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The Effect of Acrylic Acid on Ring Formation in Polyacrylonitrile

Elisha Cade Willis
University of Southern Mississippi

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The University of Southern Mississippi

The Effect of Acrylic Acid on Ring Formation in Polyacrylonitrile

by

Elisha Cade Willis

A Thesis
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The University of Southern Mississippi
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of the Requirements for the Degree of
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Approved by

Jeffrey S. Wiggins, Ph.D., Thesis Advisor
Associate Professor of Polymers

Sarah E. Morgan, Ph.D., Director
Department of Polymers and High
Performance Materials

Ellen Weinauer, Ph.D., Dean
Honors College

Abstract

The addition of comonomers into carbon fiber precursor, polyacrylonitrile (PAN), has shown to have effects on the extent of stabilization and thermal behavior.¹ Acrylic Acid (AA) was added at varying initial apparent weight percent and added via semibatch reaction to copolymerize with acrylonitrile to form carbon fiber precursor. Accompanying batch reactions were synthesized for comparison. Degradation was found to be greater in the semibatch reactions although overall was comparable to the batch reactions. Differential scanning calorimetry (DSC) confirmed the addition of higher concentrations of AA into the reaction resulted in a less intense exotherm upon cyclization, along with a greater breadth and earlier onset temperature. These findings will extend to the semibatch reactions. The extent of stabilization was also found to be comparable among all of the polymers, however, the semibatch reaction with the highest AA concentration showed a much higher extent of stabilization. This has demonstrated that semibatch reactions can create comparable polymers when compared to batch reactions as well as the feed rate has an effect on the stabilization of the product and that this can be used to tune the backbone sequence. These findings eventually coupled with the ability to control the placement of the comonomers along the backbone could lead to greater ease of processing due to the need for lower cyclization temperatures as well as a less loss of product due to the smaller exothermic reaction while being able to achieve uniform ring structure along the backbone.

Key terms: Polyacrylonitrile, cyclization, semibatch, stabilization

Dedication

To my parents, Allen and Kandis, my brother, Allec, my sister, Maranda, JoAnna, and my extended family for their love and eternal support in all I do.

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List of Abbreviations

PAN – Polyacrylonitrile

AA – Acrylic Acid

DSC – Differential Scanning Calorimetry

TGA – Thermogravimetric Analysis

FTIR – Fourier Transform Infrared Spectroscopy

RAFT – Reversible Addition-Fragmentation chain Transfer

EC – Ethylene Carbonate

DMF – N,N-dimethyl formamide

DMSO – Dimethyl sulfoxide

IA – Itaconic Acid

E_s – Extent of Stabilization

Chapter 1: Introduction

Carbon fiber is an increasingly important material in today's world, being used in products ranging from aerospace applications to prosthetics.¹ The global usage of carbon fiber has more than doubled from 16,000 tons in 2000 to 35,000 tons in 2010.² It is valued for its high tensile capabilities as well as its overall mechanical toughness.¹ Although the need for carbon fiber is increasing the need for continued advancement of capabilities is greater; state-of-the-art carbon fibers have an ultimate tensile strength of ~7 GPa, however, the theoretical strength of an ideal carbon fiber exceeds 100 GPa.^{3,4} This can be attributed to morphological disinclinations in the fiber. The distribution of the defects along the backbone controls the limitations of the properties. Factors which ultimately govern graphite morphology include precursor chemical composition, precursor fiber processing and orientation, and oxidation/carbonization heat treatments.⁵ It has been shown in literature that the addition of co-monomers, in 3-10 weight percent, during polymerization can reduce cyclization exotherm and assist in stabilization.² This study focuses on the precursor composition.

By copolymerizing PAN homopolymer, through Reversible Addition-Fragmentation chain Transfer (RAFT), with small amount of comonomers, AA, using a semibatch reaction technique and comparing the results of traditional batch reaction it is shown that the differing techniques do not limit the eventual product and semibatch reactions even provide a way for control over the sequencing along the backbone. Controlling the sequencing along the backbone will allow for greater ring formation in precursors as well as dialing in the exothermic reaction resulting from stabilization. This

could prove to be a viable technique in tailoring the sequencing of a backbone to ultimately yield optimal mechanical properties.

1.1: PAN Chemistry

To create effective and high quality carbon fiber the precursor from which it is spun must also be high quality.¹ High quality in this context implies that the precursor is of a sufficiently high molecular weight, low polydispersity, and undergoes stabilization. The most common precursor for carbon fiber is PAN.⁶ Literature has shown that sufficiently high molecular weight and low polydispersity is possible for PAN and these techniques will be utilized for the synthesis of the PAN for this study.⁷ This research topic focuses on the effect of comonomers on ring formation and stabilization.

Carbon fiber can be defined molecularly as a large carbon ring network seen in Figure 1. To create carbon fiber the precursor material, PAN, must undergo ring cyclization and stabilization, the suggested mechanism is illustrated in Scheme 1. This reaction occurs at temperatures over 200 °C and forms the ring closed ladder structure in Figure 1. This reaction has been established as one of the most important prerequisites for high performing carbon fiber.⁸ This reaction goes by the well-established free radical mechanism shown in Scheme 1.⁹ The proposed mechanism specific to this project, going by the same free radical mechanism, is shown in Scheme 2. This reaction is characterized by a rapid exotherm that can damage the molecular structure causing structural flaws in the eventual carbon fiber.¹⁰ By adding comonomers into the reaction the exotherm can be broadened and will limit the intensity of the exotherm decreasing the number of defects in the eventual product. It has been shown in literature that the addition of certain comonomers into the polymerization has caused a reduction in stabilization energy

resulting in lower temperatures at which the precursor will cyclize.¹¹ This is important because this can significantly reduce time taken to create carbon fiber. Cyclization and stabilization can also be performed at a lower temperature which reduces risk of damage to the resulting material.

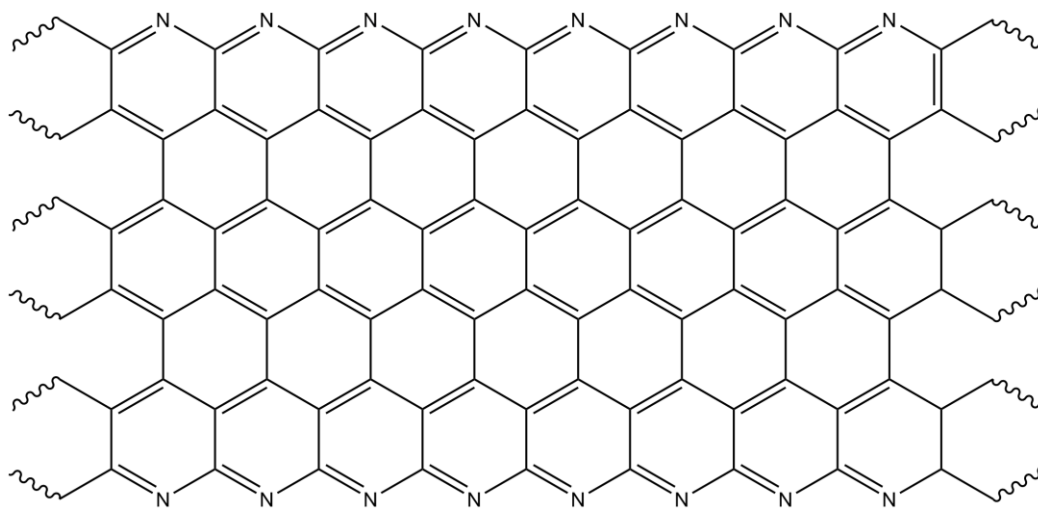
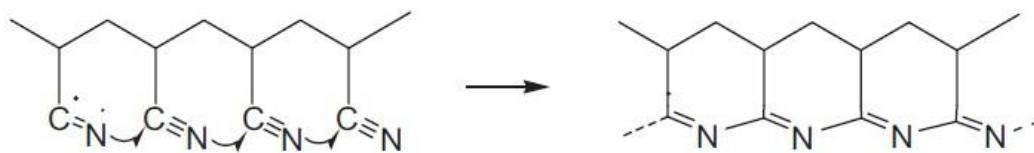
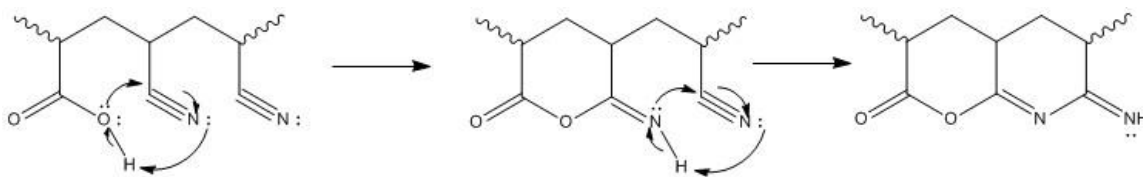


Figure 1: Carbon Fiber Network.



Scheme 1: Cyclization of PAN.⁸



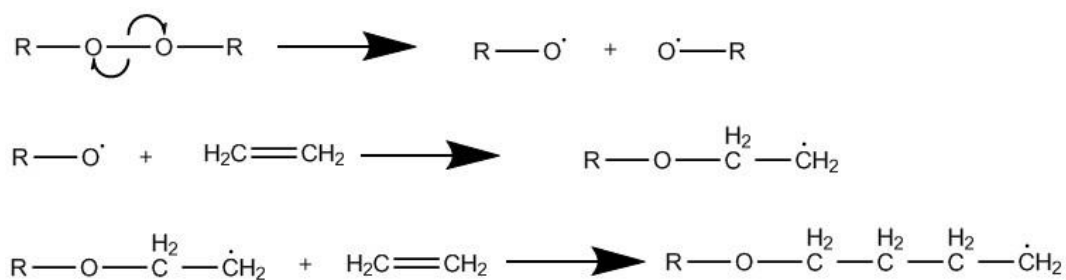
Scheme 2: Cyclization of poly(acrylonitrile-acrylic acid).

1.2: Controlled Polymerization

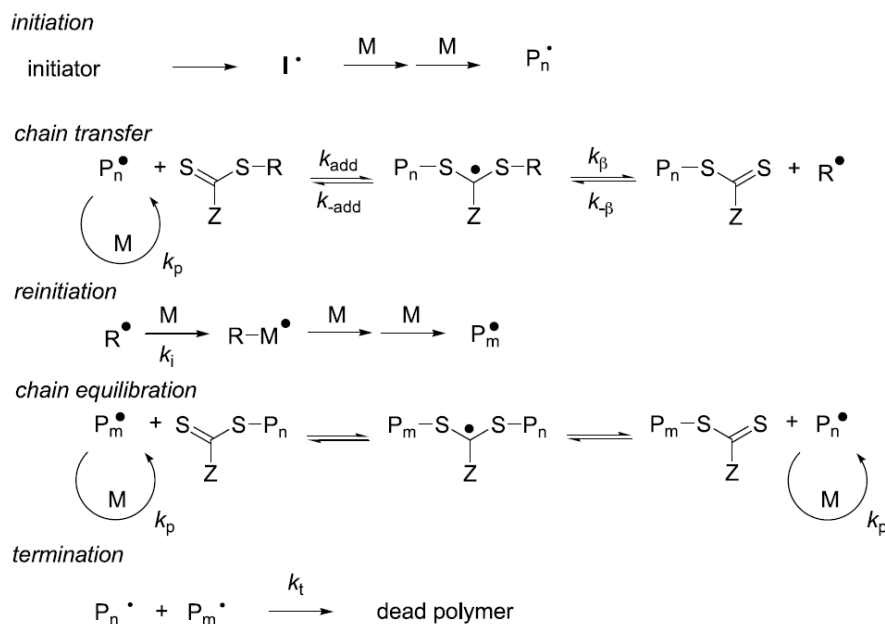
Free radical polymerization is among the most widely used and robust methods for polymerization.¹² Free radical polymerization proceeds by the mechanism seen in Scheme 1. Free radical polymerization proceeds through three phases: initiation, propagation, and termination. Initiation involves the generation of a radical by inputting energy. The initiating species will undergo homolytic dissociation, equal splitting of radicals among the initiating species. The next step is propagation. Propagation involves the addition of monomer to initiator and the subsequent addition to the chain formed. This will occur until all of the monomer is consumed or all the radicals are terminated. The final step in free radical polymerization is termination, termination occurs by two methods: coupling or disproportionation. Coupling simply involves the combination of two radicals to form a stable covalent bond. Disproportionation occurs by a radical species abstracting hydrogen from an adjacent chain. This renders the original radical species dead and forms a double bond on the abstracted species.

RAFT is a controlled free radical polymerization method that can be utilized for the creation of PAN precursor. RAFT is a versatile polymerization technique that proceeds under more mild reaction conditions, the reactions can take place at lower temperatures. RAFT usually comprises of four main components: (1) monomer for polymerization (2) initiating species (3) chain transfer agent (4) solvent. RAFT proceeds by a mechanism seen in Scheme 4. This allows for control of the monomer being added onto the polymer chain. However, PAN's insolubility and high reactivity call for careful considerations to the RAFT agent and the solvent.¹³ Trithiocarbonates were chosen as the RAFT agent due to literature studies indicating high molecular weight and low

polydispersity for polymerizations. Previous research has indicated that ethylene carbonate (EC) is a good choice for solvent.¹⁴ EC produces higher molecular weight polymer with a lower overall polydispersity when compared to traditional solvents such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) due to a lower chain transfer constant.¹⁰ A lower chain transfer means less termination of radicals which gives the desired properties as previously mentioned.



Scheme 3: General Free Radical Polymerization.



Scheme 4: RAFT polymerization mechanism.¹⁵

1.3: Stabilization

Stabilization is one of the most important steps in creating effective PAN and eventual carbon fiber.¹⁰ Stabilization in this context refers to the formation of a crystalline ring structure through various mechanisms. Stabilization goes through three main processes: oxidation, dehydrogenation, and cyclization. Cyclization is perhaps the most important. Stabilization goes by the proposed pathway seen in Figure 2. PAN stabilizes and cyclizes under intense heat.¹⁰ This can be determined by heating PAN and examining the concentration of nitrile groups as a function of time. The concentration of nitrile will decrease as cyclization increases. It has been shown in literature that the presence of comonomer in the polymer chain decreases the time taken to cyclize.¹⁰ This is an important implication in that it suggests that by copolymerizing that the time taken to cyclize and form carbon fiber can be significantly reduced. It has also been shown that the environment in which the PAN was cyclized can have significant impact on the time taken to cyclize.¹⁰ Air was shown to have a retarding effect on cyclization while the copolymerized polymer cyclized much more readily.¹⁰ This again is important as carbon fiber is typically cyclized in air as it is the most economic option.¹⁰ It has also been shown that cyclization in air is the most beneficial as it causes the greatest stabilization of the polymer network.⁶ This has been attributed to the interaction of the PAN backbone with the oxygen in the atmosphere.⁶ Two of the main factors of stabilization are cyclization and dehydrogenation reactions that are proposed to take place.⁶

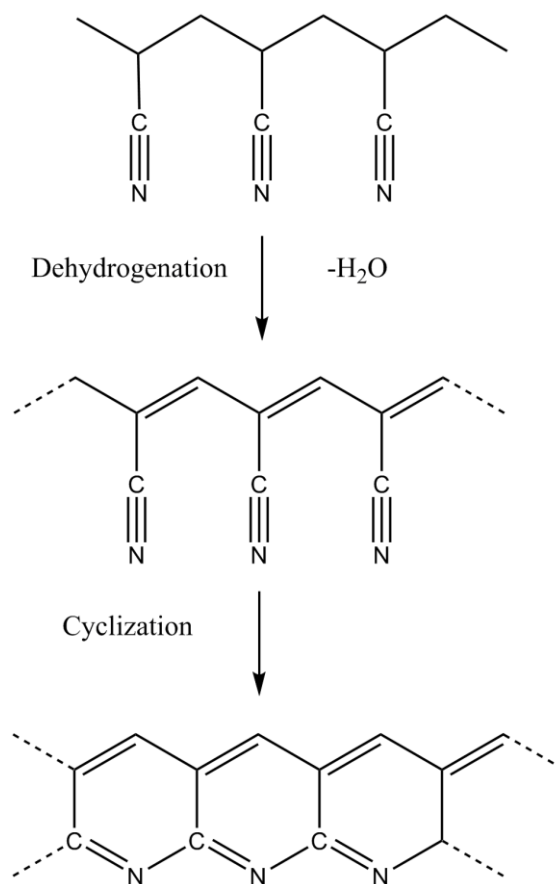


Figure 2: PAN Stabilization.

It has been shown in literature that certain comonomers, such as itaconic acid (IA), can actually facilitate reactions and therefore increase stabilization.⁶ Before it was accepted that cyclization could only be initiated at high temperatures, however, it would appear the IA's carboxylic groups can also initiate this process at a lower temperature.⁶ This again is important because it shows that the temperature at which cyclization occurs can be lowered and theoretically be controlled. Cyclization can be controlled by examining different comonomers and the rates and temperatures at which cyclization takes place.

Chapter 2: Experimental

Two copolymer carbon fiber precursors were synthesized along with two accompanying batch reactions which do not have a feed rate and will contain all of the final materials at the start of the reaction, the addition of comonomer to the reaction is what differentiates semibatch from the batch reactions. The resulting polymers will then be compared via TGA, DSC, and FTIR.

Acrylonitrile (AN, 99%, 35-45 ppm monomethyl ether hydroquinone inhibitor, SigmaAldrich Chemical Co.) was passed through a neutral aluminum oxide (50-200 μm) column to remove the inhibitor. Ethylene carbonate (EC, 98%, SigmaAldrich Chemical Co.), 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT, 97%, Sigma Aldrich Chemical Co.), Acrylic Acid (AA, 99%, Sigma Aldrich Chemical Co.), 2,2'-Azobis(4-methoxy-2.4-dimethyl valeronitrile) (V-70, Wako Pure Chemical Industries, Ltd.), and N,N Dimethylformamide (DMF, 99%, Sigma Aldrich Chemical Co.) were used as received.

2.1: RAFT Semibatch

The RAFT semibatch reaction for a molar ratio of $[\text{AN}]_0: [\text{AA}]_0: [\text{CPDT}]_0: [\text{V70}]_0 = 9800: 200: 1: 0.67$ was as follows: EC (31.1 g), AN (7.78 g), CPDT (5.2 mg, 0.015 mmol, stock solution in DMF 20 mg/mL), V70 (3.1 mg, 0.010 mmol, stock solution in tetrahydrofuran (THF) 20 mg/ml). This was charged into a 100 mL round bottom with a magnetic stir bar. The flask was capped with a rubber stopper, held in an ice bath, and purged under nitrogen flow for 30 minutes. The flask was then transferred to an oil bath set at 30 °C. Upon transfer a 3mL syringe consisting of AA (0.21 g) and EC (0.896 g) was consistently fed into the reaction vessel according to a programmed rate on a syringe

pump for 48 hours. At the end of the reaction the polymer was precipitated into a 1 L bath of 70: 30 (v:v) deionized water and methanol. The polymer was dissolved in DMF and re-precipitated into a thin film on a flat surface and coagulated by soaking in deionized water. The precipitated was then placed in a Soxhlet extractor for 24 h in methanol to remove residual solvent and then dried overnight at 60 °C via vacuum oven. This was then done for the varying comonomers content. The batch reactions were accomplished in the same manner except the amount of AA in the syringe was charged initially into the reaction flask.

2.2: TGA

TGA was recorded on a TA Instruments Discovery Thermogravimetric Analyzer to determine mass loss of the polymer samples in a nitrogen atmosphere ramped at 10 °C/min to 600 °C.

2.3: DSC

Fifteen mg of product is placed and sealed into a DSC pan and run with a TA Instruments DSC Q200 equipped with a nitrogen purge. The DSC temperature profile consists of a heating range of 100 to 350 °C at a ramp rate of 5 °C per minute.

2.4: FT-IR

FTIR spectroscopy was carried out using a Thermo Scientific Nicolet 6700 FTIR in the range of 4000-400 cm^{-1} . An infrared source was used with a KBr beam splitter and a DTGS KBr detector. Samples were prepared by dissolving 5-10 wt.% polymer in DMF and casting onto a polished 25 mm \times 4 mm NaCl salt plate. The samples were then heated overnight in a vacuum oven at 60 °C to remove DMF. The samples were then monitored in real time in a Simplex Scientific Heating Cell where 32 scans at 4 cm^{-1}

resolutions were acquired every 5 min during the cyclization reaction. The sample chamber was purged with nitrogen continuously as the temperature was raised to 225 °C and held for 5 h.

Chapter 3: Results and Discussion

The stabilization behavior of the semibatch reactions and cyclization was evaluated using TGA, DSC, and FTIR. These methods provide insight into the degradation, exotherm, and extent of stabilization of each semibatch reaction compared to each other as well as their batch counterparts. The Semibatch parameters can be found in Table 1.

Entry	t_0 (mol %) ^a	t_f (mol %) ^b	Injection rate (mL/h)	Duration of injection (h)
SB-1	0	2	0.028	48
SB-2	0	5	0.030	48
B-1	2	2	—	—
B-2	5	5	—	—

Table 1: Semibatch and batch reaction parameters.

^aThe initial amount of AA present in the reaction.

^bThe final amount of AA in the final product.

In Table 1, SB-1 refers to the semibatch reaction with 2 mol % of AA in the final product, SB-2 to the semibatch reaction with 5 mol % AA in the final product, B-1 to the batch reaction with 2 mol % AA, and B-2 to the batch reaction with 5 mol % AA. This allows for the comparison of how the method of polymerization, semibatch vs. batch, affects the thermal stability of the eventual carbon fiber precursor product.

3.1 Thermo Gravimetric Analysis (TGA)

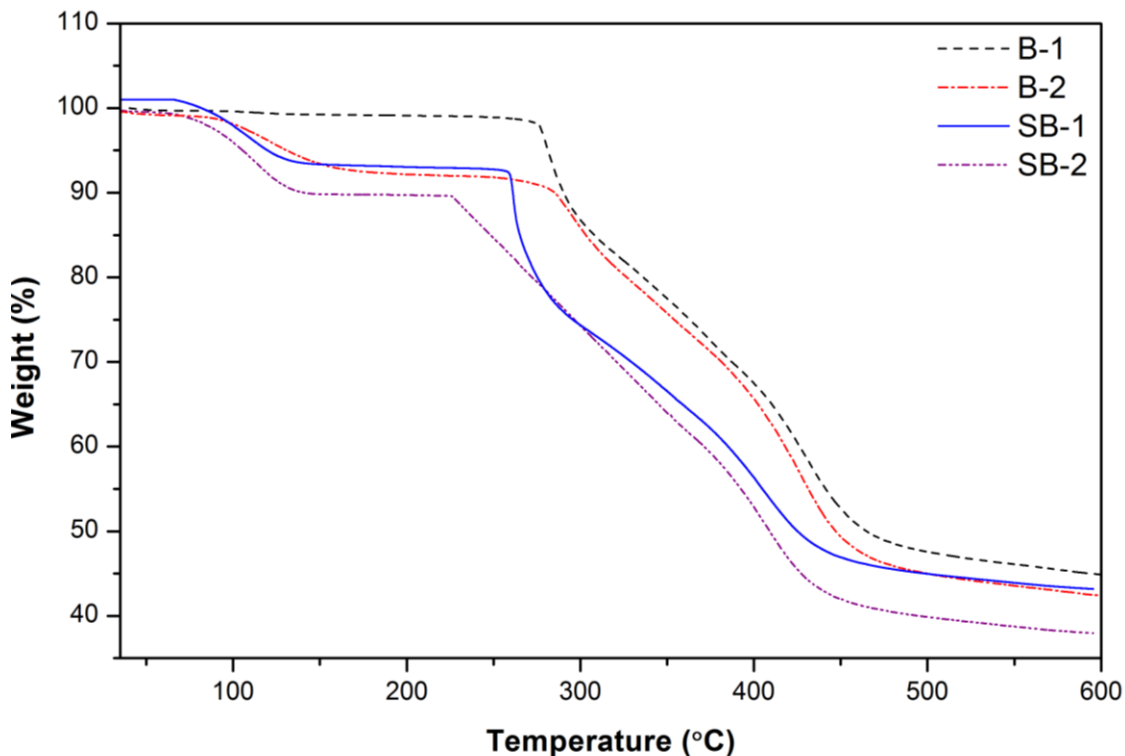


Figure 3: TGA curves of each polymer at 10 °C/min in nitrogen to 600 °C.

TGA was used to measure the thermal stability of the polymers via ramping at 10 °C/min as shown in Figure 3. Mass loss was exhibited from approximately 150–600 °C in the form of small molecules. Some of these include ammonia, hydrogen cyanide, methane, water, carbon monoxide, and carbon dioxide.¹⁶ The semibatch reactions have a higher mass loss at lower temperatures due to higher concentrations of acrylic acid on the backbone being released as carbon dioxide along with water loss. A more complex ladder structure would result in fewer impurities, less volatility, and therefore greater stability at temperatures above 800 °C. The batch reactions along with the SB-1 reaction exhibit comparable stability up to the 600 °C measured. The SB-2 reaction degrading slightly more due to the higher acrylic acid content, still this mass loss is not uncommon among

other copolymerizations. Overall, while the semibatch polymers did exhibit slightly greater degradation they were comparable to their batch counterparts, showing that they could withstand the same stabilization processes as that of the batch polymers.

3.2 Differential Scanning Calorimetry (DSC)

Entry	T_p (°C) ^a	Intensity (J/g) ^b	Heat Flow (W/g) ^c
B-1	264	1018	4.4258
B-2	241	535	2.6882

Table 2: Peak exotherm behavior.

^a Peak temperature, temperature at max heat flow.

^b Intensity is the area under the exotherm curve.

^c Maximum heat flow at a given temperature.

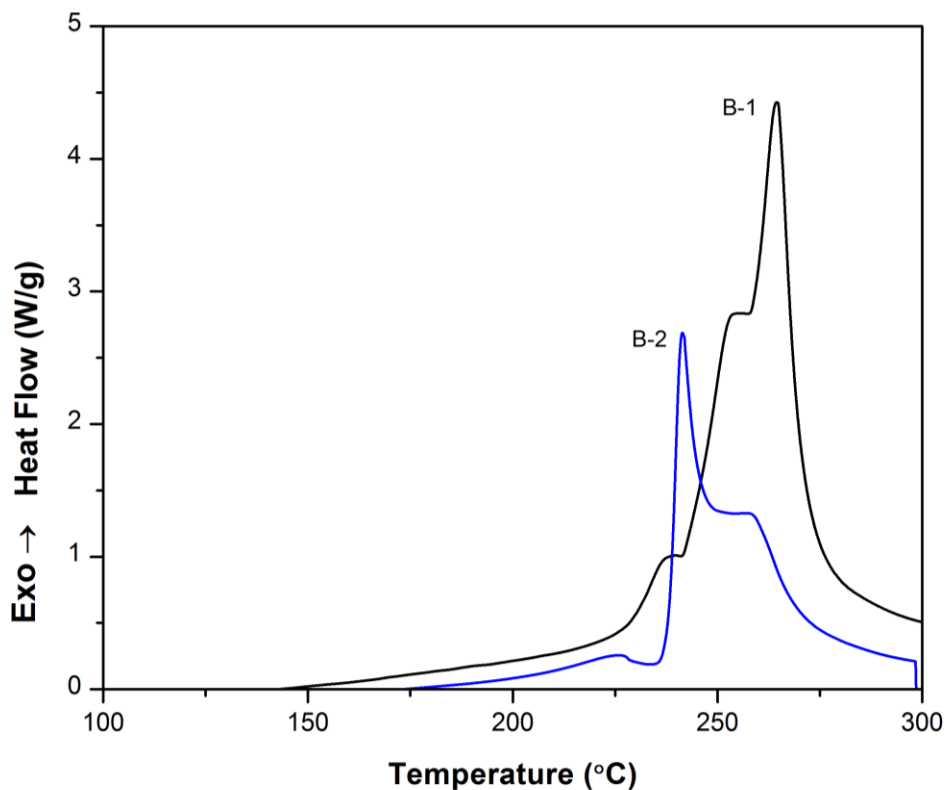


Figure 4: DSC exotherms of polymers at a 5 °C/min ramp rate.

DSC was employed to determine the exotherm characteristics of the d batch polymers. The exotherms can be found in Figure 4 and the data surmised in Table 2. Figure 4 shows that the addition of greater amounts of comonomer into the reaction significantly reduces the exotherm during stabilization B-2 with the greatest content of AA has a maximum heat flow of nearly half, as seen in Table 2. The intensity of the exotherm is also nearly halved by the addition of greater comonomers content. This would also be seen in the semibatch reactions of similar comonomer content.¹⁷ The semibatch reaction would even allow for sequencing along the backbone and could further break-up the exothermic reaction. Semibatch reactions could be implemented to further broaden the exotherm while decreasing the onset of cyclization.

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

The polymers were treated at 225 °C for 5 hours in nitrogen using a heating cell and studied in real-time via FTIR. The extent of stabilization, E_s , was then found using the equation:⁶

$$E_s = \frac{A_{1590\text{cm}^{-1}}}{A_{2240\text{cm}^{-1}}}$$

Equation 1: Extent of stabilization.

$A_{2240\text{cm}^{-1}}$ is the absorption intensity of the nitrile ($-\text{C}\equiv\text{N}$) and $A_{1500\text{cm}^{-1}}$ is the absorption intensity of the imine ($-\text{C}=\text{N}-$).⁶ The plot for the E_s is shown in Figure 5.

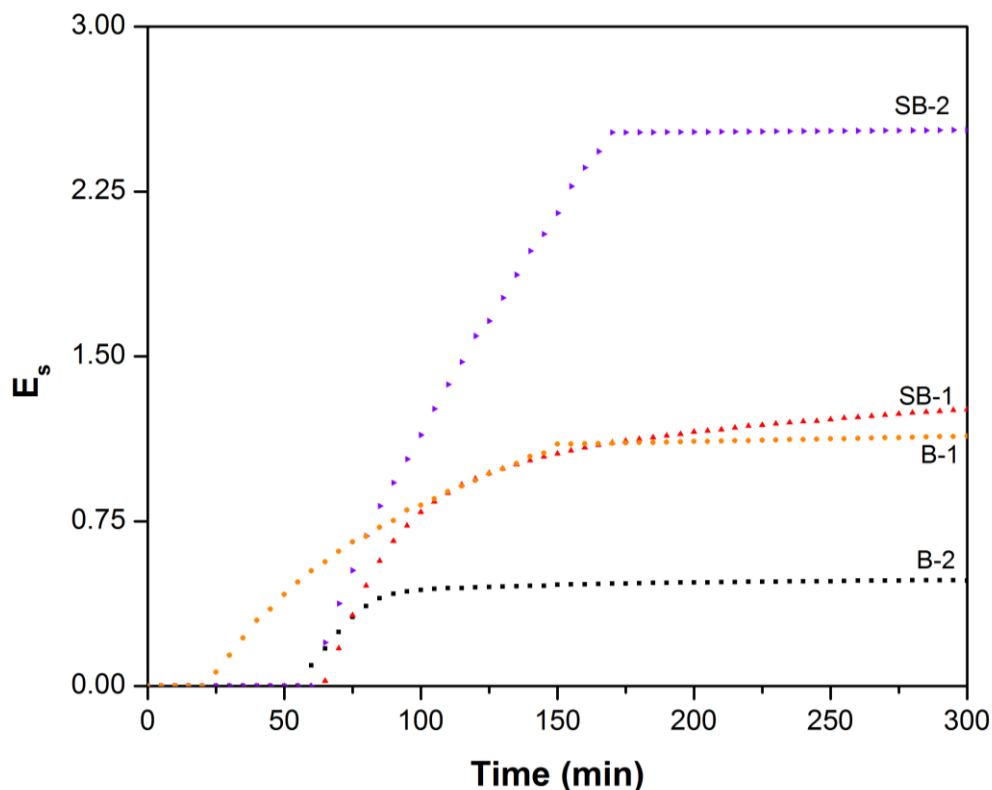


Figure 5: Extent of Stabilization for semibatch and batch copolymers treated at 225 °C for 5 h in nitrogen.

For all of the polymers the cyclization begins between 30 and 50 minutes and from there the polymers cyclize quickly plateauing around 150 minutes at 225 °C. This asymptotic behavior suggests that cyclization has been exhausted in all of the polymers with very little if any cyclization occurring after 5 hours. All of the polymers also exhibit the same general curve although the SB-2 reaction shows much greater E_s , relatively, than its batch counterpart as well as the other two reactions. This is indicative of high amount of AA on the backbone facilitating ring formation. This again shows that semibatch reactions offer the same properties when uncontrolled and could offer more tuned results with careful manipulation of comonomer along the backbone, facilitating even greater cyclization.

Chapter 4: Conclusions

Cyclization was characterized for four separate semibatch and batch reactions using TGA, DSC, and FTIR. Degradation was found to be slightly greater in the semibatch reaction when compared to their batch counterparts, however, the overall behavior was comparable and suggests that these precursor polymers would react similarly during stabilization. DSC revealed the exotherm was broadened with the addition of greater comonomer concentration and this would exhibit in the semibatch reactions as well. This could allow for greater control over the exotherm, including the onset of the exotherm by utilizing backbone composition through semibatch techniques. FTIR revealed that the semibatch and batch reactions exhibited similar cyclization behaviors, exhausting cyclization quickly. However, SB-2, with a high AA concentration, saw the greatest E_s of all the polymers. Greater cyclization could be achieved with more precise control over the addition of comonomers. These results have shown that stabilization behavior is comparable using semibatch RAFT techniques to batch RAFT techniques and that through the use of semibatch techniques could allow for tuning of backbone sequencing.

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