

# KINTEICS AND MOLECULAR WEIGHT DISTRIBUTION OF PHOTOINIFERTER-DERIVED POLYMERS AS A FUNCTION OF COMPOSITION AND LIGHT INTENSITY

Dewey Fansler, Lead Research Chemist, 3M Co., Dresser, WI Stephen Roscoe, Senior Research Specialist, 3M Co. Woodbury, MN George Griesgraber, Lead Research Chemist, 3M Co., St. Paul, MN Kevin Lewandowski, Staff Scientist, 3M Co., Inver Grove Heights, MN John Battiste, Lead Research Specialist, 3M Co., Northfield, MN Babu Gaddam, Corporate Scientist (ret), 3M Co., Woodbury, MN

## Introduction

Controlled, or living, polymerization (CRP) has been an active area of research for decades and offers many advantages over free-radical polymerization.<sup>1-8</sup> Precise control of molecular weight and distribution, monomer composition, and polymer architecture are highly sought-after properties for the synthetic polymer chemist, but traditional CRP techniques have limitations that have been a barrier for large-scale industrial applications.<sup>9-11</sup> Photopolymerization is a widely used and important technique for a variety of products including adhesives and coatings. The photoinduced CRP methods known in the art tend to be too slow and good control occurs at conversions too low to be useful for these applications.

Traditional photoinitiators generate a “free” radical under irradiation with light of the appropriate frequency. The radical adds to a monomer and forms a radical-terminated chain that keeps adding monomer until some termination event such as combination or elimination. Chain transfer agents such as thiols can be used to terminate a chain by transfer of a hydrogen atom to the radical chain end and then initiate a new chain from the resulting sulfur-based radical. Thus, the presence of a chain transfer agent reduces the average molecular weight. Once a chain has been terminated it is considered “dead”, or incapable of further monomer addition. A particular consequence of these processes is that the average molecular weight observed during a polymerization is roughly consistent through the course of the polymerization and is a function of parameters such as initiator:monomer ratio and concentration of chain transfer agent.

In contrast, Otsu discovered a class of photoinitiators he described as photoiniferters that were not only capable of **initiating** polymerization, but also of **terminating** the polymer chains reversibly, so that they could be reinitiated subsequently.<sup>12-15</sup> In practice, these two processes occur continuously throughout the polymerization as long as the light remains on. Chains are constantly being initiated, extended, terminated, and then re-initiated. There are two major consequences to this behavior; firstly, the molecular weight grows progressively throughout the polymerization in a manner similar to other living polymerization techniques such as reversible addition-fragmentation chain-transfer (RAFT) or atom transfer radical polymerization (ATRP),

and secondly, the chain ends are constantly in an activatable state. Thus, when the light is turned off, the process stops, and all chains are terminated and in a quiescent state but can be re-initiated when the light is turned back on. This allows the formation of block copolymers by the simple method of turning the light off, adding a new monomer, and turning it back on again. However, the reaction is too slow, taking many hours, to be of industrial interest.

Later work on photoiniferters continued with the use of tin and other catalysts to accelerate the polymerization rate in methacrylate polymerizations.<sup>16</sup> Although this effort was successful, the presence of tin in the polymer remained a hindrance in manufacturing and the approach was not pursued. Some work was published on the reactivity of photoiniferters as a function of molecular structure by Lalevee in 2007.<sup>9</sup> New light sources, namely UV-LED lights, inspired work exploring the field again and two factors combined to change the field and make iniferter-based polymerization much more practical. The use of much more intense LED light sources and xanthate-based iniferters both individually raise the polymerization rate and have combined to make photoiniferter-based polymerizations much more practical for manufacturing-scale polymer synthesis.<sup>17</sup>

## Experimental

### Photoiniferters

p-xylenebis(N,N-diethyldithiocarbamate) (XDC) and dibenzyl dixanthate (XDX) were used as received from TCI America. Other photoiniferters were synthesized as described below.

2-Ethylhexyl 2,2-bis(diethylcarbamoythioylsulfanyl)acetate was synthesized by a stirred solution of 2-ethylhexanol (3.00 g, 23.0 mmol, available from Sigma-Aldrich) in 50 mL of CH<sub>2</sub>Cl<sub>2</sub>, cooled to 0°C under nitrogen. To the solution were added trimethylamine (4.80 mL, 34.4 mmol) and dimethylaminopyridine (20 mg) followed by the drop-wise addition of dichloroacetyl chloride (3.74 g, 25.4 mmol). The reaction mixture was allowed to reach ambient temperature while stirring overnight. The reaction mixture was quenched with a saturated solution of NaHCO<sub>3</sub> followed by addition of 50 mL of CH<sub>2</sub>Cl<sub>2</sub>. The layers were separated, and the organic portion was washed with 5 weight percent NaH<sub>2</sub>PO<sub>4</sub> (2x) followed by brine. The organic portion was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered through a small plug of silica gel, and concentrated under reduced pressure to 5.02 g of 2-ethylhexyl 2,2-dichloroacetate as a yellow liquid.

The 2-ethylhexyl 2,2-dichloroacetate (5.02 g, 20.8 mmol) was dissolved in 50 mL of acetone and treated with sodium diethyldithiocarbamate trihydrate (9.37 g, 41.6 mmol, Sigma-Aldrich) and the mixture was stirred overnight. The reaction mixture was filtered, rinsed with acetone, and the filtrate was concentrated to give a dark brown oil. The oil was taken up in 100 mL of CH<sub>2</sub>Cl<sub>2</sub> and washed with brine. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The resulting brown syrup was passed through a small plug of silica gel eluting

with 1:1 hexanes/ $\text{CH}_2\text{Cl}_2$  and concentrated to give 7.17 g of 2-ethylhexyl 2,2-bis(diethylcarbamoythioylsulfanyl)acetate as an orange syrup.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  7.22 (s, 1H) 4.11 (dd,  $J=5.4, 10.8$  Hz, 1H), 4.07 (dd,  $J=5.9, 10.8$  Hz, 1H), 3.98 (quartet,  $J=7.1$  Hz, 4H), 3.72 (quartet,  $J=7.2$  Hz, 4H), 1.61 (m, 1H), 1.40-1.25 (m, 8H), 1.31 (t,  $J=7.2$  Hz, 6H), 1.26 (t,  $J=7.1$ , 6H), 0.89-0.86 (m, 6H).

2-Ethylhexyl 2,2-bis(isopropoxycarbothiosulfanyl)acetate was synthesized by a solution of 2-ethylhexyl 2,2-dichloroacetate (7.14 g, 29.6 mmol) dissolved in 150 mL of acetone treated with potassium isopropyl xanthate (10.3 g, 59.3 mmol) and the reaction mixture was stirred overnight. The reaction mixture was filtered, rinsed with acetone, and the filtrate was concentrated to give a brown syrup. Purification by column chromatography ( $\text{SiO}_2$ , 100 volume percent hexanes to 40 volume percent  $\text{CH}_2\text{Cl}_2$ /hexanes) gave 9.3 g of 2-ethylhexyl 2,2-bis(isopropoxycarbothioylsulfanyl)acetate as an amber colored liquid.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  6.05 (s, 1H) 5.73 (m, 2H), 4.10 (m, 2H), 1.61 (m, 1H), 1.42 (d,  $J=6.3$  Hz, 6H), 1.40 (d, 6H), 1.37 (m, 2H), 1.34-1.26 (m, 6H), 0.89 (t,  $J=6.9$ , 3H), 0.89 (t,  $J=7.4$  Hz, 3H).

### Polymerization Kinetics

A solution of 2-ethylhexyl acrylate (25.0 g, 135 mmol, BASF) and 0.137 g (0.311 mmol) of 2-ethylhexyl 2,2-bis(isopropoxycarbothiosulfanyl)acetate in ethyl acetate (25 g) was placed in a 250 mL 2-necked round bottom flask and degassed with a nitrogen stream for 15 minutes. The flask was then held under a positive pressure of nitrogen, stirred magnetically, and irradiated with a UV Lamp (Sylvania F 15T8/BLB Blacklight Blue) placed 12.7 cm above the flask. The light intensity, measured at a distance of 12.7 cm, was  $0.7 \text{ mW/cm}^2$ .

The probe of a ReactIR 15 in-situ infrared spectrometer (Mettler-Toledo Autochem, Redmond, VA) was inserted into one neck of the flask and the tip of the IR probe was maintained below the surface of the reaction solution. The lamp was turned on and an infrared spectrum was recorded every minute for the first hour, every 5 minutes for the next three hours, and 15 minutes thereafter. The percent monomer consumption was calculated by determining the peak height of the C=C stretching band at  $1639 \text{ cm}^{-1}$  defined from a two-point baseline from  $1650 \text{ cm}^{-1}$  to  $1610 \text{ cm}^{-1}$ . The weight percent monomer conversion was calculated as:  $\text{Wt\% Monomer Conversion} = 100 \times (\text{peak height}/\text{time zero peak height})$ . The times for conversion of 40 weight percent and 80 weight percent of the monomer to polymer are recorded. Physical samples were removed at intervals throughout the polymerization and molecular weights were determined by gel permeation chromatography (GPC) using differential refractive index (dRI) detection and polystyrene standards.

In systems using an LED light source the LED systems employed were either a water-cooled bank of custom designed and built by 3M Co. (500 365 nm LEDs maintained at 5W input power which yielded ~ 150 mW/cm<sup>2</sup>) mounted 3” from the flask, or a 12-LED air-cooled system from Clearstone Technologies (JL3-365G2-12 ) that gives ~ 60 mW/cm<sup>2</sup> at 50% power when mounted 1” from the flask.

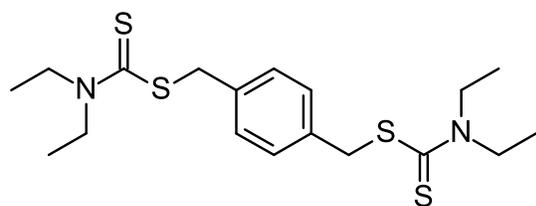
## Results and Discussion

Otsu’s archetypical photoiniferter was xlylidene bis(diethylamino) dithiocarbamate (XDC), and in Otsu’s hands XDC was able to successfully polymerize MMA and styrene with good control, albeit slowly. Thus, Mw would start low, and increase progressively throughout the polymerization. However, when the polymerization of typical acrylates such as 2-ethylhexylacrylate (EHA) or butyl acrylate (BA) was investigated, markedly different behavior was observed. With irradiation under a standard blacklight UV lamp (BLB), the Mw was very high at low conversion levels and actually dropped with increasing conversion. In order to better understand this phenomenon, four iniferters were studied in considerable detail. In particular a set of four that represent variations on two structural features: dithiocarbamate vs xanthate end groups and dibenzyl vs geminal cores. Note that all four of these iniferters possess two end groups and are capable, at least theoretically, of extending the polymer chain in two directions from a central core.

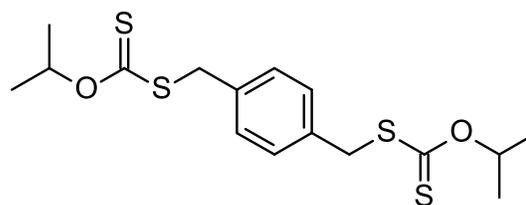
**Table 1.** Iniferter Structural Features

	Dithiocarbamate	Xanthate
Dibenzyl	Dibenzyl bis(dithiocarbamate) (XDC)	Dibenzyl dixanthate (XDX)
Geminal	Geminal bis(dithiocarbamate) (GPIT series)	Geminal dixanthate (GTEX series)

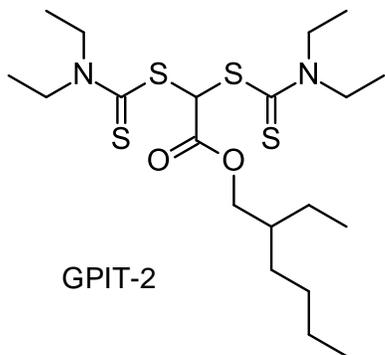
Numerous esters (and amide) derivatives based on the geminal motif have been explored in the group, but their polymerization behavior is similar so for the sake of consistency we used the 2-ethylhexyl derivatives GPIT-2 and GTEX-5.



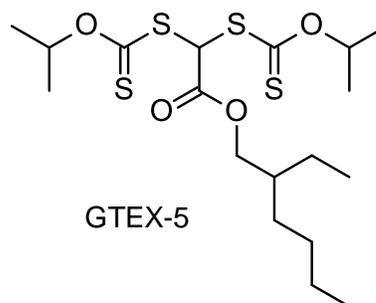
XDC



XDX



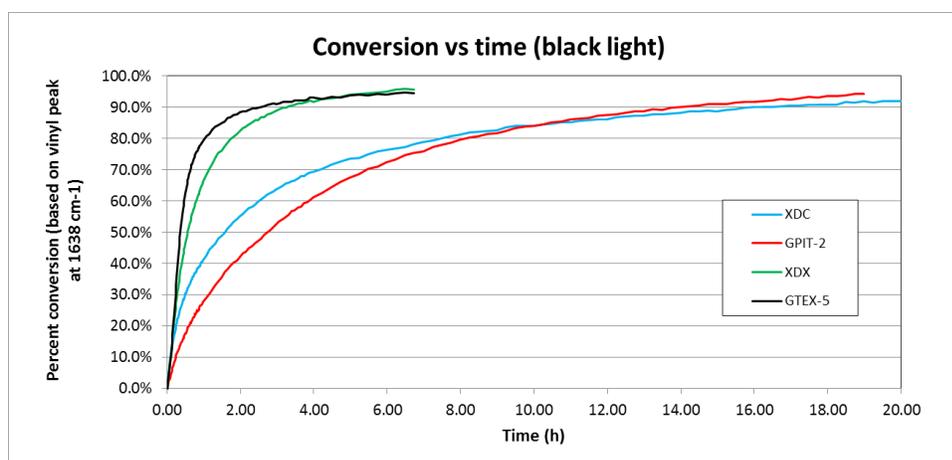
GPIT-2

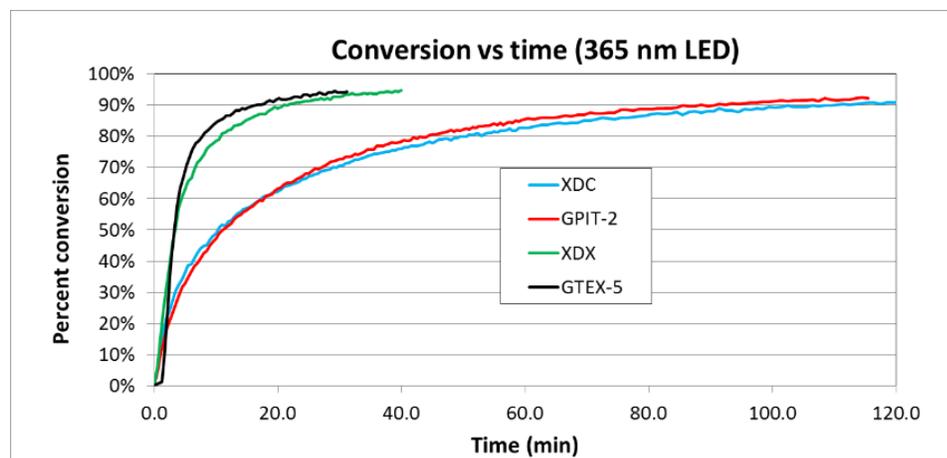


GTEX-5

**Figure 1.** Iniferter Structures

Graphs of conversion vs time for the four iniferters demonstrates that the two xanthate derivatives (GTEX-5 and XDX) polymerize 2-EHA considerable faster than the dithiocarbamates (XDC and GPIT-2).





**Figure 2.** Monomer conversion for 2-EHA polymerization with different initiators under a/ backlight and b/ LED illumination.

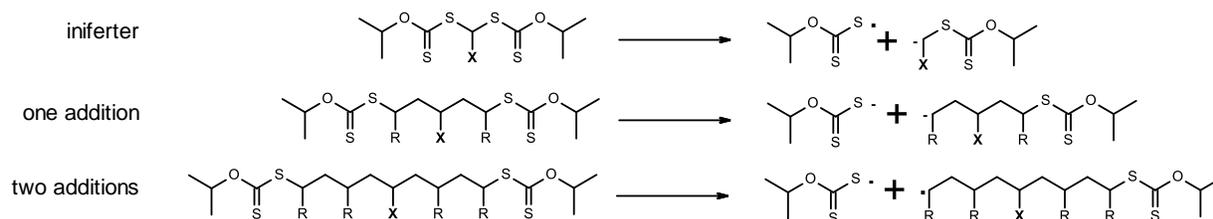
This is observed both with UV illumination ( $\sim 0.7 \text{ W/cm}^2$ ) and with 365 nm LEDs ( $150 \text{ mW/cm}^2$ ). The relative rates with different initiators and light sources can be conveniently assessed by comparing the time taken to reach 80% conversion.

**Table 2.** Time to 80% Conversion (min)

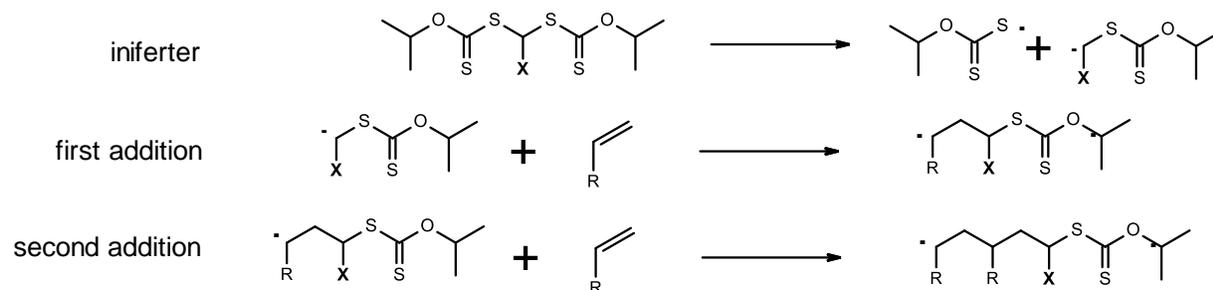
	UV	LED
<b>XDC</b>	450	49
<b>GPIT-2</b>	500	45.5
<b>XDX</b>	100	11
<b>GTEX-5</b>	66	7.5

This highlights that the polymerization rate is a function of the end group (xanthate vs dithiocarbamate), core structure (dibenzyl vs geminal) and light intensity. Of the structural components, the nature of the end group has a more significant effect on rate than the core, with xanthates GTEX-5 and XDX being 5-6 times faster to 80% conversion than the analogous dithiocarbamates (GPIT-2 and XDC, respectively) under the same conditions. The influence of the core is much smaller and variable, with XDC being faster than GPIT-2 under one condition and slower under another, while GTEX-5 is  $\sim 50\%$  faster than XDX under both light intensities. The lack of impact from the core is hardly surprising, since once a couple of monomers are added, the core is remote from the active site and should not be expected to have an impact on either the rate of photolysis or addition (Scheme 1).

Photolysis:



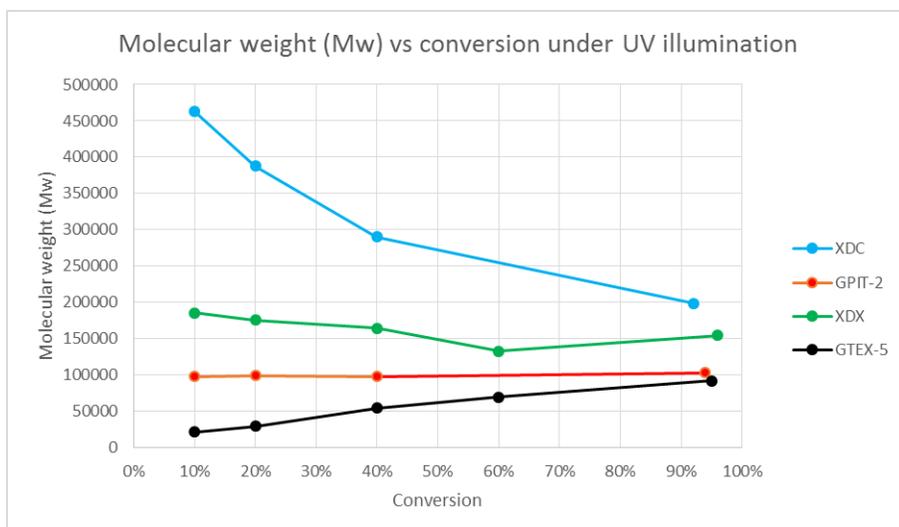
Addition:



**Scheme 1.** Photolysis of iniferter, and product after one and two additions. Also, product from photolysis after one addition of monomer to each side, and after two additions. Scheme highlights how core group becomes remote from active site at an early stage in the polymerization.

As expected, the polymerization rate increases markedly as the light intensity increases. It is worth noting however, that an increase in light intensity of ~200-fold going from UV blacklight to LED causes an increase in rate of only ~10X.

When running polymerizations under UV illumination, it was obvious that there were significant differences between the four iniferters. In particular samples polymerized with XDC would become so viscous above ~40% conversion that it was not practical to withdraw a sample by syringe for GPC. This was not true when the polymerizations were conducted under LEDs, or when GTEX-5 or XDX were used as the photoiniferter. This is readily explained by the plot of weight average molecular weight (Mw) vs conversion below, in which a reaction run with XDC as iniferter yields very high Mw at low conversions. The theoretical MW under these experimental conditions was ~80,000 yet the first sample, removed at 10% conversion, already had a weight average Mw of 450,000. As the polymerization proceeds to higher conversion, the average molecular weight drops progressively ending at less than half the initial value by the end of the experiment (Figure 3).

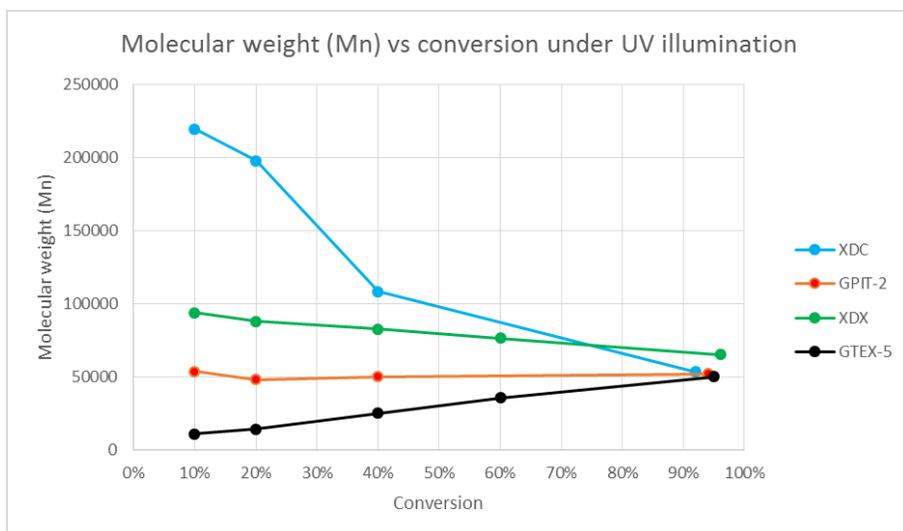


**Figure 3:** Weight average molecular weight (Mw) as a function of conversion under illumination with a UV blacklight.

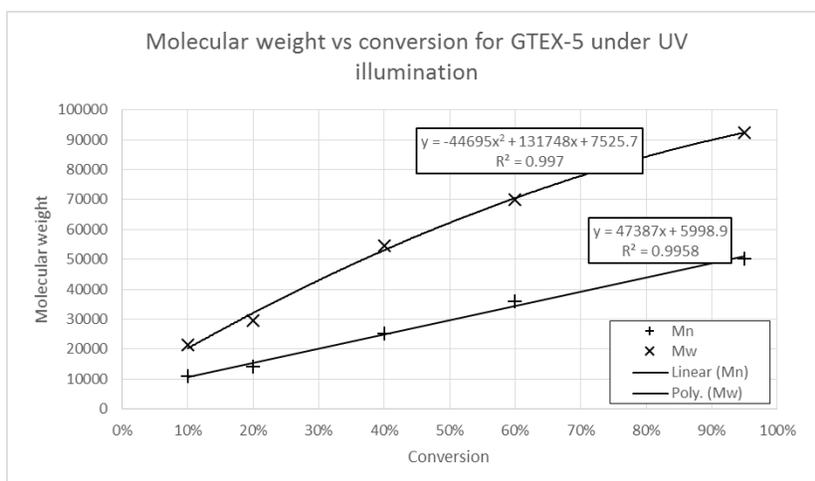
None of the other three iniferters led to such dramatically high Mw. GTEX-5 yields the expected behavior for a living polymerization, where Mw increases linearly with conversion from ~ 20k at 10%, to ~90k at 95% conversion. GPIT-2 and XDX display intermediate behavior, starting at higher than expected Mw and remaining essentially unchanged through the polymerization.

Similar results are seen in the number average molecular weights (Figure 4), with all values being significantly lower than Mw. The same general trends persist, Mw drops steeply for XDC, remains constant for XDX and GPIT-2, and rises linearly for GTEX-5. Polydispersities (PD) are ~2 in each case, except for XDC, where it rises from 2 to nearly 4 by the time the polymerization is complete.

The Mw vs conversion graphs are particularly interesting for GTEX-5. The relationship between conversion and Mn in particular is highly linear, but does not intercept the Y axis at 0, instead crossing at ~6000 which corresponds to ~ 30 monomer units. A linear fit to Mw leads to an intercept at ~15000, but it is worth noting that the slope clearly flattens out as the polymerization proceeds. The initial slope can be simply approximated with a quadratic fit which yields an intercept of 7500, close to the intercept obtained for Mn (Figure 5). This suggests that, under these conditions, roughly 30 monomers are added for each photolysis step at the beginning of the polymerization.



**Figure 4:** Number average molecular weight (Mn) as a function of conversion under illumination with a UV blacklight for four different iniferters.

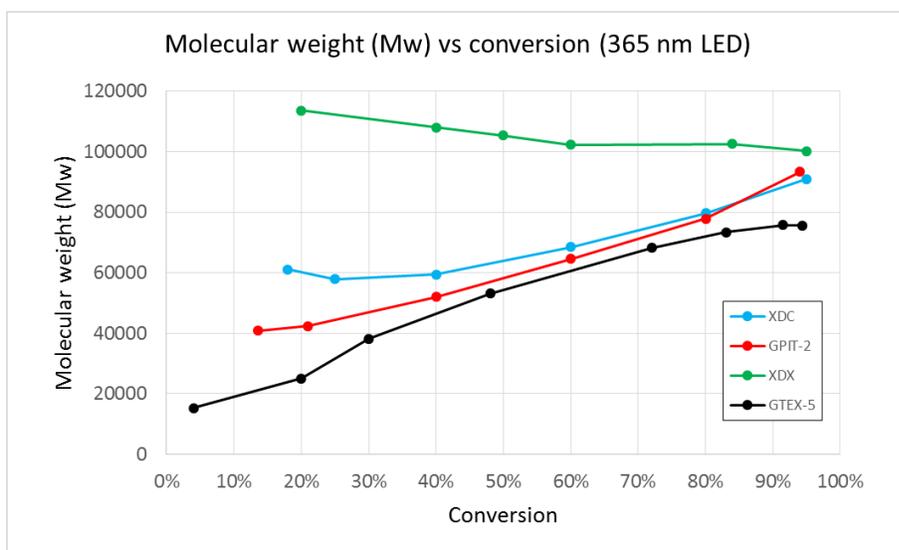


**Figure 5:** Linear fit to Mn vs conversion, and quadratic fit to Mw vs conversion for GTEX-5.

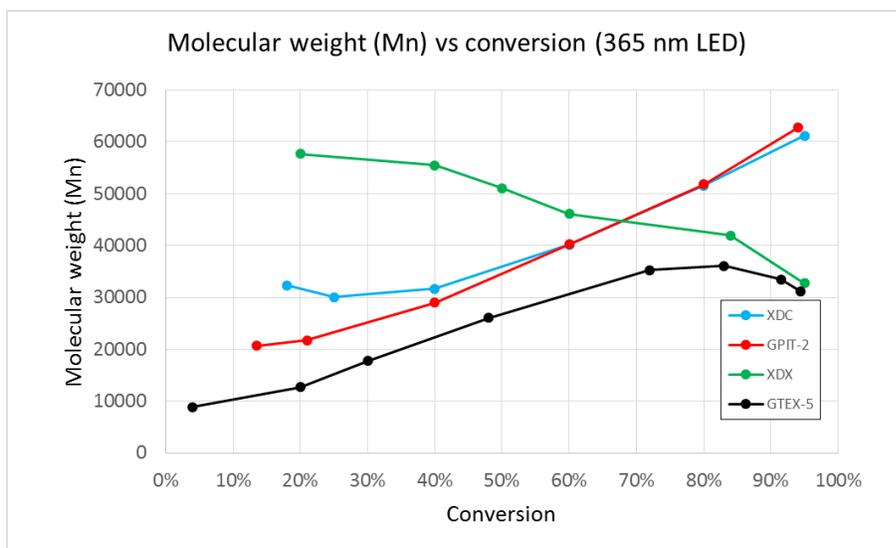
The situation changes markedly when the more intense LED light source ( $120 \text{ mW/cm}^2$ ) is used. Under these circumstances polymerizations conducted with both XDC and GPIT-2 show the expected behavior for Mw vs conversion. In both cases, Mw starts below the intended 80,000 Mw and grows throughout the polymerization. GPIT-2 displays more linear behavior than XDC, yielding  $\sim 40\text{k}$  Mw polymer at 20% conversion vs  $\sim 60\text{k}$  for XDC. The graph of Mn vs conversion provides an interesting distinction between the two end groups, xanthate and dithiocarbamate. The geminal xanthate GTEX-5 achieves the lowest initial Mw at early stages in the polymerization, indicative of a well-controlled polymerization, but at higher conversions the values tail off and above 80% conversion the number average (Mn) starts to decrease. When the

dithiocarbamates GPIT-2 and XDC are used, initial Mn values are significantly higher than with GTEX-5 but in contrast to GTEX-5 for the dithiocarbamate cases the Mw continue to increase linearly even above 90% conversion. XDX continues to be an outlier, starting at higher molecular weight than all the others and progressively lowering throughout the course of the polymerization.

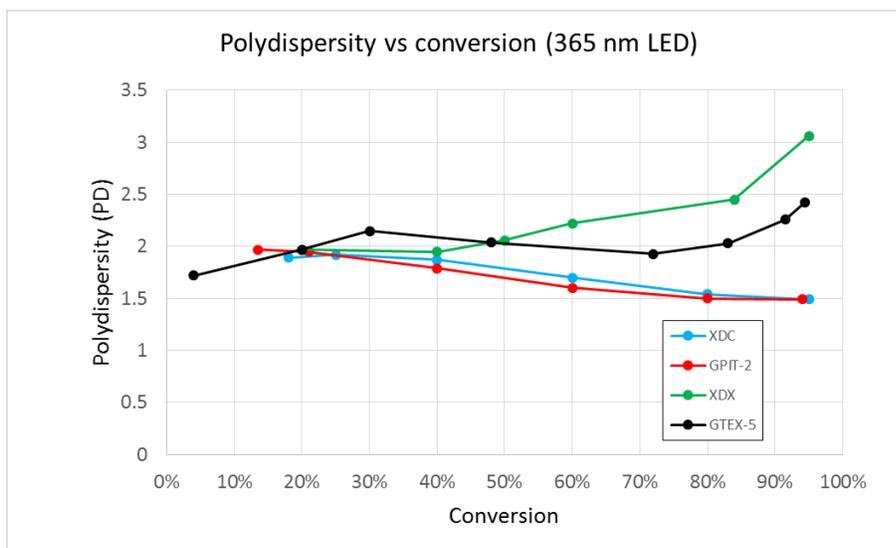
The polydispersity graph, in which all four polymerizations start at a PD of ~ 2, highlights this distinction. For the two dithiocarbamates, PD drops progressively throughout the polymerization to finish ~ 1.5 while in the case of the xanthates it goes through a pronounced upward turn in the later stages of the polymerization.



**Figure 6:** Weight average molecular weight (Mw) as a function of conversion under LED illumination.

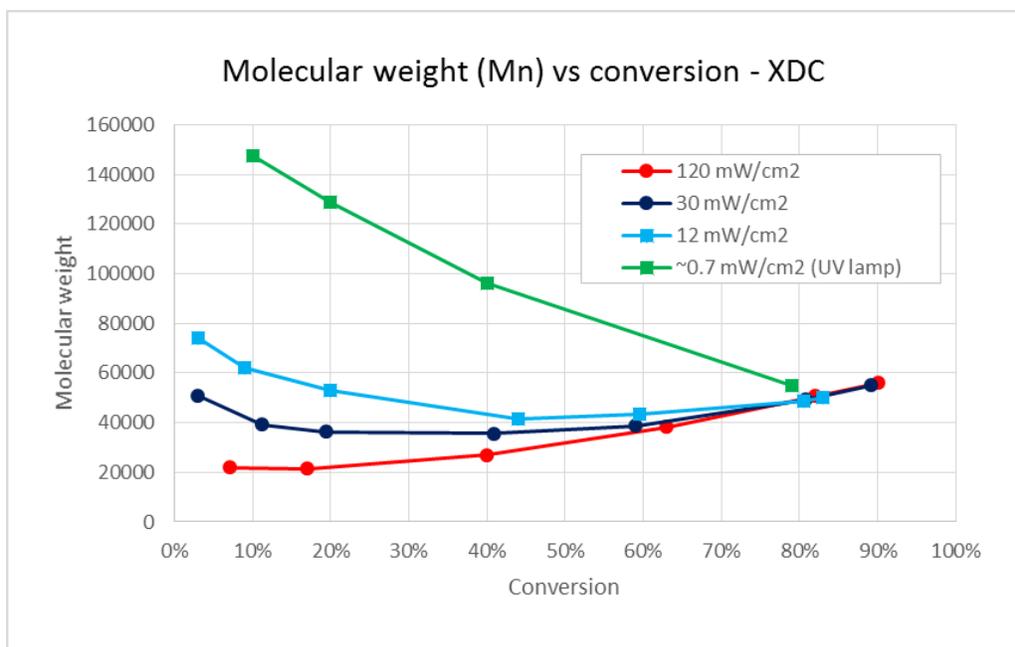


**Figure 7:** Number average molecular weight (Mn) as a function of conversion under LED illumination.



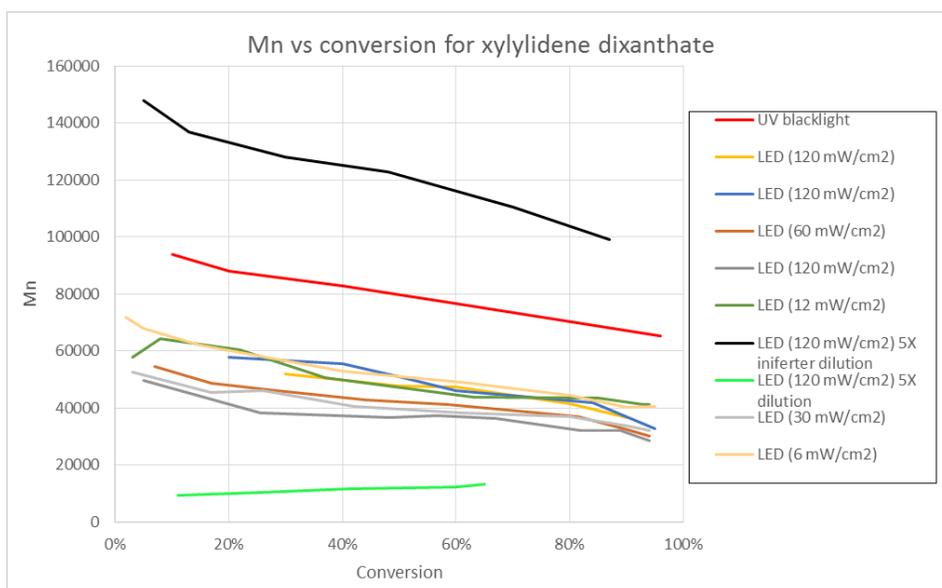
**Figure 8:** Polydispersity as a function of conversion under LED (120 mW/cm<sup>2</sup>) illumination.

The relationship between Mw progression intensity for XDX and XDC was investigated in more detail by running reaction at varying light intensity with the Clearstone LED heads. The output of these heads is linear from 100% power (120 mW/cm<sup>2</sup>) to about 15% power (18-20 mW/cm<sup>2</sup>). Lower intensities were obtained by moving the LED further away from the flask. In the case of XDX, five-fold dilutions of monomer and iniferter, or iniferter alone, were also explored.



**Figure 9:** Molecular weight (Mn) as a function of conversion for XDC under different LED light intensities.

For XDC, a smooth progression is seen as LED intensity is increased from the very high initial MW observed with the UV blacklight, to the reasonably well-controlled polymerization observed with the more intense LEDs.



**Figure 10:** Molecular weight (Mn) as a function of conversion for XDX under different LED light intensities and concentrations.

For XDX however, the behavior is quite different and largely independent of LED intensity. Where the concentrations are held constant at 50% monomer and 6 mM iniferter, there is a slight trend to lower  $M_n$  as LED intensity increases, mostly apparent in comparison to the blacklight results (red line in Figure 10). However, the relationship between  $M_w$  and conversion continues to follow a downward slope in each case. Where the iniferter alone is diluted five-fold (black line in Figure 10), the  $M_n$  value is much higher as expected, but still follows the same downward trend. Only when both monomer and iniferter are diluted 5-fold (green line) does the molecular weight start to show a slight upward trend with conversion.

Photolysis of the carbon-sulfur bond is considerably more facile in the case of xanthate end groups than dithiocarbamates. This dominates the polymerization rate throughout the entire reaction because the active radical is constantly reformed at the end group. Consequently, polymerizations initiated with GTEX progress much faster than those initiated with GPIT and those using XDX are faster than those with XDC. There is minimal difference between polymerizations using xanthates GTEX-5 and XDX, or dithiocarbamates GPIT-2 and XDC because after a few additions the core is remote from the active site and the on/off kinetics of the end group alone controls the rate of addition of monomers.

GTEX-5-initiated polymerizations are well-controlled under both high and low intensity because initiation of the geminal xanthate to a secondary radical is relatively fast even at low light intensities. Thus, initiation of all chains occurs early in the polymerization and most of the conversion of monomer occurs by extending the same number of chains. NMR studies on polymerization of butyl acrylate provide direct evidence of this. The polymerization is not ideal, with a  $PD > 1.5$  even at low conversions (Figure 8) but remains reasonably well-controlled. Numerous other geminal dioxanthates have been prepared with different ester groups (and analogous amides) and the behavior is consistent – overall polymerization rates are similar and the molecular weight starts low and progresses to near the calculated amount. The behavior of the other three iniferters (GPIT-2, XDC and XDX) is more complicated, and can be best understood in terms of the polymerization mechanism.

The high molecular weights observed early in the UV blacklight-initiated polymerization of GPIT-2 is a function of the slow on/off kinetics of the dithiocarbamate end group. As a consequence of this there is a relatively small amount of active initiator present at the start of the polymerization. Thus at low conversions the monomer:photoinitiated radical ratio is significantly higher than initial calculations would suggest, inherently leads to longer chains early in the polymerization. By the time the polymerization is complete,  $M_n$  is roughly the same as observed with GTEX-5, as expected if all initiators have reacted. Under these conditions, GPIT-2 demonstrates the unusual ability to controllably polymerize an acrylate monomer to constant  $M_w$  throughout the polymerization, while retaining active chain ends.

When the much more intense LED light source is used, dithiocarbamate on/off kinetics are considerably enhanced, leading to faster generation of initiating radicals, but in and of itself this has little impact on the MWD because the re-activation rate of already initiated chains increases similarly. The lower initial molecular weights observed under LED illumination (Figures 6 and 7) are a function of the increased rate of initiation relative to the rate of propagation. Since the rate of monomer addition to radical chain end (propagation) is a thermal process it is largely unaffected by light intensity. Thus, more chains are initiated at lower conversions under LED light and GPIT-2 behaves more like a traditional controlled initiator.

When XDC is used with UV blacklight illumination, the reduced iniferter concentration at low conversions is exacerbated by a second factor, the high energy of the primary radical produced by homolysis of the benzylic C-S bond. Consequently, in XDC-initiated polymerizations even fewer chains are initiated early at low conversions than for GPIT-2. As described above, once the chains have been initiated, and a couple of monomers added, the influence of the core structure is eliminated and all re-initiation occurs from a secondary CH<sub>2</sub>-CH-ester carbon. Thus, chains grow faster than they are initiated and molecular weights early in the polymerization are much higher again (Figures 3 and 4). New chains are initiated slowly as the reaction progresses and these new, short, chains lead to the observed reduction in molecular weight averages as a function of conversion. NMR evidence highlights that a considerable proportion of the initiator remains unreacted even at 90% monomer conversion.

When the light intensity is increased (Figure 9), initiation accelerates relative to propagation, as in the case of GPIT-2, and the initial MW drops dramatically. In both these cases, the Mw progression as a function of conversion “turns over” at high intensities and shows something approximating the conventional behavior for controlled polymerizations, where Mw starts low and ends high.

XDX provides an interesting example of the impact of differing rates. In contrast to both XDC and GPIT-2, the initial Mw values do not drop significantly at higher light intensities. Furthermore, the Mw vs conversion plot does not turn over to give a conventional chart with LEDs. This can be understood as a mismatch between initiation and re-initiation rates. At low intensities, initiation is inhibited by the formation of a high energy primary benzylic radical, and thus higher than calculated Mw polymer is formed. The initial Mw values are not as high as seen for XDC since the formation of the xanthate radical is energetically easier than the dithiocarbamate. As the reaction progresses, re-initiation occurs, and occurs more rapidly via a lower energy secondary propagating radical. Thus, irrespective of the intensity of the light source, photolysis and re-initiation of a chain always occurs faster than photolysis of unreacted iniferter and initiation of a new chain (Figure 10 and Scheme 2).



dithiocarbamate group to initiation of polymerization, and indicates the relative absence of irreversible termination.

### Summary:

The polymerization of acrylate monomers initiated by photoiniferters is convenient, rapid and capable of good molecular weight control. The use of geminal xanthates enables rapid polymerization kinetics with early initiation under a variety of light intensities.

Dithiocarbamates, in particular with geminal cores, polymerize acrylate monomers more slowly, but conversely provide a greater level of control over Mw at high conversions when polymerized with high intensity LEDs. These differing properties are likely of value in different applications, in a manufacturing environment where speed is important and precise control of Mw less so, the xanthates are most suitable.

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