

## New Comonomer Technologies

### Introduction

Increasing regulatory pressure and new applications of energy curable materials have made the development of new methacrylic monomers and oligomers more attractive. Despite their increased glass transition temperatures and hardnesses, alongside appealing safety and environmental characteristics, methacrylate monomers and oligomers also have slower cure speeds and lower ceiling temperatures than their acrylate analogues, which can often lead to their exclusion from some market segments. Monomers with rapid (photo)polymerization kinetics are also interesting from a more general perspective, as rapid polymerization coupled with slow termination reactions may lead to longer kinetic chain lengths, which can give rise to network properties that show signs of thermoplastic-like behavior, arising from network chains approaching their entanglement molecular weights.

Herein, we describe new comonomer technology that allows for a substantial increase in the rate of double-bond conversion in methacrylate-containing formulations, closing the gap in cure speed between methacrylates and their acrylate analogs. We also present a brief overview of their mechanical properties.

### Experimental

Raw materials were prepared from commercial products and used as-supplied. Differential scanning calorimetry (DSC) was conducted using a TA Instruments Q2000 DSC instrument; FT-IR spectra were acquired using a Nicolet iS50 spectrometer with a resolution of  $4\text{ cm}^{-1}$ . Samples were prepared by blending the formulation constituents in bulk using an overhead mixer with the addition of 0.1 wt% photoinitiator; diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) was used for all kinetic studies. For photo- FT-IR and photo-DSC studies, a drop of formulation was placed on the ATR objective or in the DSC pan and exposed to irradiation from a 385 nm LED for 1 s intervals and the conversion at each time point was determined. After 10 s total exposure, the sample's physical state was qualitatively assessed. Samples for mechanical property testing were prepared by blending 25 wt% of an aliphatic urethane acrylate oligomer (CN8881, Sartomer) with 75 wt% of the desired monomer, poured into ASTM D638 "dogbone"-shaped molds, heated to 60°C for two hours to remove visible air bubbles, covered with a 0.125 in. glass sheet, and cured at 100 ft/min using a "V" lamp. In order to protect Sartomer's intellectual property, the structures of these new monomers cannot be disclosed.

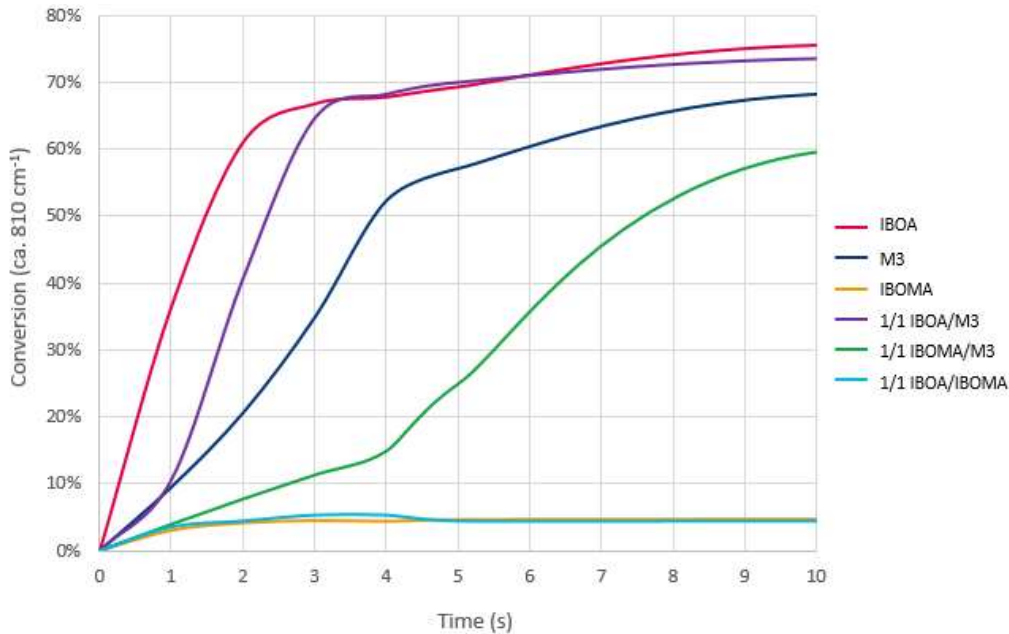
### Results and Discussion

The results of the preliminary screening of homopolymerized monomers are shown in Table 1, below:

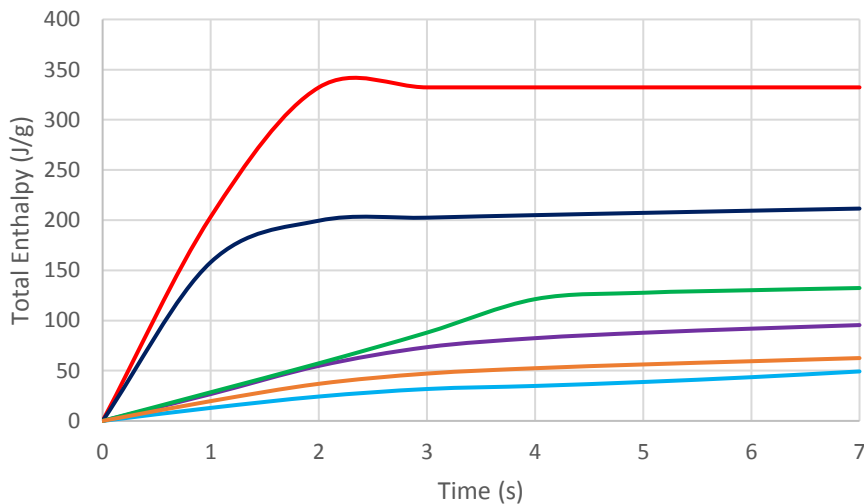
*Table 1: Qualitative Assessment of Cure Quality for Photopolymerization of New Monomers with Various Photoinitiators (0.1 wt%) and 1 s Exposure to 405 nm radiation*

	<b>BAPO</b>	<b>PL369</b>	<b>TPO</b>
<b>Monomer 1</b>	Liquid	Liquid	Liquid
<b>Monomer 2</b>	Liquid	"Gel"	Liquid
<b>Monomer 3</b>	Liquid	Tacky solid	Solid

Based on the results shown in Table 1, further studies were carried out using 0.1 wt% TPO in monomer 3 (**M3**). Monomers 1 and 2 show potential utility in different applications, but the formation of a glassy solid by the homopolymerization of **M3** (attributed to its cyclic rather than linear pendant groups) at short irradiation times allows for comparisons to be made to a well-characterized and widely used acrylate/methacrylate pair (isobornyl acrylate, IBOA/isobornyl methacrylate, IBOMA), and for qualitative (but useful) 'extent of cure for use' as well as quantitative extent of cure to be assessed.



**Figure 1.** Photo-FT-IR results for (co)polymerization of **M3** with isobornyl acrylate and isobornyl methacrylate.



**Figure 2.** Photo-DSC results for (co)polymerization of **M3** with isobornyl acrylate and isobornyl methacrylate.

The FT-IR and DSC results suggest that copolymers of monomer 3 form readily under conventional LED cure conditions with both IBOA and IBOMA. Monomer 3 shows faster initiation but apparently a more pronounced period of oxygen inhibition and a lower overall heat of polymerization than does IBOA, but the low conversion of the IBOMA homopolymerization precludes direct comparisons based on our experiments. The copolymerization of **M3** with IBOMA proceeds considerably more rapidly than does the homopolymerization of IBOMA or the copolymerization of IBOMA and IBOA, giving a soft solid and a small amount of residual liquid rather than a liquid after 10s irradiation (Table 2).

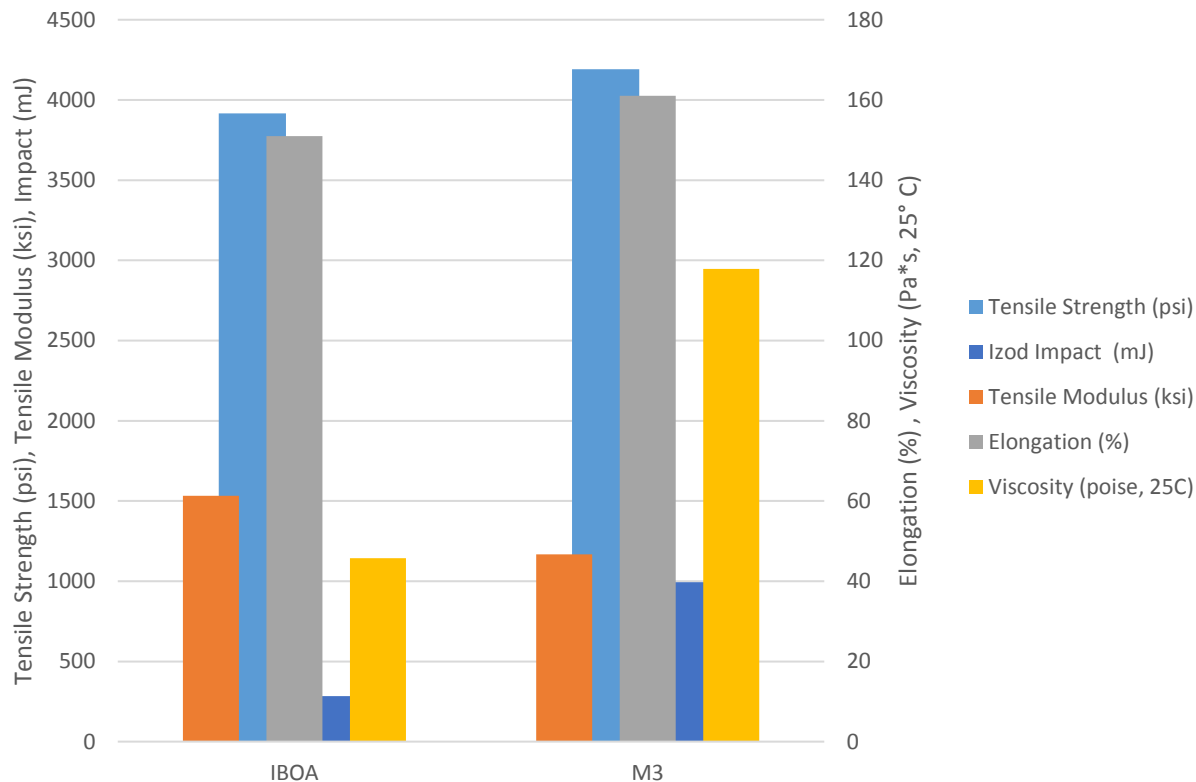
*Table 2: Physical State of TPO-initiated Homo- and Copolymers After 10s Irradiation (M3 homopolymer is a solid)*

	<b>IBOA</b>	<b>IBOMA</b>
<b>IBOA</b>	Solid	Liquid
<b>IBOMA</b>	Liquid	Liquid
<b>M3</b>	Solid	Soft solid

The long delays in autoacceleration and non-logistic double-bond consumption observed for the reactions not containing IBOA suggest that a factor other than dilution coupled with a lack of cross-propagation influences the observed polymerization rates, especially in light of the homopolymerization of **M3** proceeding at an essentially identical rate after the inhibition period ends. Several different mechanisms may be posited based on this data, suggesting the need for further kinetic study and microstructural characterization of both linear (co)polymers of **M3**, IBOA, and IBOMA, as well as their (co)polymer networks.

It is also worth remarking on the lower overall heats of polymerization for **M3** and its copolymers as compared to acrylates. Because the photopolymerization of **M3** is less exothermic than the photopolymerization of IBOA (compare the total heat evolution in Figure 2, red curve at 2 s irradiation to Figure 2, dark blue curve, at 7 s) monomers of the **M3** type may find application in areas where photocurable materials are used in direct contact with thermally sensitive substrates such as the human body.

Finally, we assessed the ability of **M3** to serve as a reactive diluent in photocurable systems (Figure 4). The mechanical properties of the **M3**-containing formulation are quite similar to those of the IBOA-containing formulation, albeit with a considerably higher viscosity and modestly higher impact resistance; **M3** may also serve as a drop-in replacement for IBOA in applications that are less sensitive to viscosity changes and where the pungency of IBOA is a limitation, as the odor of **M3** is quite mild. Despite its limited diluency, the copolymerizability of **M3** and its chemical relatives with methacrylates should allow for higher cure-speed resin systems to be formulated with both superior mechanical properties and low viscosities.



**Figure 4.** Mechanical properties of 75/25 (w/w) blends of IBOA and **M3** with an aliphatic urethane acrylate oligomer initiated with 0.1 wt% TPO.

### Conclusion

We have demonstrated the photo-copolymerizability of a new series of monomers with acrylate and methacrylate monomers and oligomers, and provided an overview of their physical properties. While copolymer formation results in improved cure speeds for methacrylate monomers under LED illumination, pronounced changes in the polymerization kinetics suggest that these copolymer networks may have structures more complex than simple statistical copolymers; further work will be needed to fully understand these kinetics in more detail, as well as to provide formulators with advice on how to optimally utilize these kinetic differences to achieve new products.