

# A Simple Process for Preparing Low Viscosity Diacrylate-Functional Epoxy Oligomers

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## Abstract

An investigation was conducted to determine if an inexpensive, simple approach to significantly reducing the viscosity of acrylate-functional oligomers could be developed. This work began with an attempt to reproduce claims of U.S. Patent 4,687,806. This patent claims that small amounts of aqueous lithium bromide (LiBr) solution will significantly reduce the viscosity of an epoxy diacrylate oligomer. The claims were not corroborated in this study, but even lower viscosities were obtained than were claimed. This paper summarizes the key claims of the patent and presents data that show that the presence of LiBr is actually detrimental and that water alone is a surprisingly effective diluent.

## Introduction

### *Historical Background*

Since the development of ultraviolet (UV) or electron beam (EB)-polymerizable systems in the 1960s, a variety of technical problems have been addressed and successfully overcome. While some technical issues remain, one problem persists that seems inherent to the nature of the raw materials; the problem of the very high viscosities of most oligomers. These high viscosities produce handling problems for the formulators and production problems for the manufacturers.

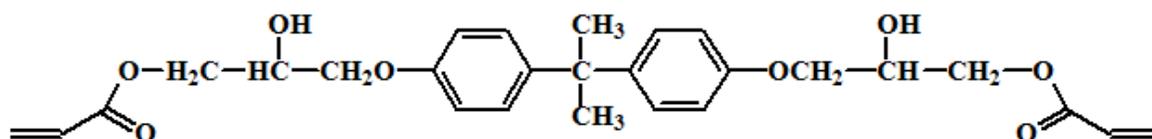
To assist their customers with this issue, oligomer manufacturers recommend holding drums for a period of time in ovens to allow the oligomer viscosities to be reduced for easier handling. Alternatively, the suppliers prepare various blends of the oligomers with acrylate-functional monomers. Neither of these approaches is ideal. Having to heat the oligomers before using them in the preparation of formulations is time and energy consuming. It also increases the risk to workers handling the drums and if done repeatedly, reduces the shelf-life of the materials. The addition of monomer to the oligomer by the manufacturer adds production costs and reduces the formulating latitude of their customer. It may also lead to product proliferation issues for the manufacturer if different formulators desire many different monomer blends for a given oligomer.

In 1987, U. S. Patent 4,687,806 was issued to Interez, Inc. (Formerly Celanese and now Cytec Surface Specialties) claiming a novel process for significantly reducing the viscosity of an acrylate-functional epoxy oligomer using small amounts of a LiBr solution in water [LiBr (aq)]<sup>1</sup>. **Figure 1** shows an idealized structure of this oligomer, which is also produced by other suppliers. The high viscosity of this oligomer results from the addition of acrylic acid to the diglycidylether of *bis*phenol-A (DGEBA) (**Figure 2**). The DGEBA starting material has a viscosity of around 12 000 cP while that of the acrylate-

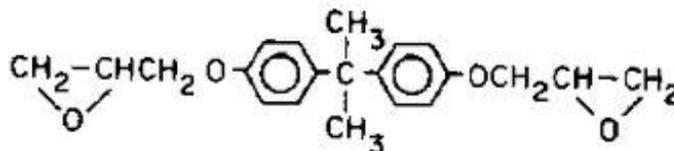
functional material is about 950 000 cP @ 25.0°C. The acrylation step in this process produces secondary -OH groups that are not present in the starting resin, resulting in significant hydrogen-bonding (H-bonding) among the different oligomer molecules. This H-bonding is responsible for the substantial increase in viscosity observed.

The work done that led to the patent was predicated on the understanding that a process for breaking up these intermolecular H-bonds would significantly lower the viscosity of epoxy-based oligomers. It was suggested that incorporating lithium ions ( $\text{Li}^+$ ) into the oligomer would “disrupt” these H-bonds. Thus, work was instituted to investigate this hypothesis. Various lithium halide salts

**Figure 1: Diacrylate Ester of the Diglycidylether of Bisphenol-A (DGEBA)**



**Figure 2: Diglycidylether of Bisphenol-A (DGEBA)**



were investigated as well as some sodium and potassium salts. But it was found that LiBr (aq) worked best and a 1.85%  $\text{H}_2\text{O}$ /0.15% LiBr/98.00% oligomer by mass formulation was optimum.<sup>1</sup> Since the viscosity of the oligomer is very high, mixing of the components was done at elevated temperatures and according to **Table II** of the patent (**Figure 3**), blending at 98°C was found to be optimum compared to results at 75°C. The second and third columns in **Table II** indicate that water was not nearly as effective at reducing the viscosity as the LiBr (aq) solution. Interestingly, **Examples 3** and **4** of the patent demonstrated that neither 2% of methanol solvent nor a LiBr solution in methanol reduced the viscosity as much as the LiBr (aq) solution did. These results led to the conclusion that  $\text{Li}^+$  was working to interfere with the H-bonding and was doing so more effectively than either pure  $\text{H}_2\text{O}$  or even the organic solvent, methanol.

Beginning in 1998, undergraduate students in the Center for Applied Polymer Science Research (CAPSR) laboratory at the University of Houston-Downtown (UH-D) began investigating the claims of the patent. They made LiBr (aq) solutions to incorporate into the acrylate-functional epoxy oligomer. However, because of the very high viscosity of the oligomer, difficulty in mixing LiBr (aq) into the oligomer was encountered. The temperature of the oligomer was raised but clear mixtures could not be prepared without incorporating a significant amount of air in the process of mixing. This entrapped air had a profound effect on the viscosity. While working against this difficulty, Mr. Victor Odu attempted to mix in 2% of LiBr without the water and got a surprising result. The sample had the properties of an elastomer - it could be stretched somewhat like a rubber band and was very high in viscosity. He had, most likely, created “ionic-crosslinks” with the  $\text{Li}^+$  ion in a system that had not yet been exposed to UV irradiation. This is directly contradictory to the belief that the  $\text{Li}^+$  ion would disrupt the intermolecular

Figure 3: Copy of Table II from U. S. 4,687,806

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**TABLE II**

**EFFECTS OF WATER AND LITHIUM BROMIDE ON THE VISCOSITY OF A BISPHENOL A DIGLYCIDYL ETHER DIACRYLATE RESIN (CELRAD 3700)**

	Weight %					
	100	EXAMPLE 5	EXAMPLE 5	EXAMPLE 5	EXAMPLE 5	EXAMPLE 6
Bisphenol A diglycidyl ether diacrylate resin (Celrad 3700)	100	98	98	98	98	98
Water	—	2	1.85	1.82	1.80	1.85
LiBr	—	—	0.15	0.18	0.20	0.15
Blend Temp. (°C.)	—	98	98	98	98	75
Viscosity @ 25° C. (cps)	1,200,000	410,000	135,000	165,000	160,000	180,000

H-bonding of the oligomer. On the contrary, it strengthened it when no water was present. Mr. Odu subsequently added water to the system, hydrating the ions and the polar –OH groups, greatly reducing the viscosity in the process. This was the first indication that the hypothesis behind the 1987 patent might not be valid. Further work, however, was not productive as the problem of mixing in air continued. Thus, the project was shelved.

In 2001, Mr. Ekong Uffort began working on this project and attempted to reproduce the “ionic crosslink” observed previously. He subsequently reported that even after two days, he was unable to get the LiBr salt to dissolve in the oligomer and that no elastomeric properties were observed. However, he attempted to reproduce the LiBr (aq) solution findings reported in the patent. He found that when a 0.15 g LiBr/1.85 g H<sub>2</sub>O mixture was added to 98.00 grams of the oligomer, the viscosity was reduced to 291 138 cP. He then found that 2.00 grams of deionized water (DI water) without any LiBr would reduce the viscosity all the way down to 198 358 cP. Thus, once again, the claims of the patent seemed to be refuted. While some meaningful results had been obtained, the problem with incorporation of air into the samples continued and the project was shelved once again.

Ultimately, the CAPSR lab acquired a high speed mixer. This instrument reduced formulation mixing time from hours or even days to minutes in the lab. It also allowed CAPSR students to mix DI water or LiBr (aq) solutions into the oligomer without whipping in air in the process. Thus, the project was resurrected once more in Fall 2010. The high speed mixer was found to be incredibly efficient at mixing the components and no evidence of entrapped air was noticed. This instrument was the key to beginning a successful project to assess the claims of U. S. 4,687,806. Initial work on this project was reported at the 2011 Photopolymerization Fundamentals Conference in Breckenridge, CO.<sup>2</sup>

**Purpose**

The purpose of this project was to assess the claims of U. S. Patent 4,687,806 and to determine whether or not acrylate-functional epoxy oligomers could be made with significantly lower viscosities using deionized water as the sole viscosity reducing material. The purpose of this paper is to present the results of this work.

## Experimental

### Materials

**Oligomer:** Ebecryl<sup>®</sup> 3700 - Bisphenol-A-based epoxy diacrylate - was provided *gratis* by Cytec Surface Specialties, Inc. and used without further purification.

**Monomers:** Octyl/Decyl Acrylate (ODA) and 1, 6-Hexanediol Diacrylate (HDODA) were also provided *gratis* by Cytec and used without further purification.

**Photoinitiators:** Irgacure<sup>®</sup> 184 (1-hydroxycyclohexyl phenyl ketone) and Darocur<sup>®</sup> 1173 (2-hydroxy-2-methyl-1-phenyl-propan-1-one) were provided *gratis* by Ciba Specialty Chemicals and were used without further purification. These products are now supplied by BASF.

**Lithium Bromide (aq):** LiBr (99%) was obtained from Aldrich Chemical Company, Inc. and used without further purification. The salt was then dissolved in deionized (DI) water.

### Equipment

**High Speed Disperser:** A Speed Mixer<sup>™</sup> was obtained from FlackTek, Inc. and used to mix the formulational components.

**Viscometer:** A Brookfield DV-III *Ultra* Programmable Rheometer was provided *gratis* by Brookfield Engineering Laboratories, Inc. Viscosities were measured at 25.00°C using a #25 spindle and a small sample adaptor (SSA). A Brookfield TC 500 temperature controlling bath was used to maintain constant temperature. Rheocalc software was used to control the measurements and to record data.

**UV Curing Station:** A 600 W/in Light Hammer<sup>®</sup> 10 UV lamp system with an H-Bulb was provided *gratis* by Fusion UV Systems, Inc. and was used to make polymer films of each of the formulations prepared in this study. The UV Total Energy Density and Peak Irradiance values used to “cure” the films were approximately 800 mJ/cm<sup>2</sup> and 1750 mW/cm<sup>2</sup>, respectively.

**Thermomechanical Properties:** The thermomechanical properties of polymerized films were characterized using a Q800 Dynamic Mechanical Analyzer (DMA) with gas cooling accessory (GCA) from TA Instruments, Inc. A temperature ramp of 5°C/min was utilized from -50°C to either 175°C or 200°C with a constant frequency of 1 Hz. The Storage Moduli at 25°C and in the “Rubbery Plateau” were measured, along with the glass transition temperature (T<sub>g</sub>) and the half-height width of the tan δ curve. The T<sub>g</sub> was taken to be at the peak of the tan δ curve and the half-height width was interpreted as indicative of the relative concentration of microgels<sup>3</sup>, a measure of homogeneity at the molecular level.

### Procedures

**Formulation Preparation:** LiBr (aq) solutions were prepared to match the composition disclosed in U. S. 4,687,806. This solution was then added in a 2%/98% mass ratio to the acrylate-

functional epoxy oligomer. This mixture was subsequently blended to a uniform consistency using the high speed disperser. Pure DI water was also blended into the oligomer in various ratios including 2%/98%. This latter DI water/oligomer mixture is referred to as “*Oligomer B*”.

Fully formulated systems were prepared using monomers, photoinitiators, and either the *neat* acrylated epoxy oligomer or *Oligomer B*. Each oligomer was placed in a container and the appropriate monomer mixture and photoinitiator were added. This mixture was then spun at very high speed to blend the components into a homogeneous composition.

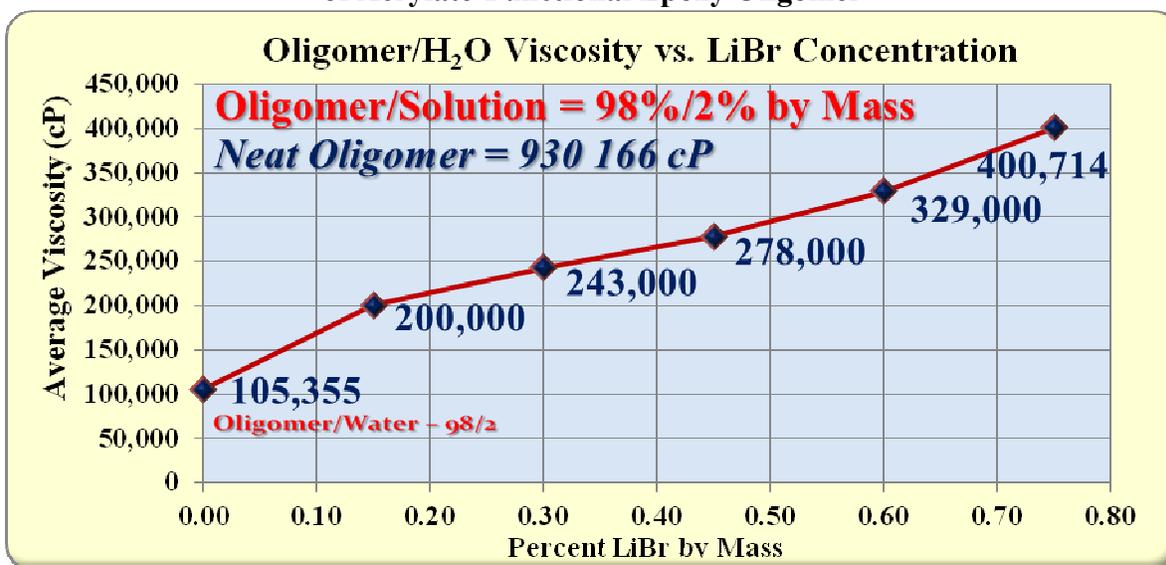
## Results and Discussion

This project was conducted in two phases: 1) Investigation of the claims of U. S. Patent 4,687,806; 2) The development and characterization of low viscosity *Oligomer B*.

### Phase 1

The initial phase of this project began with efforts to determine the effects of LiBr (aq) on the neat acrylated epoxy oligomer highlighted in the patent. The data presented in **Figure 4** show clearly that at all levels investigated, LiBr (aq) was actually counter-productive to the objective of reducing the oligomer viscosity. The optimum composition claimed in the patent (0.15% LiBr/1.85% H<sub>2</sub>O), was

**Figure 4: The Effects of LiBr (aq) on the Viscosity of Acrylate-Functional Epoxy Oligomer**

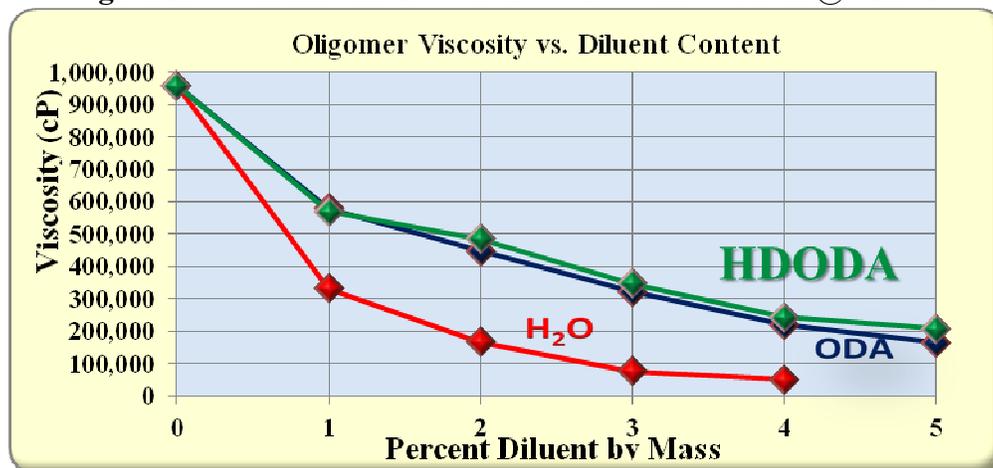


found in the current study to give a viscosity that was about 47% higher than that of the oligomer with DI water alone. These data clearly fail to corroborate the hypothesis that the intermolecular hydrogen bonds (H-bonds) can be effectively interrupted by the presence of Li<sup>+</sup> ions.

Having demonstrated that DI water was more effective than any solution of LiBr (aq), experiments were performed to test the limits of water compatibility with the acrylate-functional epoxy oligomer. These experiments indicated that the two materials were miscible in levels up to 4% by mass DI water

but were incompatible at 5%. **Figure 5** shows the diluent power of water as compared with two of the most effective acrylate-functional monomers commercially available for UV/EB applications. Even at 2% DI water, the viscosity of the blend is significantly lower than that of blends of the oligomer with 4% by mass octyl/decyl acrylate (ODA) or 1, 6-hexanediol diacrylate (HDODA). This surprising result indicates that DI water can have a profound effect on the oligomer's viscosity even at relatively insignificant levels. This opens up an opportunity for raw material suppliers to reduce the viscosity of acrylate-functional epoxy oligomers without resorting to the incorporation of functional monomers. It also, obviously, improves the handling characteristics for formulators.

**Figure 5: DI Water vs. ODA and HDODA as Diluents @ 25.0°C**



## Phase 2

The viscosity-reducing power of DI water compared with that of the two acrylate-functional monomers was quite significant, but it raised the question of how compatible the water contained in **Oligomer B** would be when monomers with relatively low polarity were mixed with it. The six methylene (-CH<sub>2</sub>-) groups bridging the two acrylate groups in HDODA are non-polar (hydrophobic) while ODA has an even larger segment of hydrophobic moieties. Thus, there was concern that the use of low polarity monomers in formulating would cause the DI water in the oligomer to phase out of solution. **Figures 6 & 7** indicate that this concern was unwarranted. At every level up to 50% monomer, the **Oligomer B**-based formulations remained transparent and homogeneous and their viscosities were lower than the corresponding neat oligomer blend viscosities. These results indicated that **Oligomer B** would be completely compatible with commercially available monomers and would, therefore, facilitate the work of formulators. Thus, an experimental design was developed that involved a comparison of **Oligomer B** with the neat oligomer in more realistic formulations containing one or both of these monomers and a photoinitiator.

**Tables 1 and 2** show the formulations chosen for further characterization along with their 25.0°C viscosities and their average functionality – the average number of moles of acrylate groups in the formulation. The average functionality was expected to have effects on the thermal and thermo-mechanical properties of the polymer films as well as the viscosities. The formulations in **Table 1** were all prepared using 2-hydroxy-2-methyl-1-phenyl-propan-1-one as the photoinitiator (**PI 1**). **Table 2** shows comparable formulations using 1-hydroxycyclohexyl phenyl ketone photoinitiator (**PI 2**).

Figure 6: HDODA Dilution Curves

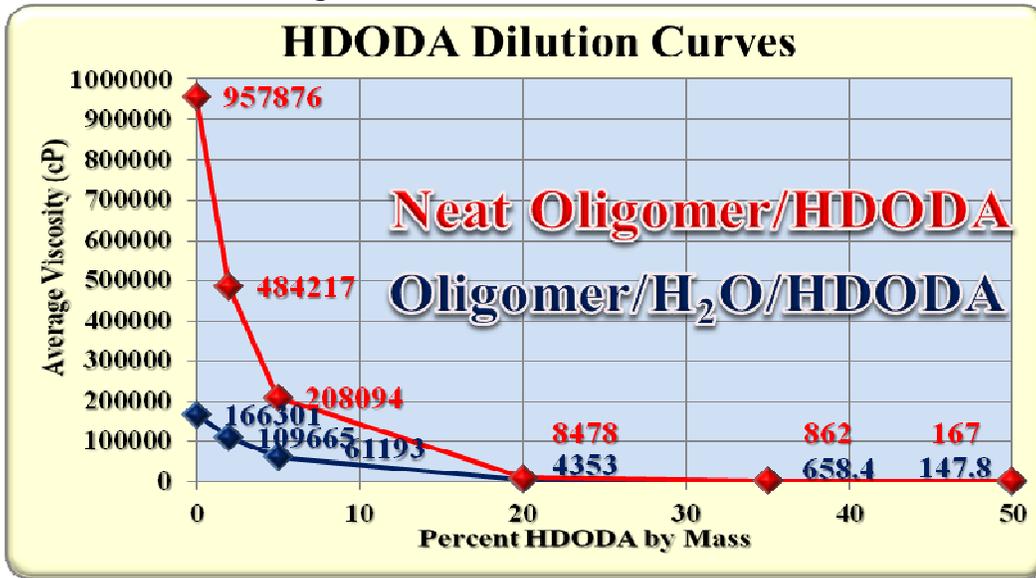
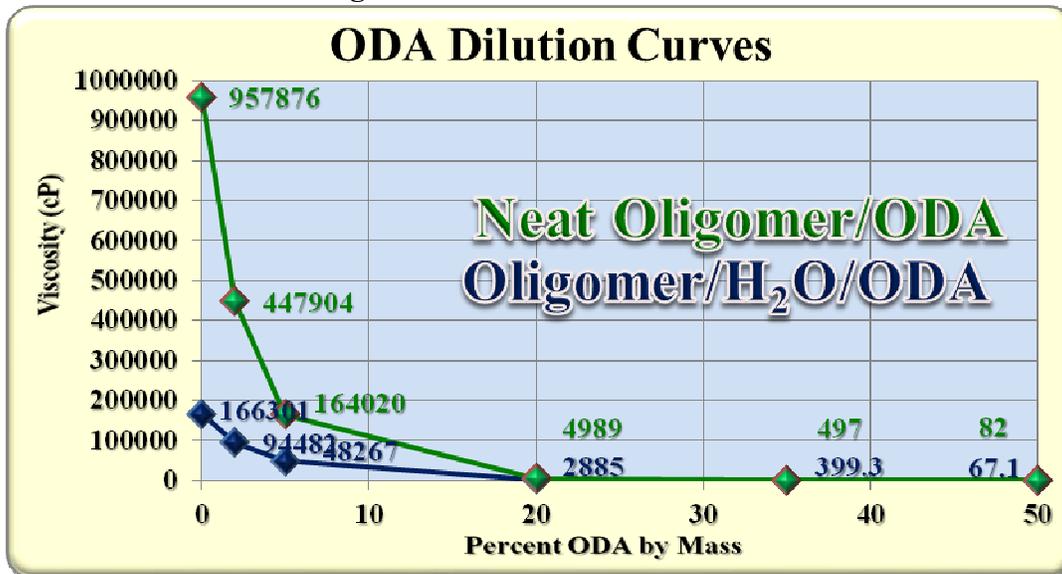


Figure 7: ODA Dilution Curves



Several trends are apparent in these data. First of all, it is obvious from the data in both tables that all formulations based on *Oligomer B* are significantly lower in viscosity than the comparable formulations made using the neat oligomer. Also, careful comparison among the formulations indicates that as the concentration of HDODA is increased, the viscosity increases, as does the average functionality. This is true, regardless of which of the two photoinitiators is used and is consistent with early work reported by Christmas and Zey.<sup>4</sup> Finally, the viscosities for all formulations containing **PI 2** are higher than the corresponding formulations containing **PI 1**. These differences between the two photoinitiators average 14.3%. While **PI 1** is a liquid and **PI 2** is a solid, these physical state differences are not likely to reflect directly their solution properties. Whether liquid or solid, photoinitiators do contribute somewhat to the reduction in viscosity of a UV-polymerizable formulation.

**Table 1**  
**Formulation Compositions (w/PI 1)**

Formulation Identity	A	J	C	D	I	B
Neat Olig. (Mass %)	70.00	---	70.00	---	70.00	---
<i>Oligomer B</i> (Mass %)	---	70.00	---	70.00	---	70.00
ODA (Mass %)	30.00	30.00	15.00	15.00	---	---
HDODA (Mass %)	---	---	15.00	15.00	30.00	30.00
PI 1 (ppm)	3.00	3.00	3.00	3.00	3.00	3.00
PI 2 (ppm)	---	---	---	---	---	---
<b>25.0°C Viscosity (rpm)</b>	<b>900</b>	<b>508</b>	<b>1146</b>	<b>787</b>	<b>1656</b>	<b>1100</b>
Avg. Functionality	1.49	1.48	1.74	1.73	2.00	2.00

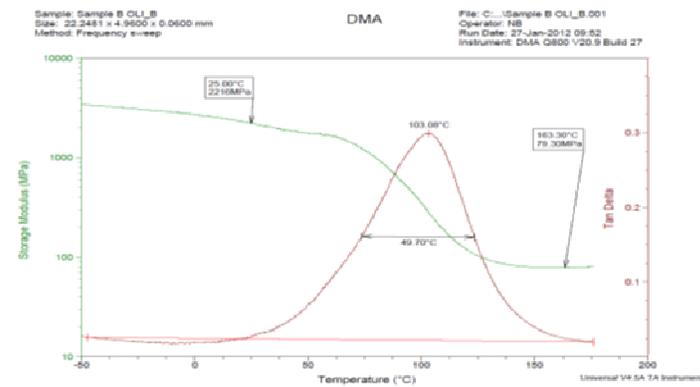
**Table 2**  
**Formulation Compositions (w/PI 2)**

Formulation Identity	E	L	G	H	K	F
Neat Olig. (Mass %)	70.00	---	70.00	---	70.00	---
<i>Oligomer B</i> (Mass %)	---	70.00	---	70.00	---	70.00
ODA (Mass %)	30.00	30.00	15.00	15.00	---	---
HDODA (Mass %)	---	---	15.00	15.00	30.00	30.00
PI 1 (ppm)	---	---	---	---	---	---
PI 2 (ppm)	3.00	3.00	3.00	3.00	3.00	3.00
<b>25.0°C Viscosity (rpm)</b>	<b>1071</b>	<b>608</b>	<b>1241</b>	<b>889</b>	<b>1860</b>	<b>1251</b>
Avg. Functionality	1.49	1.48	1.74	1.73	2.00	2.00

While the primary dependent variable in this investigation was viscosity, the thermomechanical properties of the polymer films made from these 12 formulations were also of interest. As previously stated, these properties were measured using dynamic mechanical analysis (DMA) methodology. Polymers have both “liquid like” and “solid like” properties at the same time and these respective properties are typical of the nature of “viscoelastic” materials. In the DMA, the relationship between these properties is expressed as a “damping factor” or “tan  $\delta$ ”. **Figure 8** shows a typical DMA scan including the storage modulus curve and the tan  $\delta$  curve.

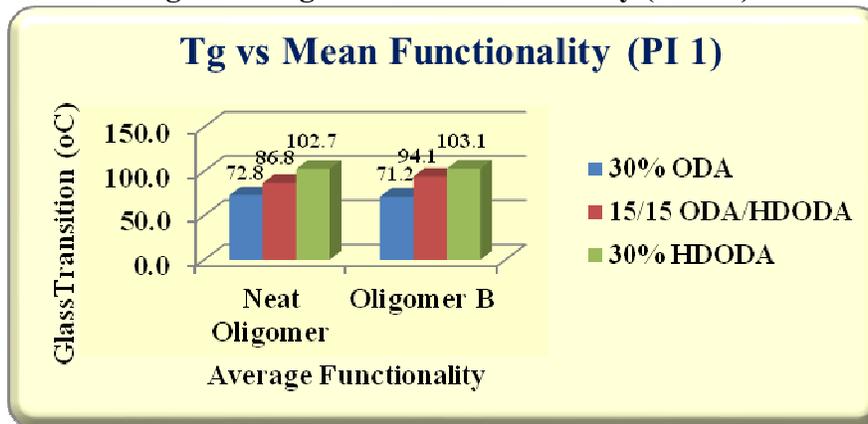
The glass transition temperatures (T<sub>g</sub>s) were taken to be the temperature at the peak of the tan  $\delta$  curve in the DMA scan. **Figures 9** and **10** show that as the average functionality of the formulations increased, the T<sub>g</sub>s increased. This is fully expected since increased functionality is assumed to produce increased crosslink density. The two oligomers failed to show very significant differences in T<sub>g</sub> results but in general, the *Oligomer B* samples produced somewhat higher T<sub>g</sub>s, this in spite of the fact that they had slightly lower average functionality. Also, it was assumed that water would act as a plasticizer, lowering the T<sub>g</sub>. The reasons for why the *Oligomer B* formulations had higher T<sub>g</sub>s are not clear. Perhaps the lower formulation viscosities allow for better diffusion of reactive species, resulting in a higher percent conversion. This would then result in a higher crosslink density and a higher T<sub>g</sub>. Also,

**Figure 8: Typical DMA Scan**



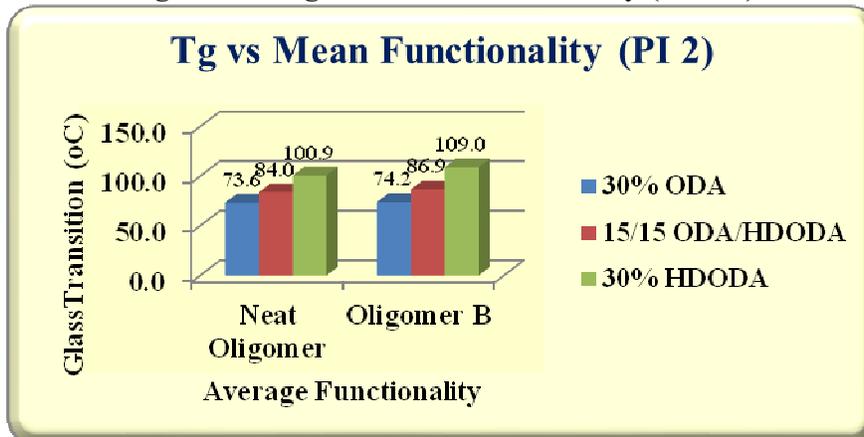
with any thermal characterization method, one would expect the removal of water, causing the plasticizing effect to be minimized. In actuality, the differences are small and they may not be significant. Comparisons of **Figures 9** and **10** also indicate little differences in Tg values obtained with **PI 1** versus **PI 2**.

**Figure 9: Tg vs. Mean Functionality (w/PI 1)**



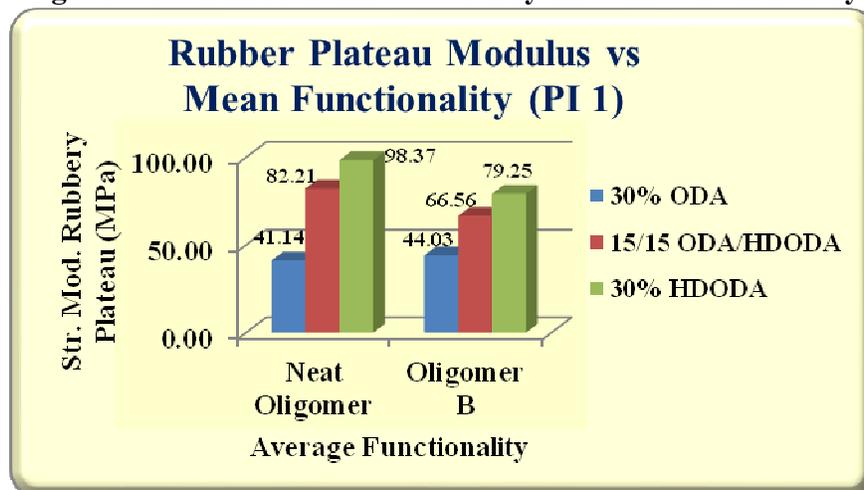
The storage modulus value of a polymer recorded in the “rubbery plateau” above the Tg gives a relative measure of the crosslink density when the polymers are essentially identical, other than for crosslink density. **Figure 11** gives values for the storage moduli in the rubbery plateau for the six formulations containing **PI 1**. These data indicate, again, that as the average functionality goes up, so does the crosslink density, for both oligomers. However, they also indicate that contrary to the Tg data, the crosslink densities of the **Oligomer B**-based formulations may be lower than those of the neat oligomer. This effect is more pronounced as HDODA monomer is added. With 30% ODA monomer, the effect is small but the opposite. ODA is not only a monofunctional, non-crosslinking monomer, but it is also a flexibilizing monomer forming relatively long pendant side-groups on the polymer matrix. So, the data indicate that with a crosslinking monomer (HDODA), the **Oligomer B** formulations have marginally lower crosslink density, while for the non-crosslinking monomer (ODA), they have slightly higher crosslink densities than those based on the neat oligomer.

Figure 10: Tg vs. Mean Functionality (w/PI 2)



The parallel study with **PI 2**, interestingly, gave different results. Increasing the average functionality did increase the apparent crosslink density (with one exception with *Oligomer B*), but the effects seen in comparing the neat oligomer formulations to those of *Oligomer B* were the opposite. With 30% by mass ODA monomer, the *Oligomer B* formulations gave lower apparent crosslink densities while they appeared to be more crosslinked when HDODA was involved. This seems to indicate a possible photoinitiator effect. In reality, all of these polymer films have relatively low crosslink densities. Therefore, the observed differences may not be significant. Further studies are needed to clarify this issue.

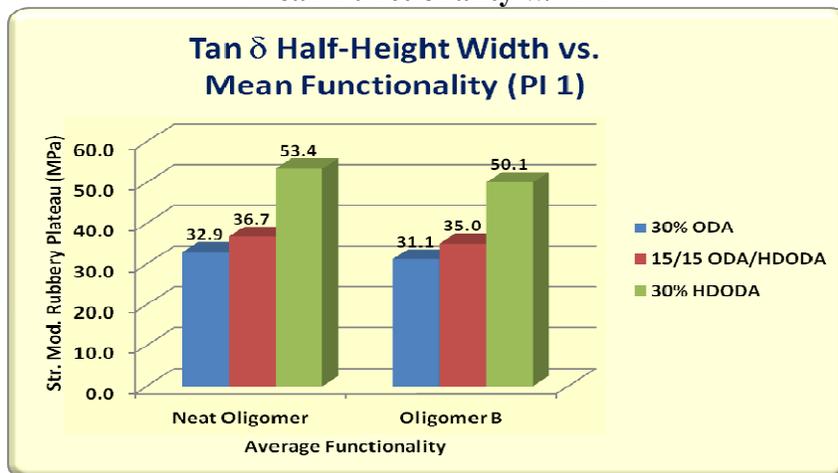
Figure 11: Relative Crosslink Density vs. Mean Functionality



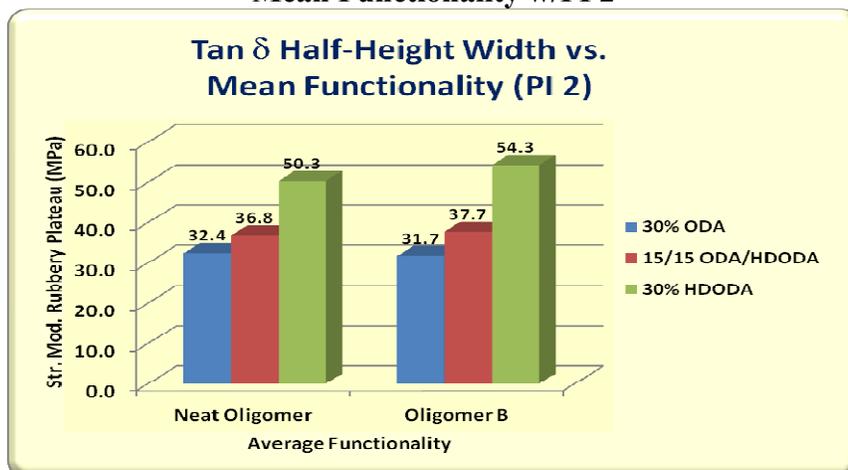
In addition to Tgs and apparent crosslink densities, the width of the  $\tan \delta$  curve at its half-height was measured for each formulation. These values are indicative of the concentration of microgels (actually “nanogels”<sup>3,5</sup>) at the molecular level. The broader the  $\tan \delta$  peak, the more heterogeneous the polymer. **Figures 12** and **13** give comparisons of 25°C storage moduli and apparent microgel concentration for formulations containing **PI 1** and **PI 2**, respectively. For both sets of formulations, as the average functionality increases, the relative concentration of microgels increases. This is consistent with

the literature where it has been reported that higher functional monomers increase microgelation in UV free radical polymerization<sup>5,6</sup>. Also, the data are consistent, regardless of oligomer or photoinitiator.

**Figure 12: Relative Microgel Concentration vs. Mean Functionality w/PI 1**



**Figure 13: Relative Microgel Concentration vs. Mean Functionality w/PI 2**



## Summary and Conclusions

The data reported in this paper demonstrate that the claims of U.S. Patent 4,687,806 concerning the utility of LiBr (aq) solutions for reducing the viscosity of acrylate-functional epoxy-based oligomers are not accurate. To the contrary, the data indicate that DI water alone is significantly better at reducing the viscosity than any level of LiBr (aq). Concentrations of DI water up to 4% by mass were found to be compatible with the oligomer. In amounts as little as 2% by mass, DI water was also shown to be significantly more effective at reducing viscosity than two of the best acrylate-functional oligomers for diluency, ODA and HDODA. Further, the oligomer containing DI water (*Oligomer B*) was perfectly compatible with the monomers and photoinitiators in comparably formulated systems and provided lower formulation viscosities than did the neat oligomer. The UV-cured polymer films made from formulations based on both oligomers had comparable thermomechanical properties though some

differences were observed. Thus, all indications are that **Oligomer B** is fully comparable to the diglycidyl ether of bisphenol-A diacrylate oligomer in properties, while having a viscosity nearly 80% lower at room temperature. This development provides a material for the UV-polymerization industry that can benefit oligomer suppliers and formulators alike.

## Acknowledgements

The authors would like to acknowledge the following people and organizations for their support of this research project.

1. The Robert A. Welch Foundation of Texas, Grant No. **BJ-0027**, for financial support.
2. Fusion UV Systems, Inc. for the donation of the UV curing station and lamps.
3. Cytec Surface Specialties for the donation of the oligomer and monomers.
4. Ciba Specialty Chemicals for the donation of the photoinitiators.
5. Brookfield Engineering Laboratories for the donation of a DV-III *Ultra* Rheometer.
6. The Department of Natural Sciences of UH-*Downtown* for continuing support of CAPSR.
7. EIT, Inc. for providing radiometry calibration work *gratis*.
8. V. Odu, E. Uffort, J. Carmichael, R.Barbosa, D. Silva, N. Abousaoui, and M. Villescas, UH-D.

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