



Effect of Polymerization Temperature on Polymethyl Methacrylate Stereochemistry and Molecular Weight: A Polymer Chemistry Laboratory Procedure



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Abstract

Polymethylmethacrylate (PMMA) is a popular commercial polymer. PMMA's mechanical properties correlate with its bulk structure which is influenced by the stereochemistry of the chiral centers along the chain; this is known as polymer tacticity. The purpose of this research was to develop a laboratory experiment to provide students taking polymer chemistry at Winona State University, the opportunity to analyze *a)* how polymerization temperature affects stereochemistry within polymer chains and *b)* how to determine polymer tacticity using ^1H NMR spectroscopy. For supplemental purposes, viscometry was taken to obtain the average molecular weight per chain and demonstrate the relationship between molecular weight and polymerization temperature. The experimental portion of the research involved synthesizing 10 PMMA samples by bulk radical polymerization at temperatures ranging from 60-100°C. During the analysis portion of the research, tacticity was measured by integrating the α -methyl protons, while molecular weight was determined by solution viscometry. The results concluded with a stagnancy of both syndiotactic and isotactic proportions as polymerization temperature varied, and as polymerization temperature increased, molecular weight decreased. Although the data did not present a change in stereochemical trend, the project itself proved to be practical as an undergraduate polymer laboratory experiment.

Introduction

More commonly known as acrylic or plexiglass, this colorless, translucent material has versatile uses in biotechnology as dentures or bone implants, as well as practical everyday uses in smartphone screens and windows. This versatility is derived from the bulk structure, which is ultimately based on the intermolecular forces between polymer chains and stereochemical patterns of adjacent centers.¹ To orient or stack these chains requires specific stereochemical patterns within the chain, also known as tacticity. There are 3 types of stereochemical patterns referred to as isotacticity, syndiotacticity, and heterotacticity. Patterns of tacticity are ultimately based on the behavior of adjacent chiral centers along a chain. When analyzing stereochemistry, adjacent centers can be compared in groups of 2 (diad), 3 (triad), and so on. Adjacent groups are labelled in terms of meso ("m") and racemic ("r") terminology; where meso refers to adjacent centers maintaining a stereochemical configuration. Whereas racemic refers to a reversed stereochemical configuration relative to the other center. More specifically, triads are labelled mm, mr, or rr relating to either isotacticity, heterotacticity, or syndiotacticity, respectively. Meanwhile diads are labelled as simply m or r.

Characterizing polymers by NMR may be approached differently than smaller molecules due to the repeat units and multitude of functional groups; causing overlap in some regions of the spectra, as well as less distinct peaks. Variables that can affect tacticity patterns in polymers include but are not limited to polymerization temperature and solvent choice. The variable throughout the experiment was temperature as it not only affects tacticity, but molecular weight as well, which involves the other method of analysis; viscometry.

Experimental

Synthesis

5 mL of methyl methacrylate was dispensed dropwise into an alumina column to remove the inhibitor. The monomer was deoxygenated under inert gas (N_2) for ~10 minutes. Once deoxygenation was complete, samples were submerged in an oil bath set to temperatures ranging from 60-100°C. 50 mg of benzoyl peroxide was used as a radical initiator for trials polymerized at 70-100°C, whereas 60°C trials utilized AIBN. The test tube was periodically observed for viscosity changes and once changes were apparent, the test tube was removed, followed by the addition of 7.5 mL of acetone with swirling to ensure homogeneity. This mixture was then emptied into a beaker with 100 mL of distilled water to isolate the polymer. Contents were vigorously stirred until the polymer solidified. The samples were then oven dried at 80°C and left in the oven for 1 day. The samples were pulverized using a mortar and pestle to small bits that were readily soluble in organic solutions.

Viscometry

To begin viscometry, a standard curve using 3 commercial PMMA samples was constructed. The 3 commercial samples contained molecular weights of 15,000 g/mol, 120,000 g/mol, and 350,000 g/mol. Each sample was weighed to 50 mg and dissolved in 10 mL of DCM. A water bath was set at a constant 25°C and an Ostwald-Fenske Viscometer was cleaned thoroughly with DCM. Initially, only DCM was tested to calculate the relative viscosity. Each commercial sample was then assessed by viscometry in triplicate (followed by the experimental samples), where the average of the values was used to calculate the inherent viscosity. Inherent viscosity was then plotted against literature molecular weight, where a linear equation was generated. Once both relative and inherent viscosity values were obtained for all samples, molecular weight was calculated using the equation from the standard curve.

^1H NMR

^1H NMR sample preparation consisted of weighing 10 mg of polymer followed by saturation in CDCl_3 . Each spectra was obtained from 32 scans.

Figure 1. Structure of methyl methacrylate repeat unit.

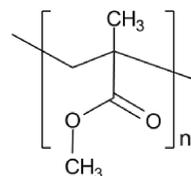
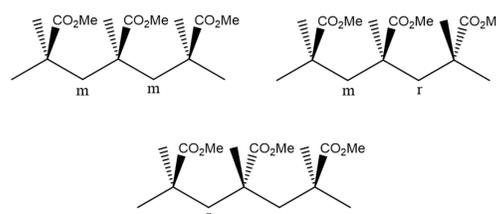


Figure 2. Stereochemistry of PMMA represented in triads of isotacticity (mm), heterotactic (mr), and syndiotacticity (rr).



Results and Discussion

^1H NMR

Figure 3. The 1st 80 °C sample's ^1H NMR spectra with labels corresponding to triad types of mm, mr, and rr; correlating with isotacticity, heterotacticity, and syndiotacticity, respectively.

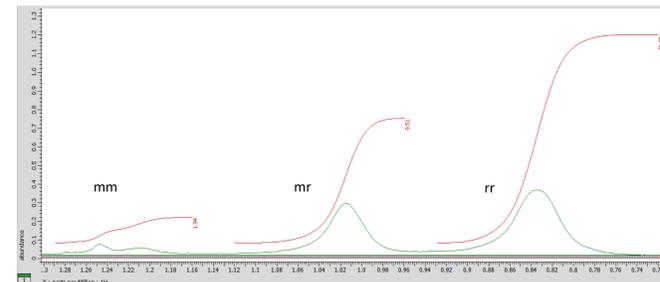


Figure 4. A plot representing percentages of the total integration values for each peak within the interval of 0.72-1.29 ppm; each representing a triad type.

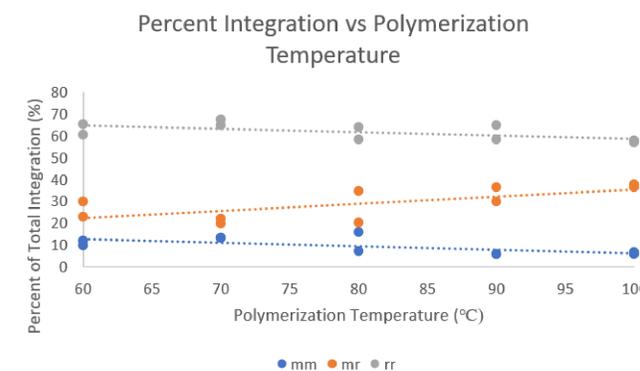
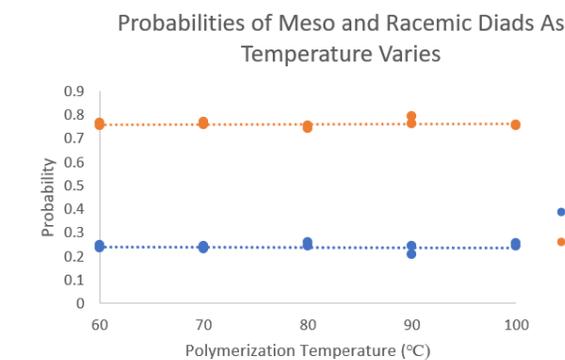


Figure 5. Using the integration percentages, the probabilities of meso-diads (isotactic) and racemic diads (syndiotactic) with respect to heterotacticity are plotted as a function of polymerization temperature.



The 0.7-1.3 ppm α -methyl region of the NMR spectra was integrated in 3 areas with consistency (Figure 3). Each of the 3 integration values were divided by the sum of all peaks to obtain the percent predominance of each triad-type. These percent values were then plotted against polymerization temperature (Figure 4). The literature³ source used the percent integration values (in decimalized form) to obtain the probability of meso-diads (isotactic) and racemic-diads (syndiotactic) with respect to heterotacticity (mr). These P-values were plotted as a function of polymerization temperature (Figure 5) and the trends appeared to be stagnant with nearly undetectable changes in proportions. With that, Figure 4 does show fluctuation in mm, mr, and rr triad proportions and expresses an increase in syndiotacticity as temperature decreases. However, Figure 5 presents no variation in proportions between meso and racemic diads.

Viscometry

Figure 6. A standard curve constructed from 3 commercial polymer samples of 15,000 g/mol, 120,000 g/mol, and 350,000 g/mol.

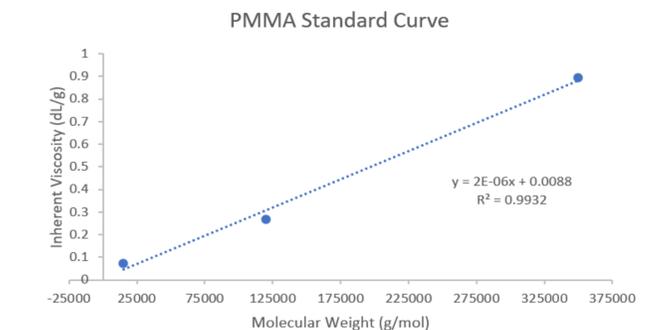
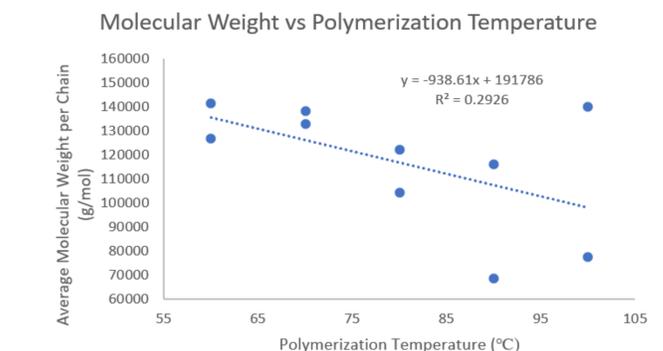


Figure 7. Plot of the calculated molecular weights vs polymerization temperature for all 10 samples.



Using the standard curve in Figure 6, the molecular weights for each sample were calculated and plotted against polymerization temperature (Figure 7). The resulting coefficient of determination was 0.29 and expressed a lack of precision. Lack of precision may be due to the risk of auto-acceleration, which involves uncontrolled conversion in bulk polymerization. However, there is nevertheless a downward trend, summarizing the inverse relationship that as polymerization temperature increases, molecular weight decreases. The inverse proportionality can be justified using a modified equation regarding kinetic chain length in which the steady-state approximation is utilized for monomer and initiator concentration. Mode of termination also may affect chain length, let alone molecular weight. The tendency for disproportionation to occur increases as temperature increases, which prevents developing polymer chains from combining and resulting in a greater (2-fold) molecular weight.

Conclusion

The findings relating to viscometry aligned with the kinetics of polymerization and can be reasonably justified by the kinetic chain equation when incorporating the steady-state approximation. The data in reference to ^1H NMR show stagnancy for isotactic and syndiotactic proportions as temperature is varied. According to literature, syndiotacticity should have expressed slight predominance in probability as polymerization temperature decreased. Nevertheless, this experiment successfully demonstrated its practicality to serve as an undergraduate laboratory exercise.

References

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