Continuous Flow Polymerization: Energy Usage and Characterization of Functional Copolymers

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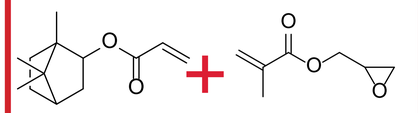
Introduction

In the information age, the demand for higher efficiency at lower cost has never been greater; it benefits manufacturers, consumers, and the environment alike. As microelectronics continue to evolve, there is an increasing need for materials that demonstrate high energy storage capability with high energy efficiency. This project explores the synthesis, characterization, and energy usage of a novel copolymer with the potential to meet these demands.

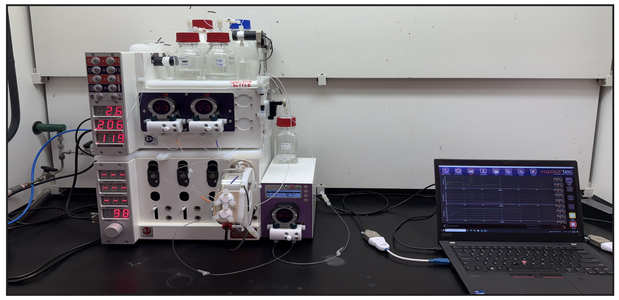
The product is a copolymer between *iso-Bornyl Acrylate (iBoA)* and *Glycidyl Methacrylate (GMA)*. The reaction occurs in a **continuous flow reactor** which allows us to control the reaction with high precision and efficiency compared to that of a batch reactor.

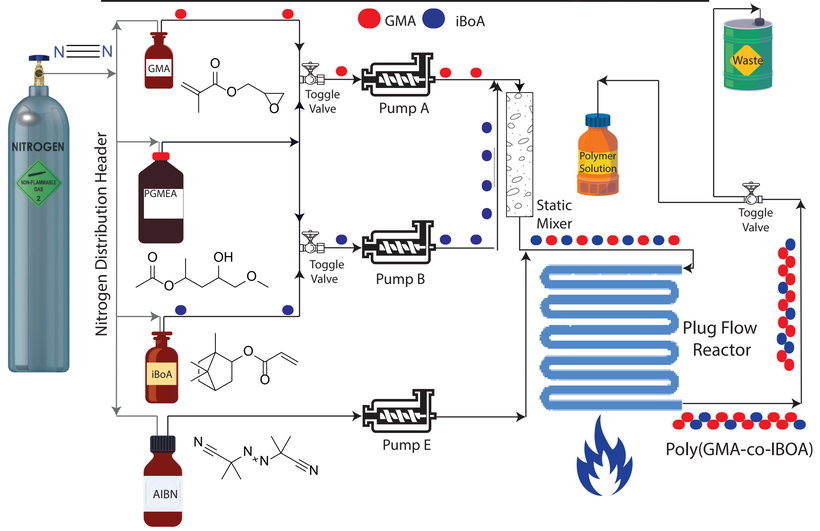


The use of acrylate-based copolymers in microelectronic chip manufacturing has been increasingly explored, with studies examining various materials such as poly(MSEMA-co-GMA). The idea of utilizing iso-Bornyl Acrylate for this process comes from previous research on the acrylate which highlights its ability to be a binding and structural agent in the process of manufacturing solid polymer electrolytes. Having high polymer quality and structural precision are highly desired in the process of extreme ultraviolet lithography, therefore, iBoA has the potential to be a suitable monomer.

Continuous Flow Reactor

Utilizing a continuous flow process enables high-precision control and scalability. By adjusting the flow rates of individual reagents, including the initiator, we can control both the stoichiometry and the quantity of product and waste. The following experiment was performed at 98 degrees Celsius with *GMA*, *iBoA*, and *AIBN* flowing at 0.15 mL/min, 0.175 mL/min, and 0.175 mL/min respectively. This arrangement of flow rates and the composition of the solutions used gives our product an approximately 1:1 molar ratio. This balanced ratio allows the analysis to be moderate and skewed in neither favor of the reactants. Our reactor is composed of four components: ***R4 Reactor***, ***R2S Pumping module***, ***SF-10 Pump***, and a laptop with ***VapourTec*** software.



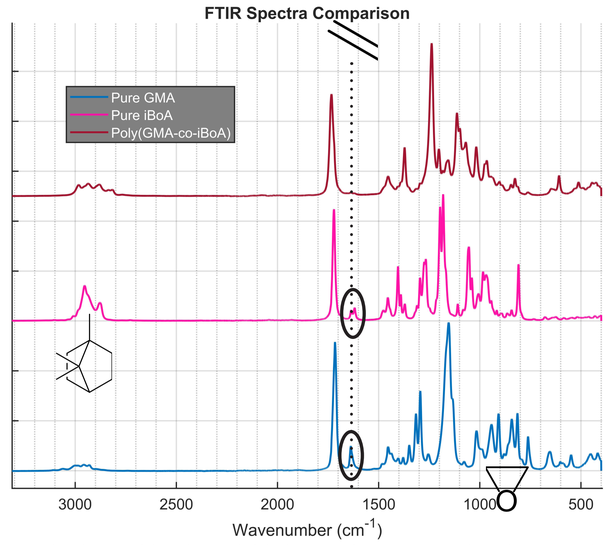


Characterization

The characterization of the solution confirms the accuracy of our technique, reaction, and information. The utilized methods of characterization are the *Fourier Transform Infrared Spectroscopy (FTIR)* for molecular bond identification, *Gel Permeation Chromatography (GPC)* for molecular weight distribution, and *Infrared Spectroscopy Thermogravimetric Analysis (IRTGA)* for thermal stability analysis.

Chemical Fingerprint

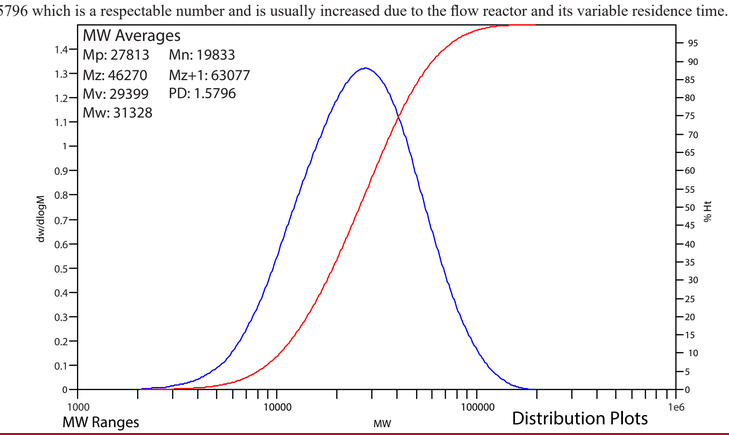
The Fourier Transform Infrared Spectroscopy is a technique that identifies chemical bonds by measuring the absorption of infrared light. By looking at peaks in corresponding wavenumbers, the bonds within the molecule can be determined.



Above are three graphs with two of them, blue and pink, demonstrating pure GMA and pure iBoA respectively. GMA has a few peaks around 910 cm^{-1} which represents the ring stretching and deformation of an **epoxy group**. iBoA has peaks around 1,400 cm^{-1} and intense stretching in the 2,900 cm^{-1} area demonstrating the **cyclic structure** that it holds. Above those two graphs (scarlet) is the polymer formed from each of the substances below it, demonstrating characteristics from both GMA and iBoA. The biggest identifier of the copolymer would be the absence of the **vinyl group** (C=C bond) that would be demonstrated by a peak just past the 1,600 cm^{-1} mark. This disappearance confirms the consumption of the double bonds during the free radical copolymerization process.

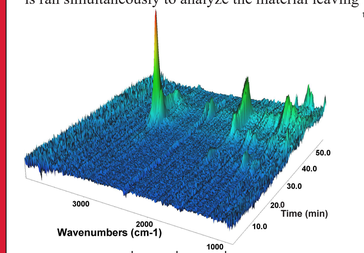
Molecular Weight Distribution

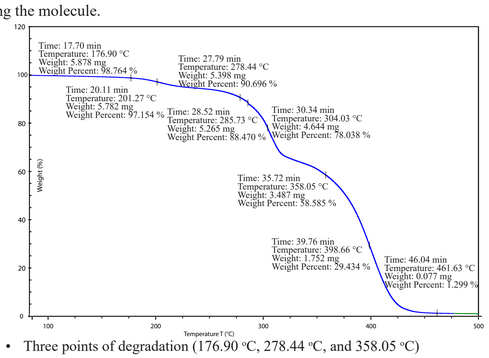
Gel Permeation Chromatography measures molecular weight distribution. Large molecules pass through a packed column faster than smaller molecules which gives insight into the molecules' size and uniformity. The red line is the cumulative amount of sample passing through the column while the blue line is the distribution of molecular weight in grams per mol. The peak molecular weight (Mp) is 27,813 g/mol and the polydispersity index is 1.5796. The closer the polydispersity index can be to one is preferrable as it represents uniformity in polymer chain lengths throughout the product. The measured PD is 1.5796 which is a respectable number and is usually increased due to the flow reactor and its variable residence time.



Thermal Stability Analysis

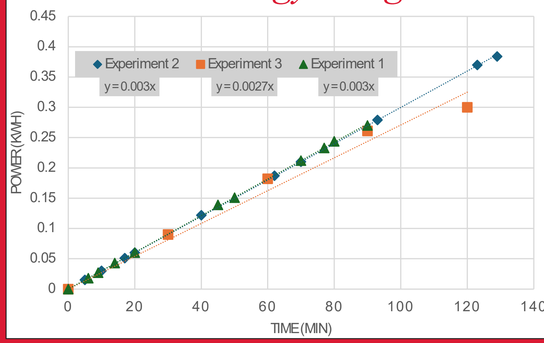
Thermogravimetric Analysis measures the weight loss (degradation) of a sample as it absorbs heat. An Infrared Spectroscopy is ran simultaneously to analyze the material leaving the molecule.





- Three points of degradation (176.90 °C, 278.44 °C, and 358.05 °C)
- IR analyzed at each point (displayed left)
- T = 21.17 min: CO_2 and H_2O (2350 cm^{-1} and 1600 cm^{-1} respectively)
- T = 31.88 min: Aliphatic Structure (2900-3000 cm^{-1}) and esters/ketones (1700-1750 cm^{-1})
- T = 38.60 min: Carbonyl group (1700-1750 cm^{-1}), Ester/ether group (1000-1200 cm^{-1}), and more aliphatic structure (2800-3000 cm^{-1})

Energy Usage



We performed reactions at 98 degrees Celsius. The average power usage of the reactor was determined to be approximately 0.003 KWh per minute of usage. The average cost of a KWh is 8.84 cents in Nebraska, making the cost rate 0.02652 cents/min. That makes a two hour (120 min) reaction cost 3.1824 cents because the reactor consumes 0.36 KWh in that time. During a 125.68 minute reaction we produced 48.76 mL of steady-state product. This makes 1mL of product cost approximately 14.629 cents and 1 L equivalent to 146.29 USD.

Conclusion/Future Work

The synthesis and composition of the copolymer were confirmed through FTIR and GPC analysis, while TGA was used to assess its thermal stability. The energy consumption was measured to be 0.003 KWh per minute of reactor operation. This value can be compared to that of a batch reactor in future studies to evaluate which method offers greater efficiency. The synthesis method for this novel copolymer was outlined and can therefore be used as foundation for future projects involving flow synthesis.
Future work can focus on evaluating the suitability of this copolymer for use in microelectronic chip manufacturing via photolithography. Its potential would be assessed based on its energy storage and overall energy efficiency. Also, comparisons with more common copolymers like poly(GMA-co-MMA) could help evaluate its structural integrity and functional performance providing a basis that would lead to further optimization and experimentation.

Acknowledgments

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