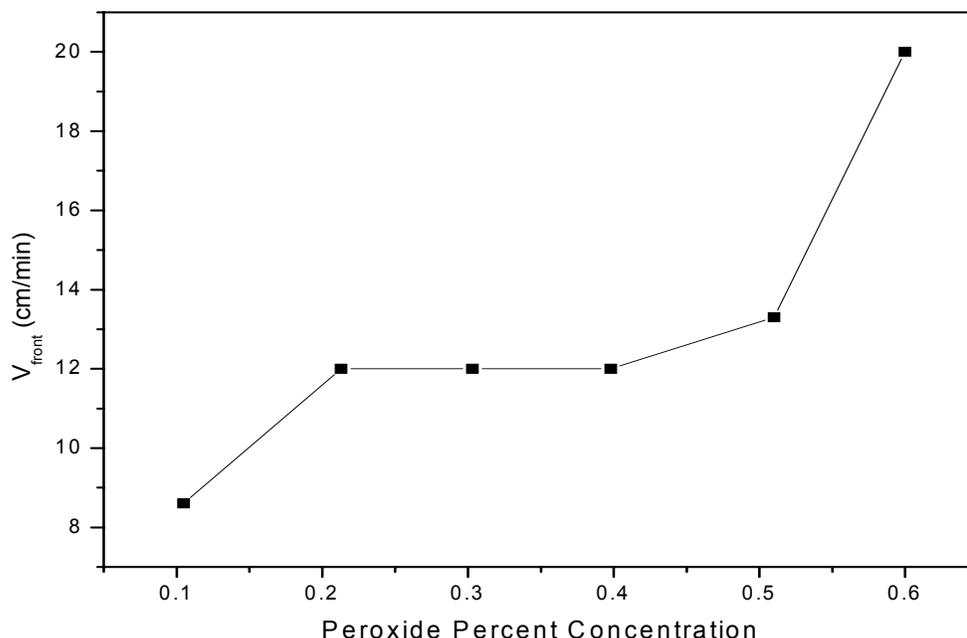


Figure 6. V_{front} of TMPTA as a function of peroxide concentration; 1 wt% Darocur 4265; In air; irradiance of 5 mW/cm².

Conclusions

Photo-DSC was used to record exotherms of the photopolymerization of (meth)acrylates. The results were used to correlate with the data collected from the frontal polymerization of each monomer. Monomers that had a high H_{max} and a low T_{max} exhibited fast frontal velocity. Due to steric effects and stability of the radical, methacrylates had a very slow frontal velocity. TMPTA, which had the fastest frontal velocity, was chosen for further evaluation. The time to start the front as a function of both thermal and photoinitiator concentration was recorded. 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. The frontal velocity was plotted as function of thermal initiator concentration, and it was found that the velocity increased as the thermal initiator concentration increased. We have shown that thick materials can be produced by UV-induced frontal polymerization.

Acknowledgements

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