# Poly(ethylene) Blends With Acrylonitrile Co/Terpolymers as Barrier Materials

Amardeep Gill 260376264

Department of Chemical Engineering McGill University Montreal, Quebec, Canada

# August 2015

A thesis submitted to McGill University in partial fulfillment of the requirements of the degree of Master of Engineering

© Amardeep Gill 2015

Table	of	Contents
LUDIC	UL.	Contento

Abstract	i
<u>Résumé</u>	ii
Acknowledgments	iii
Preface & Contribution of Authors	iv
<u>Glossary</u>	iv
<b><u>1.</u></b> <u>General Introduction</u>	1
<b>1.1 Background Information</b>	1
Barrier Polymers	1
Polymer Blends	1
Compatibilization	2
Radical Polymerization	4
<u>1.2 Objective</u>	6
2. <u>Reactive Compatibilization of Poly(Methyl Acrylate-co-Acrylonitrile)</u>	
/Poly(ethylene) Blends Through the Amine-Maleic Anhydride Reaction	8
<b>2.1. Manuscript Introduction</b>	8
2.2. Experimental Section	10
2.2.1. Materials	10
<b>2.2.2. Methods</b>	10
2.2.3. Characterization	12
2.3. Results & Discussion	15
2.3.1. Synthesis of Methyl Acrylate/Acrylonitrile Copolymers	15
2.3.2. Synthesis of (MA/AN/PAS) Terpolymers	17
2.3.3. Extrusion & SEM Analysis	21
2.3.4 Rheology	24
2.4. Conclusion	26
3. <u>Reactive Compatibilization of Poly(styrene-ran-acrylonitrile) (SAN)/</u>	
Poly(ethylene) Blends Through the Acid-Epoxy Reaction	27
3.1. Manuscript Preface	27
3.2. Manuscript Introduction	27
3.3. Experimental Section	28
3.3.1. Materials	28

<u>3.3.2. Methods</u>	
3.3.3. Characterization	
3.4. Results & Discussion	
3.4.1. Synthesis of Styrene/Acrylonitrile Copolymers	
3.4.2. Synthesis of Styrene/Acrylonitrile/Acrylic Acid Terpolymers	
3.4.3. Synthesis of Styrene/Acrylonitrile Copolymers by NMP	
3.4.4. Synthesis of Block Copolymers using SAN copolymers	
3.4.5. Extrusion & SEM analysis	
<u>3.4.6 Rheology</u>	
3.5. Conclusion	
<u>4. Future Considerations</u>	
5. <u>Conclusions</u>	
References	

# List of Figures

Figure 1.1: Anhydride-Amine Coupling	4
Figure 1.2: Mechanism of Conventional Radical Polymerization	5
Figure 2.1: <sup>1</sup> HNMR spectrum of MA_AN_Exp1	16
<i>Figure 2.2:</i> Superimposed ART-FTIR spectrum of MA/AN copolymer (blue) MA/AN/PAS terpolymer (red)	and 18
<i>Figure 2.3:</i> <sup>1</sup> H NMR spectrum of the terpolymer MA_AN_PAS_Exp1	19
Figure 2.4: Thermal degradation of an MA/AN/PAS terpolymer	21
Figure 2.5: SEM images of MA/AN & MA/AN/PAS blends with PE-g-MA	23
Figure 2.6: Viscosity measurements of MA/AN, MA/AN/PAS, and PE-g-MA	25
Figure 3.1: <sup>1</sup> H NMR spectrum of S_AN_Exp1	35
Figure 3.2: <sup>1</sup> H NMR spectrum of S_AN_AA_9	38
Figure 3.3: DSC analysis of S_AN_AA_1	40
<i>Figure 3.4</i> : TGA analysis of S_AN_AA_1	41
<i>Figure 3.5</i> : Kinetic plots of $\ln[(1-x)^{-1}]$ versus time for SAN copolymers	43

Figure 3.6: M <sub>n</sub> vs conversion plots for SAN copolymers	.44
Figure 3.7: GPC chromatograph for chain extension of SAN macro-initiator	.46
Figure 3.8: SEM images SAN & SAN-b-SAA polymer blends with PE-g-GMA	.48
Figure 3.9: Viscosity measurements for PE-g-GMA, SAN, and SAN-b- SAA	50

# List of Tables

Table 2.1: Characterization of MA/AN Copolymers Synthesized by Conventional Radica         Polymerization	1
Table 2.2: Reaction Formulations for MA/AN/PAS Terpolymerizations	
Table 2.3: Molecular Weight Characterization of MA/AN/PAS Terpolymers	
Table 2.4: Interaction Parameters of the Blending Pairs	
Table 2.5: Particle Analysis of SEM Images	
Table 3.1:         Characterization         Of         Non-Reactive         SAN         Copolymers         Synthesized         by           Conventional radical polymerization	y
Table       3.2:       Formulations       for       the       Synthesis       of       Styrene/Acrylonitrile/Acrylic       Acid         Terpolymers by Conventional Radical Polymerization	b
Table       3.3:       Characterization       of       Styrene/Acrylonitrile/Acrylic       Acid       Terpolymer         Synthesized by Conventional Radical Polymerization	S
Table 3.4: Glass transition Temperatures of the Terpolymers40	)
Table 3.5: Characterization of SAN Copolymers Synthesized by NMP	2
Table 3.6: Formulation and Characterization of SAN macro-initiator       45	5
Table 3.7: Formulation and Characterization of SAN-b-S/t-BA46	5
Table 3.8: Interaction Parameters of the Blending Pairs	7
Table 9: Particle Analysis of SEM Images    49	9

# **Abstract**

Methyl acrylate/acrylonitrile copolymers (MA/AN) were reactively compatibilized as the dispersed phase with poly(ethylene) for potential barrier material application. The MA/AN was made reactive by including p-aminostyrene (PAS), yielding terpolymers (MA/AN/PAS) with pendant primary amine functionality (number average molecular weight  $\overline{M}_n = 65{\text{-}}133 \text{ kg mol}^{-1}$ , dispersity  $\overline{D} = 1.83{\text{-}}2.53$ , molar composition of PAS in copolymer F<sub>PAS</sub> =0.03{\text{-}}0.14). The non-functional MA/AN and amino functional MA/AN/PAS were each melt blended into poly(ethylene) grafted with maleic anhydride (PE-g-MA) at 200°C at 70:30 PE-g-MA:co/terpolymer. After extrusion, the dispersed phase particle size (volume to surface area diameter  $\langle D \rangle_{vs}$ ) was 12.6 µm for the non-reactive blend whereas it was much lower for the reactive blend ( $\langle D \rangle_{vs} = 1.2 \ \mu m$ .). Coarsening during annealing at 150°C was slow, but the domain sizes increased only slightly for both cases. The reactive blend was deemed sufficiently stable.

A second reaction coupling, the acid-epoxy coupling, was also studied. Styrene/acrylonitrile (SAN) copolymers with number average molecular weight  $(M_n) = 10-20 \text{ kg mol}^{-1}$  and dispersity D = 1.18-1.25 were synthesized by nitroxide mediated polymerization. The SAN ( $M_n = 10 \text{ kg mol}^{-1}$ ) was chain extended with a styrene/*tert*-butyl acrylate mixture. The block copolymer had a  $M_n = 36.6 \text{ kg mol}^{-1}$  and D = 1.34. The *tert*-butyl protecting groups were converted to acid groups (SAN-b-S/AA). SAN and SAN-b-S/AA were each melt blended with poly(ethylene) grafted with glycidyl methacrylate groups (PE-g-GMA) at 160°C in a twin screw extruder at a mass ratio of 70:30 (PE-g-GMA:polymer). The non-reactive PE-g-GMA/SAN blend had a volume to surface area diameter ( $<D>_{VS}$ ) of 3.0 µm while the reactive blend (the epoxy groups can react with the acid groups to form a graft copolymer in situ to stabilize the morphology) (PE-g-GMA/SAN-b-SAA) had  $<D>_{VS} = 1.7$ µm. After thermal annealing at 150°C for x hours, however, the non-reactive blend coarsened dramatically while the reactive blend showed no sign of coarsening suggesting that the coupling reaction was responsible for the stable morphology.

# <u>Résumé</u>

Une deuxième réaction entre l'anhydride maléique et l'amine a été enquêté, Les copolymères de l'acrylate de méthyle et acrylonitrile (MA/AN) ont été synthétisé par la polymérisation radicale conventionnelle. p-aminostyrene (PAS) a été additionné pour créer un polymère de trois unités (MA/AN/PAS) avec une  $M_n$ =65-133kg/mol, et de D=1.83-2.53. MA/AN et MA/AN/PAS ont été mélanger avec poly(éthylène) qui était modifiée avec des groupes d'anhydride maléique (PE-g-MA) à 200°C dans une extrudeuse. Il y avait 70% à 30% PE-g-MA à polymère (MA/AN ou MA/AN/PAS) par rapport à la masse totale insérée dans l'extrudeuse.  $<D>_{VS}$  pour la mélange de PE-g-MA avec MA/AN était 12.6µm et pour la mélange de PE-g-MA et MA/AN/PAS était 1.2µm. Après avoir recuit les échantillons à 150°C, les domaines pour les deux mélanges ont agrandi un peu donc la réaction entre l'anhydride maléique et l'amine était responsable pour la petite des domaines.

Une deuxième réaction entre l'acide carboxylique et l'epoxy a été étudié. Des copolymères de styrene et acrylonitrile (SAN) avec une masse moléculaire moyenne en nombre ( $M_n$ ) de 10-20kg/mol et dispersité ( $\oplus$ ) de 1.18-1.25 ont été synthétisé par la polymérisation contrôlée par les nitroxydes (NMP). SAN (M<sub>n</sub>=10kg/mol) a été grandi par une solution (50/50% mol) de styrene/acrylate de tert-butyle. Le produit, SAN-b-S/t-BA avait une M<sub>n</sub>=36.6 kg/mol et de Đ=1.34. Les groupes d'acrylate de tert-butyle ont étés transformé aux groupes d'acides (SAN-b-SAA). SAN et SAN-b-SAA ont été mélangé avec poly(éthylène) qui était modifié avec des groupes d'époxy (PE-g-GMA) à 160°C dans une extrudeuse. Il y avait 70% à 30% PE-g-GMA à polymère (SAN ou SAN-b-SAA) par rapport à la masse totale insérée dans l'extrudeuse. Le volume divisé par l'aire  $(<D>_{VS})$  était 3.0µum quand SAN a été mélangé avec PE-g-GMA.  $(<D>_{VS})$  a été 1.7µm quand SAN-b-SAA a été mélangé avec PE-g-GMA. Après avoir recuit les échantillons à 150°C, les domaines n'ont pas agrandi pour la mélange de SAN-b-AA et PE-g-GMA mais elles ont agrandi sévèrement pour la mélange de SAN et PE=g-GMA. Ces résultats suggèrent que la réaction entre les groupes d'acides et les groupes d'époxy a été responsable pour la morphologie stable.

# **Acknowledgments**

I would like to thank my supervisor, Prof. Marić for not only answering the questions I had, but also for his constant input every step of the way throughout the project. His guidance throughout the project was very greatly appreciated and paved the way to the results. Furthermore, I'd like to also extend my thanks to my numerous colleagues who each trained me and/or took their time to discuss possible solutions for problems that arose during the project. Specifically, I'd like to thank Celestine Hong, for her excellent work and report during Summer 2014, which paved the way for the first half of the second half of the second manuscript of which, she is a co-author.

I would like to express my thanks to Frederick Morin and Peter Fiurasek from the department of Chemistry at McGill. Fred provided not only training for NMR, but also advised on which techniques and instruments would be better suited for my specific samples. Peter not only trained me for FTIR, TGA and DSC analysis, but also made sure that optimal conditions were found for each of the three instruments.

I would like to also give my thanks to David Liu of the Physics department at McGill. He was responsible for training me on the SEM sample preparation and analysis.

I would like to thank Hanno Erythropel for running the rheology experiments.

Finally, I would like to thank Imperial Oil and McGill University for their generous funding for which the project would not be possible.

# **Preface & Contribution of Authors**

This thesis is a manuscript-based thesis comprised of two manuscripts (chapters 2 & 3). Both manuscripts are in the process of being submitted to the Journal of Macromolecular Materials & Engineering. The first manuscript titled "Reactive Compatibilization of Poly(Methyl Acrylate-co-Acrylonitrile) /Poly(ethylene) Blends Through the Amine-Maleic Anhydride Reaction", was written by me and edited by Prof. Milan Marić. I performed all of the syntheses, characterization, analysis, and extrusion. The rheology was performed by Hanno Erythropel as previously mentioned.

The second manuscript titled "Reactive Compatibilization of Poly(styrene-ranacrylonitrile) (SAN)/ Poly(ethylene) Blends Through the Acid-Epoxy Reaction",was written by me and edited by Prof. Milan Marić. Celestine Hong, who is a co-author, performed all of the syntheses and characterization for all of the polymers synthesized by conventional radical polymerization under my supervision in summer 2015. Furthermore, sections 3.3.1 & 3.3.2 of the thesis are based on her final reported she submitted at the conclusion of her work. The rheology was run by Hanno Erythropel.

Additionally, I would like to also recognize Daniel Gromadzki, whose work was the basis for the synthesis of the block copolymer in chapter 3. While none of the samples or data presented in the manuscript are of his work, the samples and data presented are a by-product of the work he began before me. He is listed as a co-author of the manuscript as well.

# **Glossary**

AA: Acrylic acid AIBN: Azobisisbutyronitrile AN: Acrylonitrile ATR-FTIR: Attenuated reflection fourier transform infared spectroscopy BB: BlocBuilder BPO: Benzyl peroxide CDCl<sub>3</sub>: Deuterated chloroform D: Polydispersity index

<D>vs=Volume to surface area particle diameter

DMF: Dimethylformamide

DMSO-d<sub>6</sub>: Deuterated dimethyl sulfoxide

DSC: Different scanning calorimetry

 $f_{i,0}$ : Feed composition of compound i

Fi: Polymer composition of compound i

 $\Delta G_{mix}$ : Gibbs free energy of mixing

GPC: Gel permeation chromatography

<sup>1</sup>H NMR: Proton nuclear magnetic resonance

 $\Delta H_{mix}$ :Enthalpy of mixing

K=Equilibrium constant between the active and dormant state

k<sub>p</sub>: Propagation rate constant

MA: Methyl acrylate

MA/AN: Methyl acrylate/acrylonitrile copolymer

MA/AN/PAS: Methyl acrylate/acrylonitrile/p-aminostyrene terpolymer

M<sub>n</sub>: Number average molecular weight

η: Viscosity ratio

N: Degree of polymerization

NHS-BB: BlocBuilder terminated by a succidimidyl ester group

NMP: Nitroxide mediated polymerization

PAN: Poly(acrylonitrile)

PAS: p-aminostryene

PE: Poly(ethylene)

PE-g-GMA: Poly(ethylene) grafted glycidyl methacrylate

PE-g-MA: Poly(ethylene) grafted maleic anhydride

PMMA: Poly(methyl methacrylate)

PP: Poly(propylene)

R: Gas constant

- δ: Hildebrand solubility parameter
- S: Styrene

 $\Delta S_{mix}$ : Entropy of mixing

- SAN: Styrene/acrylonitrile copolymer
- SAN-b-SAA: Styrene/acrylonitrile-block-Styrene/Acrylic acid block copolymer
- S/AN/AA: Styrene/acrylonitrile/acrylic acid terpolymer
- SEM: Scanning electron microscopy
- SG1: Persistent radical group of Blocbuilder
- SN<sub>2</sub>: Nucleophilic substitution (second order)
- t-BA: *Tert*-butyl acrylate
- T: Temperature
- Tg: Glass transition temperature
- TGA: Thermal gravimetric analysis
- THF: Tetrahydrofuran
- μ: Chemical potential
- *v*: Wavenumbers (for ATR-FTIR)
- *v*: Molar volume (for polymer thermodynamics)
- x: Conversion
- $\chi$ : Interaction parameter

# **1. General Introduction**

# **1.1 Background Information**

#### **Barrier Polymers**

Barrier polymers are polymers used to prevent the penetration of liquids, gases or vapors in storage containers and food packaging.<sup>[1]</sup> Traditionally, metals were used to fabricate storage containers. Polymers, being much lighter and generally less expensive became more attractive for storage containers (eg. gas tanks, food and drug containers). The most commonly used polymer is poly(ethylene) (PE) for not only storage containers but plastic bags, bottles and, films. While it is extremely cheap, its hydrophobic structure gives it poor barrier properties against hydrocarbons and other hydrophobic compounds. The target application of this research is fuel tanks, and minimizing gasoline loss from PE based fuel tanks. One typical solution is blending polymers by layering them (eg. multilayer packaging for films). Each layer brings about different properties to create a material with a wide variety of properties that can be suitable for many applications. Layering could be costly if multiple extruders are used. In some applications, the multilayer approach is not needed, and thus simply like the classical approach, blending, two polymers together in an extruder, followed by appropriate dies, can create desirable structures to obtain barrier properties. The classical blending approach is to blend hydrophilic polymers such as polyesters and polyamides with the hydrophobic PE.<sup>[2]</sup> Although these polymers are immiscible, the brick like morphology creates a tortuous structure that minimizes PE loss.<sup>[2]</sup> No one polymer possess ideal barrier properties against every class of compounds while being cheap, recyclable, with strong mechanical and thermal properties so blending is favored.<sup>[1]</sup> However, in order to apply polymer blends, the underlying thermodynamics that govern the domain size and morphological stability must be addressed.

#### **Polymer Blends**

Polymer blending is the process of taking separate polymers with a unique set of properties and mixing them together at elevated temperatures to create a polymer blend with a combined set of properties from the original polymers. For equilibrium and therefore, phase stability to occur for a blend of polymers, as morphological stability dictates the properties, the Gibbs free energy must be minimized as shown in Equation 1.<sup>[3]</sup> Also, the chemical potentials for each component in each phase must be equal as shown in Equation 2.

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} < 0 \tag{1}$$

$$\mu_i^a = \mu_i^b \quad i = 1, 2, 3 \dots n \tag{2}$$

In Equation 1,  $\Delta G_{mix}$  is the Gibbs free energy of mixing,  $\Delta H_{mix}$  is the enthalpy of mixing and  $\Delta S_{mix}$  is the entropy of mixing. In Equation 2,  $\mu$  is the chemical potential, i is used to denote a specific component in the blend, n is the total number of components and, the superscripts a and b denote the different phases present. A polymer blend is considered miscible (one homogenous phase) if Equations 1 and 2 are both satisfied.<sup>[3]</sup> If either Equation 1 or 2 is not satisfied, the polymer blend is considered immiscible (two separate phases). Like any mixture, models are used to approximate not only thermodynamic properties such as  $\Delta G_{mix}$ , but the stability of the system as well. The most common and often simplest model used for polymer blends is the Flory Huggins equation. It introduces  $\chi$ , the enthalpic interaction parameter, in addition to the concentration and the degrees of polymerization. A negative interaction parameter indicates that the polymers are interacting through strong interactions such as: dipole-dipole, hydrogen bonding, dipoleionic, ionic-ionic interactions, etc...<sup>[3]</sup> Blends with a positive interaction parameter (weak interaction) can still yield miscible blends under very strict and limited conditions. Most polymer mixing combinations yield immiscible blends because these specific interactions are not present. Immiscible blends lead to phase instability and thus poor properties, particularly mechanical properties. Immiscible blends however still can be of use and yield high performance materials if the separate phases can be stabilized/compatibilized.<sup>[3, 4]</sup>

#### Compatibilization

In an immiscible blend, there are two separate phases. The interfacial energy between them is too high for them to favor mixing (use oil and water as an example). This results in a coarse, unstable morphology, and very low adhesion between the two phases. Compatibilization of a blend means to decrease the interfacial tension/energy at the interface of the two (or more) polymers so that the polymers interact with one another rather themselves. Also, it constructs a desirable stable morphology during forming.<sup>[3]</sup> Finally, it enhances adhesion between the two phases in the solid state.<sup>[4]</sup> There are two main methods for compatibilization: the addition of a pre-made compatibilizer and reactive compatibilization.<sup>[4-6]</sup>

#### Addition Method

A compatibilizer is a block co-polymer which has one block that can interact with one phase, and another block which can interact with the other phase.<sup>[4-8]</sup> Here it is expected that the compatibilizer diffuses to the interface between the two polymers creating adhesion between the respective phases and prevents coalescence, like a surfactant, leading to a finer morphology and better dispersion. Coalescence is when the dispersed phase domains agglomerate and coarsen. While adding a pre-made compatibilizer obtains a desirable and stable morphology, it has a few disadvantages. Firstly, because the compatibilization process depends on the compatibilizer diffusing to the interface, this process is mass transport limited.<sup>[3, 4]</sup>It could be entirely possible that the compatibilizer forms micelles instead of going to the interface, which reduces its effectiveness.<sup>[4, 6, 9]</sup> Finally, the correct architecture and monomers required to compatibilize two disparate polymers may not be accessible. Pre-made copolymers are thus rarely used industrially; instead, reactive compatibilization is most often applied.<sup>[9]</sup>

### Reactive Compatibilization

Reactive compatibilization is a strategy that takes advantage of pre-existing functional groups being present on the polymers to be blended. Some examples are poly(amides) and poly(esters), which have the terminal groups from the polymerization process used to make them. Generally, polymers do not have the requisite functional groups on them, but may be modified (i.e. grafting or copolymerization) such as PE, which can be grafted with maleic anhydride with peroxide addition. Thus, the complementary functional groups can be added to the polymers that will permit graft copolymer formation in the melt during blending. Figure 1 demonstrates a typical functional group coupling.



# Figure 1: Anhydride-Amine Coupling<sup>[10]</sup>

Due to this coupling reaction, the interfacial tension between the two immiscible polymers will be lowered.<sup>[5, 9, 11]</sup>Additionally, coalescence can be prevented/reduced due to the formation of the copolymer brush at the interface. Reactive compatibilization does not imply that immiscibility was overcome.<sup>[4]</sup> However, it links the two phases physically via bonding and creates a stable morphology. An issue arises on deciding which functional group coupling to use. The reaction must occur at a relatively fast rate compared to the residence time spent in the extruder<sup>[3, 11]</sup> While any functional group coupling can be used (as long as the reaction can occur within the residence time of the extruder), the most commonly used couplings are: amine-anhydride, amine-carboxylic acid, amine-epoxy, isocyanate-hydroxyl, oxazoline-carboxylic acid and epoxy-carboxylic acid<sup>[12]</sup> Of these reactive pairs, the kinetics of the amine-anhydride (primary amine to be specific) coupling is the fastest.<sup>[11, 12]</sup>

It should be emphasized that copolymer formation is accomplished *in situ* at the interface between the two polymers, and thus no mass transport limitations exist. The only requirement for reactive compatibilization is the presence of compatible functional groups. While there are many chemical pathways for functional groups to be added, radical copolymerization is a versatile and simple method to use.

### **Radical Polymerization**

Radical polymerization makes use of radicals, which are highly reactive species, to polymerize vinylic monomers, forming macroradicals and eventually high molecular weight polymers. Because radicals react strongly with double bonds, the extensive set of monomers containing a vinyl group can be readily polymerized by a radical mechanism. There are many different types of radical polymerization, but this work focuses on conventional radical polymerization and nitroxide mediated polymerization (NMP).

#### Conventional Radical Polymerization

Conventional radical polymerization uses initiators such as azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO). These initiators are activated (release radicals) at elevated temperatures. Other types of initiators can also be used, such as initiators that are activated with light for example. The release of radicals (initiation) is the first step of the polymerization process as shown in Figure 2.





Once a radical is formed, it can begin to attack monomers with double bonds. When a monomer is attacked by a radical, it forms a new radical species, and the radical is transferred to the  $\beta$ -carbon of the monomer. This new unit with the radical on the  $\beta$ -carbon can consequently attack another monomer with a double bond to extend the chain. This cycle can continue to repeat and is known as propagation. Because radicals are not selective, instead of reacting with monomers, they can combine with another propagating chain, which would destroy the radicals, and cause the two chains to stop growing. It is also possible that a newly initiated radical combines with a growing chain, which destroys both radicals and stops growth. These two scenarios are known as chain termination. The chains are considered dead because they cannot continue to grow as they have lost their radical nature. As it was mentioned, radicals are highly reactive and not selective, so the phenomenon of chain transfer is likely to occurring during the polymerization. Chain transfer means that the radical has transferred to another species,

leaving the species, which originally possessed the radical, dead. Chain transfer to monomer, polymer or solvent are all possible. Because of the high possibility of chain transfer and chain termination, the size distribution of the chains also known as the polydispersity index (Đ), is generally broad. Đ of unity indicates that all the chains are the same size (length), but for conventional radical polymerization, typical theoretical values are 1.5>D>2.0. Significant broadening in the size distribution can lead to uneven properties in the polymer. NMP can be used to reduce the Đ.

#### Nitroxide Mediated Polymerization

NMP has the same possible steps as conventional radical polymerization(initiation, propagation, termination and chain transfer). The one key difference however is that NMP occurs in a controlled manner. In conventional radical polymerization, the radical is free to attack and termination is very likely to occur. In NMP, the radical is continuously capped by a persistent radical (persistent radical effect) so that the possibility of termination or chain transfer is drastically reduced.<sup>[13]</sup> In fact, kinetics of the equilibrium between the active and dormant state favor the dormant state so that the radical is capped (deactivated) by the persistent radical for the majority of the time.<sup>[14-18]</sup> When the radical is uncapped (activated) it attacks a few monomers and is capped once again by the persistent radical, significantly reducing the chance of chain transfer or termination. This results in polymers with more uniform chain length distribution, and chain end fidelity, which permits the ability to form block copolymers.<sup>[13]</sup> The latter feature has been traditionally associated with mechanisms like living ionic polymerization, which have an indefinitely active chain end (truly living as opposed to NMP, where there are still irreversible chain termination events during the course of the polymerization). However the key attractive feature of NMP is that it has the same requirements as conventional radical polymerization with a high tolerance towards impurities and oxygen, a trait not shared by many living polymerization techniques, which require oxygen and moisture free environments and copious purification of reagents.<sup>[13]</sup>

# **1.2 Objective**

The main objective of this project is to develop PE based barrier materials with barrier properties against hydrocarbons (gasoline specifically) using acrylonitrile based

polymers. PE is used as the matrix material (cheap and easy to process) while the acrylonitrile based polymers provide the polar domains dispersed as elongated brick-like morphologies, analogous to barrier blends made from poly(esters)or poly(amides).<sup>[2]</sup> To make such blends stable, functional groups will be inserted into the polymers to ensure interactions producing fine, stable domain sizes. The functional groups will be inserted by polymerizing monomers by both conventional radical polymerization and NMP. Two different functional group pairings will be tested to determine which pairing yields finer domain sizes. The first pairing is the amine-maleic anhydride pairing and the epoxy-carboxylic acid pairing is the second. These couplings were chosen over other possibilities because they have among the fastest kinetics available. Chapters 2 & 3 describe the objectives and the results obtained from experimentation. Both chapters are manuscripts, which are in the process of being submitted to the Journal of Macromolecular Materials & Engineering.

# 2. Reactive Compatibilization of Poly(Methyl Acrylate-co-Acrylonitrile) /Poly(ethylene) Blends Through the Amine-Maleic Anhydride Reaction

# 2.1. Manuscript Introduction

Barrier polymers are used to prevent penetration of liquids, gases or vapors in materials used often for storage containers and food packaging.<sup>[1]</sup> Materials such as ethylene-vinyl alcohol copolymers, poly(acrylonitrile) (PAN), vinylidene chloride copolymers, poly(chlorotrifluoroethylene), polyesters, and polyamides are just some common polymers used for barriers (sometimes in blends with other polymers) against gases and/or moisture<sup>[1]</sup>. Traditionally, metals were the choice to fabricate storage/transport containers. However, the light weight of polymers in addition to relatively low processing temperatures compared to metals made them attractive alternatives. Consequently, polymers such as PE or poly(propylene) (PP) have been used.<sup>[1, 19]</sup> However, using polyolefins such as PE or PP, despite their attractive mechanical strength, physical properties and cost, may not be effective as barrier materials solely and thus requires the addition of other polymers in the form of a blend.

While blending can deliver a material combined with the desirable properties of two or more polymers, it often leads to phase separation upon further processing due to incompatibility between the constituent polymer phases.<sup>[3, 4]</sup> Phase separation is indicated by coalescence, leading to large dispersed phase particle sizes, low interfacial area, and, subsequent poor mechanical and other physical properties. To overcome coalescence and improve phase stability, compatibilization is used.<sup>[4, 6, 20]</sup> Many groups have shown that adding compatibilizers to polymer blends reduces the size of the dispersed phase significantly (which is crucial for many properties) and reduces coalescence.<sup>[3, 5, 7, 21-33]</sup> By far, the most common method to compatibilize polymer blends is reactive compatibilization.<sup>[4, 6]</sup>

Reactive compatibilization uses complementary functional groups on the respective polymers to reduce the interfacial tension and suppress coalescence, resulting in stable morphologies.<sup>[20]</sup> Examples of compatibilization reactions are amine-anhydride, amine-carboxylic acid, amine-epoxy, isocyanate-hydroxyl, oxazoline-carboxylic acid and

epoxy-carboxylic acid.<sup>[12]</sup> The coalescence rate is dependent on, among other variables, the kinetics of the coupling reaction.<sup>[6, 34]</sup> It is therefore important to choose a reaction that has a relatively rapid coupling rate compared to the residence time of the extrusion process. Out of these reactive pairs, the kinetics of the amine-anhydride (primary amine to be specific) coupling is the fastest.<sup>[12]</sup>

PAN has been extensively studied and used for its very good barrier properties against the noble gases along with oxygen and carbon dioxide.<sup>[35]</sup> Furthermore, in the food industry, it has been used to block the permeation of aromas and/or flavors along with other hydrophobic compounds.<sup>[36]</sup> Its hydrophilic structure however, limits its absorption against water vapor.<sup>[25]</sup>. However, this hydrophilicity is useful as a barrier against hydrocarbon liquids such as the case of dispersing nylon into PE as dispersed, elongated domains.<sup>[2]</sup> Using nylons or polyesters is useful, as the terminal functional groups left as residues from the step-wise polymerization mechanism used to make the polymers can be applied towards reactive blending. PAN, in contrast, is made most often by a free-radical polymerization mechanism, and is further amenable to controlled polymerization methods, which provide the potential for more sophisticated microstructures and consequently opportunities for more extensive tailoring of mechanical and physical properties. The only missing component is the inclusion of a functional group in PAN for reactive blending. Further, acrylonitrile is often copolymerized with another monomer to improve thermal stability; often styrene and methyl acrylate are used.<sup>[37]</sup> In fact, copolymers of styrene and acrylonitrile and of methyl acrylate and acrylonitrile are commercially available as barrier materials synthesized by conventional radical polymerization.<sup>[37]</sup> We previously made styrene-acrylonitrile (SAN) copolymers where we placed a single reactive amine group at the chain end.<sup>[10]</sup> The amine-terminated SAN was effective in compatibilization with maleic anhydride grafted PE (PE-g-MA) and we were able to form elongated SAN domains in the PE.<sup>[10]</sup> However, the dispersed phase particle size was limited to about 1-2 µm and further modulation could potentially be accessed by making the acrylonitrile-containing copolymer with man pendant functional groups. The following study first describes the conventional radical polymerization of methyl acrylate, acrylonitrile, and p-aminostyrene terpolymers (MA/AN/PAS) to give

9

pendant amino functionality and then describes its reactive blending and phase stability after blending with (PE-g-MA).

# 2.2. Experimental Section

# 2.2.1. Materials

Methyl acrylate (MA) (99%) and acrylonitrile (AN) (99%) were obtained from Sigma-Aldrich, purified by passing the monomers through a column of basic aluminium oxide (Brockmann, Type 1, 150 mesh) and calcium hydride (90-95% reagent grade) (5 wt% CaH<sub>2</sub>: 95 wt%Al<sub>2</sub>O<sub>3</sub>), which were also obtained from Sigma Aldrich), and stored under a head of nitrogen prior to use. AIBN was obtained from Du Pont, dissolved in methanol, and purified by re-crystallization before use. p-aminostyrene (PAS) was obtained from Oakwood Chemicals and used as received. Deuterated chloroform (99.8 atom%) (CDCl<sub>3</sub>), deuterated dimethylsulfoxide (DMSO-d<sub>6</sub>), trimethylsilyldiazomethane in 2M hexanes solution, and phenyl isocyanate (98%) were obtained from Sigma Aldrich and were used as received. N,N-dimethylformamide (DMF) ACS grade (99%) was obtained from Fisher and used as received. HPLC grade DMF (99.5%) was obtained from Fisher as the mobile phase for gel permeation chromatography (GPC). Lithium bromide was added to the DMF at a concentration of  $1 \text{ g L}^{-1}$  for GPC.<sup>[38]</sup> PE-g-MA with a melt flow index of 1.5 g (10 min)<sup>-1</sup> at 190°C, density of 0.91g ml<sup>-1</sup> and, a melting point of 123°C was obtained from Arkema and used as received. Other chemicals used for cleaning purposes such as acetone (99.5%) and methanol (99.8%) were obtained from Fisher and used as received unless otherwise mentioned.

### 2.2.2. Methods

# 2.2.2.1. Synthesis of Methyl Acrylate/Acrylonitrile Copolymers

MA and AN were copolymerized using DMF as the solvent in a three necked 50 ml reactor with a nitrogen purge, thermocouple/thermowell and, reflux condenser. The reactor sat on top of a stirring plate and heating mantle. Appropriate amounts of AIBN, MA, AN, and DMF were measured out and poured into the reactor with the formulation for MA\_AN\_Exp1 (see Table 1) shown as an example. For this particular experiment, 0.1137 g (0.692 mmol) AIBN, 5.1163 g (59.43 mmol) MA, 3.3177 g (62.53 mmol) AN,

and 7.9164 g (108.31mmol) DMF were measured and poured into the reactor. The reactor solution was purged with nitrogen for at least 30 minutes prior to starting the reaction and maintained throughout the reaction. The set point of the reaction was set to 65°C to ensure significant decomposition of AIBN.<sup>[39]</sup> The chiller was set to 4°C. Once the reaction was complete (reaction time of about 3-4 hours), the polymer was precipitated the first time in about 300ml of deionized water, re-dissolved in a minimum amount of solvent, and precipitated a second time in about 50ml of deionized water to remove unreacted monomers. Finally, the polymer was vacuum dried in the oven at 50-60°C overnight. This particular copolymer had a number average molecular weight (M<sub>n</sub>) of 90.9 kg mol<sup>-1</sup> and Đ of 2.71 relative to poly(methyl methacrylate) (PMMA) standards in DMF at 50 °C. The copolymer had a MA molar composition of 0.51, which was determined by Proton Nuclear Magnetic Resonance (<sup>1</sup>H NMR) (300 MHz, DMSO-d6,  $\delta$ ): 3.6 (s, 3H, O-CH<sub>3</sub>), 1.2-2 (m, 2H, backbone CH<sub>2</sub>).

#### 2.2.2.2. Synthesis of Methyl Acrylate/Acrylonitrile/p-aminostyrene Terpolymers

MA, AN and PAS were terpolymerized in a three necked 50ml reactor with a nitrogen purge, thermocouple/thermowell and, reflux condenser. The reactor sat on top of a stirring plate and heating mantle. The solvent was DMF. Appropriate amounts of AIBN, MA, AN, PAS, and DMF were measured out and poured into the reactor, with the formulation for MA\_AN\_PAS\_Exp1 (see Table 2) shown as an example. For this particular experiment, 0.107 g (0.652 mmol) AIBN, 7.1598 g (71.46 mmol) MA, 1.335 g (25.16 mmol) AN, 0.6016 g (5.05 mmol) PAS, and, 9.7982 g (134.06 mmol) DMF were measured and poured into the reactor. The reactor solution was purged with nitrogen for at least 30 minutes prior to starting the reaction and maintained throughout the reaction. The set point of the reaction was set to 65°C to ensure sufficient initiator decomposition.<sup>[39]</sup> Once the reaction was complete (reaction time of 1.5 hours), the polymer was precipitated the first time in about 300 ml of deionized water, re-dissolved in a minimum amount of solvent and precipitated a second time in about 50 ml of deionized water to remove unreacted monomers. Finally, the polymer was vacuum dried overnight in the oven at 50-60°C. This particular terpolymer had a  $M_n$  of 114.1 kg mol<sup>-1</sup> and Đ of 2.14 relative to PMMA standards in DMF at 50 °C. The terpolymer had a MA and AN molar composition of 0.68 and 0.24 respectively, which were calculated by

11

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 6.9-7.5 (m, 4H, Ar H), 0.8-2 (m, 3H, CH-CH<sub>2</sub>), 3.6 (s, 3H, O-CH<sub>3</sub>).

# 2.2.3. Characterization

# 2.2.3.1. <u>Proton Nuclear Magnetic Resonance (<sup>1</sup>HNMR)</u>

<sup>1</sup>H NMR (Varian 300 MHz) was used to characterize the composition of all copolymers and terpolymers. The peaks of interest for MA/AN copolymers were at  $\delta = 3.6$  ppm for the methyl protons for MA and  $\delta = 1.2$ -2 ppm for the backbone protons. The peaks of interest for MA/AN/PAS terpolymers were at  $\delta = 3.6$  ppm for the methyl protons for MA,  $\delta = 0.8$ -2 ppm for the backbone protons and  $\delta = 6.5$ -7 ppm for the styrenic protons of PAS. For all polymers, the AN content was calculated using the backbone protons, rather than solely the proton on the  $\alpha$ -carbon.<sup>[40, 41]</sup> CDCl<sub>3</sub> was used for <sup>1</sup>NMR analysis for the terpolymers, whereas deuterated DMSO-d<sub>6</sub> was used for the copolymers.

# 2.2.3.2. <u>Gel Permeation Chromatography (GPC)</u>

All polymers were analyzed using a Waters Breeze system equipped with two ResiPore (3  $\mu$ m MULTI pore type 250x4.6 mm<sup>2</sup>) columns along with a ResiPore guard column (3  $\mu$ m, 50x4.6mm<sup>2</sup>) from Polymer Laboratories. The flow rate was 0.3ml min<sup>-1</sup>. The GPC was equipped with a differential refractive index (RI 2410) detector. MA/AN copolymers and MA/AN/PAS terpolymers required DMF with 1g L<sup>-1</sup> lithium bromide as the mobile phase and a column temperature of 50°C. The molecular weights were measured relative to PMMA standards. Prior to analysis, polymer samples containing PAS were quenched with phenyl isocyanate to prevent sticking of the amine groups onto the column.<sup>[9, 20, 40, 41]</sup>

2.3.3. <u>Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR)</u> A Perkin-Elmer spectrum TWO with UATR accessory (also from Perkin-Elmer) and diamond as the ATR crystal was used to qualitatively analyze MA/AN and MA/AN/PAS co/terpolymerizations. The peaks of interest for MA/AN copolymers were at v = 1600-1800 cm<sup>-1</sup> for the carbonyl stretch of MA and v = 2200-2400 cm<sup>-1</sup> for the nitrile stretch in AN.<sup>[42]</sup> The peaks of interest for MA/AN/PAS terpolymers were at v = 1600-1800cm<sup>-1</sup> for the carbonyl stretch of MA, v = 2200-2400 cm<sup>-1</sup> for the nitrile stretch for AN and, v = 3300-3500 cm<sup>-1</sup> for the N-H stretch of the primary amine of PAS.<sup>[42]</sup>

# 2.2.3.4. Thermal Gravimetric Analysis (TGA)

A TGA Q500 (TA Instruments) was used to determine the minimum degradation temperature and degradation profiles of the MA/AN/PAS terpolymers. The analysis began at ambient temperature (35-40°C) and proceeded to 550°C at a heating rate of 10 °C min<sup>-1</sup>. The analysis was done under oxygen rather than nitrogen to simulate the environment in an extruder.

# 2.2.3.5. Differential Scanning Calorimetry (DSC)

A DSC Q2000 from TA Instruments was used to approximate the glass transition temperature ( $T_g$ ) of the MA/AN/PAS terpolymers. The analysis was comprised of two heating cycles and one cooling cycle. Heating cycles began at -20 °C and went to 180 °C at a rate of 20 °C min<sup>-1</sup>. The cooling cycle began at 180 °C and went to -20 °C at a rate of 20 °C min<sup>-1</sup>. The measurements were done in an aluminum *t-zero* pan and were calibrated to an empty aluminum *t-zero* pan.

# 2.2.3.6. Rheology

Sample discs (~0.7g) of MA/AN copolymer and MA/AN/PAS terpolymer were prepared in a Carver Model 3857 hot press at 200°C. The discs were 1 mm in thickness and 25 mm in diameter. The discs were prepared between teflon plates at a clamping force of 12 tons. The pressing time was 10 minutes with quick releases at 3 minute intervals to remove any gas bubbles. The discs were cooled to room temperature at rate of about 35°C min<sup>-1</sup>.

Rheology measurements were performed on the prepared discs using an Anton Parr MCR 302 parallel plate rheometer using a frequency sweep at 200°C for MA/AN copolymers and MA/AN/PAS terpolymers discs under nitrogen. The strain was kept below 10% to stay within the linear viscoelastic regime and the angular frequency was varied between 0.01 and 300 s<sup>-1</sup>.

### 2.2.3.7. Extrusion and Scanning Electron Microscopy (SEM)

MA/AN/PAS terpolymers and MA/AN copolymers were melt blended with PE-g-MA in a Haake MiniLab II twin screw extruder in counter-rotating mode. A 70:30 mass ratio of PE-g-MA;co/terpolymer was used. The mixture was mechanically mixed by hand with a spatula prior to feeding it to the extruder. The operating conditions were set at 200°C at 50 rpm. The material was passed through the extruder a total of three passes before the product was collected (a total residence time of about 2-3 minutes). The product was quenched in liquid nitrogen within the first 10-20 seconds as it exited the extruder (after the third pass) to freeze the morphology. A sample of the product was then freeze-fractured and was put into a beaker of DMF (and stirred) for a minimum of 36 hours to ensure the dispersed phase was etched. The samples were dried and glued onto aluminum stubs with cyanoacrylate glue. The samples were then coated with a 2 nm layer of platinum to make the sample conductive for SEM analysis. A FEI Inspect F-50 FE SEM was used to analyze the surfaces of the extruded polymers at 1-2kV (significant charging occurred at higher settings). Finally, ImageJ software was used analyze the images. A minimum of 350 particles were used in determining the volume to surface area diameter ( $\langle D \rangle_{vs}$ ). The particles were manually picked out using the ROI manager rather than letting the software automatically detect particles. The background was subtracted before adjusting the threshold.

Because a 2-D surface of a 3-D sample is analyzed by SEM, the calculated diameter does not represent the true size of the domains. Stereological corrections can be done and previous studies have shown that an increase of 10-15% in domain sizes is typical.<sup>[5, 6, 9]</sup>  $\langle D \rangle_{\rm vs}$  was calculated by using Equation 3 found in the literature.<sup>[6]</sup>

$$_{VS} = \frac{\sum_{i=1}^{k} n_i D_i^3}{\sum_{i=1}^{k} n_i D_i^2}$$
(3)

where  $n_i$  is the number of particles and  $D_i$  is the diameter of the spherical particle extracted from its area.  $\langle D \rangle_{vs}$  estimates the ratio of volume to interfacial area. It is an indicator of how well the immiscible polymers are interacting at the interface. Smaller values of  $\langle D \rangle_{vs}$  indicate that the polymers in the blend are interacting strongly with one another and vice versa.  $\langle D \rangle_{vs}$  was calculated by assuming that the particles were spherical (in 3-D) and circular (in 2-D) so that their diameter could be extracted from their area.

# 2.3. Results & Discussion

# 2.3.1. Synthesis of Methyl Acrylate/Acrylonitrile Copolymers

MA was copolymerized with AN with AIBN as the initiator. These copolymers were previously studied for carbon fiber applications.<sup>[40, 41]</sup> The goal for our synthesis was to make copolymers (and ideally terpolymers with a reactive functionality such as an amine) that had a sufficiently high AN composition to be useful as a barrier material (typically ~ 40-50 mol% AN based on SAN copolymers)<sup>[37]</sup> and to use the binary system as the model non-reactive polymer for blending studies with PE-g-MA. Feed compositions were thus varied to cover a broad composition range as seen in Table 1.

	Feed Composition				Characterization			
Experiment I.D.	[AIBN] x10 <sup>2</sup> (M)	[MA] (M) <sup>a</sup>	[AN] (M) <sup>a</sup>	fMA,0 <sup>b</sup>	<b>F</b> MA <sup>c</sup>	Mn (kg mol <sup>-1</sup> ) <sup>d</sup>	Đď	
MA_AN_Exp1	3.88	3.33	3.50	0.48	0.51	90.9	2.71	
MA_AN_Exp2	3.73	1.58	5.03	0.24	0.14	29.3	2.54	
MA_AN_Exp3	3.36	4.84	1.48	0.77	0.71	52.0	4.23	
MA_AN_Exp4	3.57	4.27	1.83	0.70	0.66	61.2	2.46	

*Table 1*: Characterization of MA/AN Copolymers Synthesized by Conventional Radical Polymerization.

<sup>a</sup> 50:50 wt% monomers to solvent ratio<sup>; b</sup> Initial feed composition of MA; <sup>c</sup> Copolymer composition of MA calculated using <sup>1</sup>H NMR; <sup>d</sup> Obtained by GPC using DMF as mobile solvent with respect to PMMA standards at 50°C

Table 1 shows that varying the feed compositions still results in significant AN incorporation. The compositions were calculated using <sup>1</sup>H NMR with a typical spectrum shown in Figure 1 as an example.



*Figure 1*: <sup>1</sup>HNMR spectrum of MA\_AN\_Exp1.

The spectrum shows residual DMSO-d<sub>5</sub> at 2.5ppm indicating that the solvent used was not 100% pure.<sup>[43]</sup> Furthermore, the appearance of the water peak at 3.3 ppm has two possible sources. It is either residual water that did not evaporate during the drying step or it is residual water in the solvent itself.<sup>[43]</sup>

The compositions were calculated by examining the peak areas of the methyl protons of MA labelled in Figure 1 as "A", and the backbone protons labelled as "B" using the following previously published method:<sup>[41]</sup>

n = moles of MA present in copolymer=
$$\frac{A}{3}$$

m = moles of AN present in copolymer=
$$\frac{B}{2} - n$$

Molar compositions of MA and AN in the copolymer,  $F_{MA}$  and  $F_{AN}$ , respectively, were calculated using the following.

$$F_{MA} = \frac{n}{n+m}$$

 $F_{AN}=1-F_{MA}$ .

Table 1 shows that the copolymer compositions are similar to the feed compositions. The reported reactivity ratios are  $r_{AN} = 1.29$  and  $r_{MA} = 0.96$  implying that a statistically random copolymer was likely, which seems to be in fair agreement with our results.<sup>[40]</sup> With the incorporation of AN confirmed, terpolymerizations were attempted to also incorporate functional amine pendant groups into the copolymer, which is necessary for reactive compatibilization into the PE matrix.

# 2.3.2. Synthesis of (MA/AN/PAS) Terpolymers

Terpolymers using a feed of MA, AN and PAS were polymerized with AIBN as the initiator. Others have polymerized PAS in its protected form by ionic polymerization, anionic polymerization, conventional radical polymerization and even by atom transfer radical polymerization.<sup>[44-46]</sup> According to these previous studies, there is a possible resonance structure where the electron density from the amino group shifts through the aromatic group, leaving a negative charge on the  $\alpha$ -carbon of the vinyl group.<sup>[45-46]</sup> This is the reason why polymerizing PAS in its unprotected form is difficult to a significant conversion. A previous study however, illustrated that PAS in its protected acrylamide form incorporated much less into a copolymer using NMP compared to the non-protected form.<sup>[47]</sup> PAS was chosen as it can couple to anhydrides, acids and epoxies.<sup>[12]</sup> The different formulations are presented below in Table 2.

Experiment I.D.	[AIBN] x10 <sup>2</sup>	[MA]	[AN]	[PAS]	f <sub>MA,0</sub>	fan,0
	( <b>M</b> )	( <b>M</b> ) <sup>a</sup>	( <b>M</b> ) <sup>a</sup>	(M) <sup>a</sup>		
MA_AN_PAS Exp1	3.23	3.54	1.25	0.25	0.70	0.25
MA_AN_PAS Exp2	4.02	4.14	0.59	0.25	0.83	0.12
MA_AN_PAS Exp3	5.29	3.15	2.18	0.31	0.56	0.39
MA_AN_PAS Exp4	3.03	3.56	1.26	0.26	0.70	0.25
MA_AN_PAS Exp5	2.90	3.94	0.81	0.28	0.78	0.16
MA_AN_PAS Exp6	2.95	3.99	0.47	0.28	0.84	0.10
MA_AN_PAS Exp7	3.35	3.67	1.30	0.19	0.71	0.25

Table 2: Reaction Formulations for MA/AN/PAS Terpolymerizations

<sup>a</sup> 50:50 wt% monomers to solvent ratio

Compositions were limited to contain a fairly low concentration of PAS (5-10 mol%) since it is required only for compatibilization during blending while AN composition should be sufficient to be an effective barrier material. Excessive AN incorporation may make processing difficult (which is why MA was incorporated).<sup>[20, 48-51]</sup> Qualitative analysis using ATR-FTIR was done to confirm the presence of the amino group from PAS. Figure 2 is a typical spectrum of a terpolymer compared to binary copolymer without PAS.



*Figure 2*: Superimposed ART-FTIR spectrum of MA/AN copolymer (blue) and MA/AN/PAS terpolymer (red).

In Figure 2, the overlapping spectra of the copolymer and terpolymers are identical except for two peaks. The peak at about  $v = 1500 \text{ cm}^{-1}$  represents the N-H bend and the doublet at  $v = 3400 \text{ cm}^{-1}$  represents the signature N-H stretch of the primary amine.<sup>[42]</sup> Figure 3 shows no residual PAS monomer (no vinyl peaks) and therefore, it can be concluded that PAS was incorporated into the terpolymer. <sup>1</sup>H NMR was then used to quantitatively estimate the terpolymer composition.



The polymer compositions were determined examining the peak for the styrenic protons of PAS (A at  $\delta = 6.5$ -7 ppm), along with the peak for the methyl protons of MA (B at  $\delta = 3.6$  ppm) and the backbone protons (D at  $\delta = 1.2$  -2.2 ppm). The approach is outlined below:

X = moles of PAS in terpolymer = 
$$\frac{A}{4}$$

Y = moles of MA in terpolymer =  $\frac{B}{3}$ 

Z = moles of AN in terpolymer = 
$$\frac{D}{3} - X - Y$$

It should be noted that the doublet at  $\sim$  3 ppm represents the solvent, DMF. The terpolymers had to be washed several times to reduce the solvent trapped in the resin. The characterization of all of the terpolymers is shown in Table 3.

Experiment I.D.	F <sub>MA</sub> <sup>a</sup>	F <sub>AN</sub> <sup>a</sup>	Mn (kg mol <sup>-1</sup> ) <sup>b</sup>	Ð Þ	Tg (°C)
MA_AN_PAS Exp1	0.68	0.24	114.1	2.14	11.2
MA_AN_PAS Exp2	0.67	0.27	117.1	1.95	4.2
MA_AN_PAS Exp3	0.44	0.52	66.9	2.23	28.3
MA_AN_PAS Exp4	0.70	0.27	65.8	2.58	7.0
MA_AN_PAS Exp5	0.47	0.39	162.5	1.83	21.0
MA_AN_PAS Exp6	0.69	0.20	133.0	2.09	10.2
MA_AN_PAS Exp7	0.63	0.29	102.4	2.51	9.0

Table 3: Molecular Weight Characterization of MA/AN/PAS Terpolymers

<sup>a</sup> Obtained by <sup>1</sup>HNMR; <sup>b</sup> Obtained by GPC using DMF as the mobile phase relative to PMMA standards at 50°C

The AN content of the terpolymers varied from 27-52 mol % and the PAS content varied from 3-14 mol%. Furthermore, there are approximately 30-290 amino groups per polymer chain. In most cases the polymer compositions are relatively consistent when similar feed compositions are used. The slight differences in polymer compositions can be attributed to the polymers having different conversions (different M<sub>n</sub>), possibly different heating history and discrepancies in processing the <sup>1</sup>H NMR spectra for analysis (different phasing and baseline adjustment, for example). Therefore, repeatability does not seem to be an issue despite the high reactivity of PAS. In summary, the functional monomer can be incorporated in relatively low concentrations into the terpolymer (3-14 mol%, 30-290 amino groups per chain).

TGA was done to determine the degradation profiles of the terpolymers. Figure 4 shows a typical spectrum.



*Figure 4*: Thermal degradation of an MA/AN/PAS terpolymer under atmospheric conditions.

There is an immediate mass loss at about 50°C-100°C, which can be attributed to the moisture absorbed by the polymer from the humidity in the air. There is further weight loss up to 140°C, which is the residual DMF solvent that was not removed during the vacuum drying stage. For further evidence of this, the <sup>1</sup>H NMR does show DMF peaks at about  $\delta = 2.8$ -3 ppm. Previous work has indicated poly(MA) to begin to slowly degrade at about 200°C under oxygen and vacuum conditions, so it is was not expected to degrade much before 200°C.<sup>[52]</sup> From 300°C and onwards, degradation of MA and AN in the polymer is most likely occurring,<sup>[52, 53]</sup> with most of PAS in the polymer not being degraded at all as it is reported to degrade after 500-550°C.<sup>[54]</sup> Therefore, the upper limit that these terpolymers can be extruded at without significant decomposition occurring is about 250-275°C. T<sub>g</sub>s were also analyzed using DSC (see Table 3). The analysis showed that the T<sub>g</sub> of the terpolymers varied between 4-28 °C. This was expected as PMA the major component, has a T<sub>g</sub> of 8 °C.<sup>[55]</sup> It is also worth noting that the higher the MA composition, the lower the T<sub>g</sub> as expected.

# 2.3.3. Extrusion & SEM Analysis

Blends of the amine functionalized terpolymer and the non-functional MA/AN copolymer were prepared with PE-g-MA at 200°C at 30 wt% of the dispersed phase.

Blend miscibility can be determined theoretically by evaluating a blend pair's interaction parameter ( $\chi_{blend}$ ), which can be calculated by the Equation 4.<sup>[56]</sup>

$$\chi_{blend} = \chi_{A/B} = \frac{v}{RT} * (\delta_A - \delta_B)^2$$
(4)

where  $\chi_{blend}$  is the interaction parameter between PE-g-MA (A) and the co/terpolymer (B), R is the gas constant, T is absolute temperature of the blend, *v* is the molar volume and  $\delta$  is the Hildebrand solubility parameter.  $\chi_{blend}$  for both the reactive and non-reactive blend is shown in Table 4.

Blend	δΑ	δв	Xblend
	$(cal^{1/2}cm^{-3/2})$	$(cal^{1/2}cm^{-3/2})$	
PE-g-MA & MA/AN	7.90	10.51	0.60
PE-g-MA & MA/AN/PAS	7.90	10.00	0.41

Table 4: Interaction Parameters of the Blending Pairs

 $\chi_{blend}$  for both the non-reactive and reactive blends is quite high at approximately 0.4-0.6 indicating that the blends are indeed immiscible.<sup>[57]</sup> The molar mass of the polymer repeat unit was calculated (using the polymer compositions as the weights) approximately to be 83 g mol<sup>-1</sup> and 86 g mol<sup>-1</sup> for the non-reactive and reactive blends respectively. The density was also calculated using the polymer composition as weights and was 0.90 g ml<sup>-1</sup> and 0.91 g ml<sup>-1</sup> for the non-reactive and reactive blends respectively. The molar volumes were calculated from the mass of the repeat units and the densities. Furthermore,  $\delta$  was determined by using a weighted average (using the polymer compositions as the weights) of the solubility parameters found in the literature for the homopolymers.<sup>[56]</sup> The solubility parameter of PAS was not found in the literature so the group contribution method was used to estimate it according to the approach described by van Krevelen.<sup>[58]</sup>

Table 5 summarizes the blends studied. The matrix was PE-g-MA in all cases, and the dispersed phase consisted of varying levels of functional terpolymer (MA/AN/PAS\_Exp7) with a non-functional copolymer (MA/AN\_Exp4). The cases with 100% MA/AN/PAS\_Exp7 or with only MA/AN\_Exp4 were also done with the latter

serving as the non-reactive blend). Figure 5 shows the SEM images of the reactive and non-reactive blends.



*Figure 5*: (SEM images of A) 70wt% PE-g-MA, 30wt% MA/AN\_Exp4 after extrusion and freeze fracturing, B) 70wt% PE-g-MA, 15wt% MA/AN\_Exp4 and 15wt% MA/AN/PAS\_Exp7 after extrusion and freeze fracturing, C) 70wt% PE-g-MA, 30wt%

MA/AN/PAS\_Exp7 after extrusion and freeze fracturing. D) 70wt% PE-g-MA, 30wt% MA/AN\_Exp4 post-annealing E) 70wt% PE-g-MA, 15wt% MA/AN\_Exp4 copolymer and 15wt% MA/AN/PAS\_Exp7 post-annealing, F) 70wt% PE-g-MA, 30wt% MA/AN/PAS\_Exp7 post-annealing.

From Figure 5 a)-c), the non-reactive blend has much larger dispersed phase domains, compared to the reactive cases, being greater than 10  $\mu$ m. The particle size is nearly halved when the dispersed phase consists of 50:50 wt% MA/AN/PAS terpolymer: MA/AN copolymer. When the dispersed phase is solely the terpolymer, the particle size is 10 times smaller compared to the non-reactive case, being about 1.2  $\mu$ m. Thus, the effect of reaction was substantial. Furthermore,  $\langle D \rangle_{vs}$  can be used to estimate how much graft copolymer is formed at the interface provided that the blended polymers have a common solvent for GPC analysis.<sup>[10]</sup> The polymers studied do not have a common solvent so SEM was used to analyze the results.

		<b>Blend Ratio</b>			Characterization
SEM	PE-g-MA	MA/AN/PAS	MA/AN	Annealing	<d>vs</d>
Image	(wt%)	(wt%)	(wt%)	Conditions	(µm)
А	70	0	30	None	12.5
В	70	15	15	None	4.6
С	70	30	0	None	1.2
D	70	0	30	20hrs at 150°C	14.1
Е	70	15	15	20hrs at 150°C	5.1
F	70	30	0	20hrs at 150°C	1.4

Seeing that  $\langle D \rangle_{vs}$  for the functionalized blends decreased relative to the nonfunctionalized blend, it suggests that morphology was stabilized due to the coupling reaction as was suggested by previous studies.<sup>[10, 20]</sup> Conversely, the small increase in  $\langle D \rangle_{vs}$  after annealing indicates that coalescence was very slow, and that slight variations in  $\langle D \rangle_{vs}$  were more likely to be caused by analysis of the particles rather than the process of coalescence itself.<sup>[10]</sup>

# 2.3.4 Rheology

Complex viscosity measurements versus frequency are shown in Figure 6.



*Figure* 6: Complex viscosity measurements of MA/AN (blue), MA/AN/PAS (orange) and PE-g-MA.

For the particular extruder used, the shear rate was approximated using the largest and smallest sections of the screws. The shear rates were approximated as 9 and 27 s<sup>-1</sup> at 50 rpm for the region with the shortest and widest gap distance, respectively by using the screw speed, channel depth and, screw diameter. Using the data obtained and data previously measured,<sup>[10]</sup> it can be seen that the viscosity ratio ( $\eta$ ) of co/terpolymer to PE-g-MA is approximately 0.3-0.6 respectively at the shear rates estimated.  $\eta$  of 1 theoretically minimizes the domain sizes.<sup>[10, 59-62]</sup> It is therefore possible that the minimum domain size was not achieved even though an effective reaction was used. Previous studies demonstrated that the amine-maleic anhydride coupling achieved a submicron domain size.<sup>[9, 63]</sup> While no indication of  $\eta$  was given, M<sub>n</sub> of the polymers used were similar size to the ones used in this study. Another study also showed that a submicron domain size could be achieved using the same reaction coupling.<sup>[5]</sup> It is therefore possible that the domain sizes could be decreased with a different setup or operating conditions.

# 2.4. Conclusion

In this study, AN-containing polymers with and without an amine functionality were synthesized and were melt blended with PE-g-MA, poly(ethylene) grafted with maleic anhydride. The domain size of the dispersed phase was  $1.2\mu m$  and  $12.5\mu m$  when functional MA/AN was and was not used respectively. Upon annealing, evidence of a slow coalescence rate was seen for all blends. It was concluded that the reaction coupling was responsible for the stable morphology and smaller domain sizes.

# 3. Reactive Compatibilization of Poly(styrene-ranacrylonitrile) (SAN)/ Poly(ethylene) Blends Through the Acid-Epoxy Reaction

# 3.1. Manuscript Preface

The amine-maleic anhydride reaction coupling showed that a stable morphology and nearly sub-micron domain sizes could be achieved. However, as it was previously mentioned, studies have obtained sub-micron domain sizes with this reaction coupling and so, further improvements in the results can be achieved. While the results are positive, PAS is an expensive monomer to use to obtain the amine functionality dispersed in a polymer. Therefore, a cheaper alternative for reactive compatibilization, the epoxy-carboxylic acid coupling was investigated to determine the domain sizes it can yield and compare it to the amine-anhydride coupling. The drawback to this cheaper option is that the kinetics of this coupling are about 10 times slower, which was previously reported.<sup>[11]</sup>

# **3.2. Manuscript Introduction**

PAN has been extensively studied and used for its very good barrier properties against gases such as oxygen and carbon dioxide.<sup>[35]</sup> Furthermore, in the food industry, it has been used to block the permeation of aromas and/or flavors in addition to hydrophobic compounds.<sup>[24]</sup> Its hydrophilic nature however, limits its barrier properties/absorption against water vapor.<sup>[24]</sup> One key limitation of PAN is its inability to be processed easily. The homopolymer degrades before it melts, making processing very difficult.<sup>[48-51]</sup> Therefore, many groups have focused their efforts into copolymerizing AN with different monomers.<sup>[24, 27, 40, 41, 49, 51, 64-66]</sup> While not all of the studies were done for the purpose of barrier materials, these studies suggest opportunities to use the barrier properties of AN in the form of a copolymer. Besides statistical copolymerization, block copolymers containing AN have been made.<sup>[21-23, 25, 26, 29, 30, 33, 67-69]</sup> The ability to polymerize acrylonitrile by radical polymerization techniques makes it an interesting polymer for barrier materials as the microstructure can be tuned in many possible ways. Also, additional properties can be further combined into the AN containing (co)polymers by

blending with other polymers. However, many cases have demonstrated the instability and/or large domains of the dispersed phase when blending either homopolymers, copolymers, or a mixture of both.<sup>[1, 3, 6, 9, 10, 70-72]</sup> While much research has been done on adding compatibilizers,<sup>[3, 5, 51, 70-79]</sup> most industrial blends are reactively compatibilized and we have focused on using this latter method, like many others.<sup>[8-10, 63, 76, 80-84]</sup> Our focus has been to synthesize AN-rich copolymers by NMP, which can be further tuned/manipulated by reactive blending. We have focused on amine functional SAN copolymers blended with poly(ethylene) grafted with maleic anhydride, which revealed a significant decrease in domain size and a stable morphology.<sup>[9]</sup> In this work, we investigate SAN copolymers with an acid functionality (via incorporation of acrylic acid (AA)) to use with poly(ethylene) grafted glycidyl methacrylate (PE-g-GMA). The SAN and acid functional terpolymer S/AN/AA system were first investigated by conventional radical polymerization first to understand the copolymerization system, incorporation of functional groups and to test for reactive compatibilization. Afterwards, a more controlled synthesis technique, NMP, was used to make the SAN copolymers and by the means of chain extension, incorporate the acid groups on one end of the chain. In contrast to earlier work, where a single functionality was located terminally as a single unit, this study attempts to place several acid groups throughout the SAN copolymer. Functional groups located terminally are more reactive than ones placed randomly in the polymer.<sup>[85]</sup> With much more reaction sites, the probability of the reaction is expected to increase, leading to more graft copolymer being formed *in situ* and better stabilization of the dispersed SAN phase.

# **3.3. Experimental Section**

#### 3.3.1. Materials

Styrene (99%), *tert*-butyl acrylate (99%, t-BA), and AN (99%) were obtained from Sigma-Aldrich and purified by passing them through a column of aluminium oxide (Brockmann, Type 1, 150 mesh, Sigma Aldrich) and calcium hydride (90-95% reagent grade, Sigma Aldrich) which were mixed at a mass ratio of 5:0.25 respectively and stored under a head of nitrogen prior to use. AIBN was obtained from Dupont, dissolved in methanol, and re-crystallized before use. AA (99%), trifluroacetic acid (99%), CDCl<sub>3</sub> (99.8 atom%), and DMSO-d<sub>6</sub> (99.96 atom%) were obtained from Sigma-Aldrich and were used as received. BlocBuilder (BB) was provided by Arkema and was transformed to a succinimidyl ester functionalized form of BB known as NHS-BlocBuilder (NHS-BB) using an established protocol.<sup>[86]</sup> 1,4-dioxane (99%) and n-hexanes (98.5%) were obtained from Fisher and were used as received. Finally, HPLC grade tetrahydrofuran (THF, 99.9%) was obtained from Fisher as the mobile phase for GPC and was used as received. PE grafted with glycidyl methacrylate (PE-g-GMA) with a melt flow index of 4.88g (10 min)<sup>-1</sup> at 190°C, density of 0.94 g ml<sup>-1</sup>, and melting point of 106°C was obtained from Arkema and used as received. Other chemicals used for cleaning purposes such as acetone (99.5%) and methanol (99.8%) were obtained from Fisher and used as received.

#### 3.3.2. Methods

#### 3.3.2.1 Synthesis of Styrene/Acrylonitrile Copolymers

Styrene (S) and AN were copolymerized via conventional radical polymerization using 1,4-dioxane as the solvent in a three necked 50 ml reactor with a nitrogen purge, thermocouple/thermowell and, reflux condenser. The reactor sat on top of a stirring plate and heating mantle. Appropriate amounts of the AIBN initiator, S, AN, and 1-4 dioxane were weighed and poured into the reactor, with the formulation for S\_AN\_Exp1 (See Table 1) shown as an example. For this particular experiment, 0.1217 g (0.740 mmol) AIBN, 4.8471 g (46.54 mmol) S, 1.50 g (28.27 mmol) AN, and 6.7582 g (76.70 mmol) 1,4-dioxane were measured and poured into the reactor. The reactor solution was purged with nitrogen for at least 30 minutes prior to starting the reaction and maintained throughout the reaction. The set point of the reactor was set to 70°C to ensure significant decomposition of the initiator.<sup>[39]</sup> The chiller was set to 4°C. Once the reaction was complete (reaction time of 3-4 hours), the polymer was precipitated the first time in about 200 ml of hexane, re-dissolved in a minimum amount of solvent, and precipitated a second time in about 50ml of hexane to further remove unreacted monomers. Finally, the polymer was vacuum dried in an oven at 50-60°C overnight. This particular copolymer had a  $M_n$  of 62.7kg mol<sup>-1</sup> and  $\tilde{D}$  of 1.76 relative to PMMA standards at 40°C in THF. The copolymer had a S molar composition of 0.63 which was determined by <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 6.9-7.5 (m, 5H, Ar H), 1.2-2 (m, 2H, CH<sub>2</sub>).

29

#### 3.3.2.2. Synthesis of Styrene/Acrylonitrile/Acrylic Acid Terpolymers

S, AN and, AA were polymerized via conventional radical polymerization using 1,4dioxane as the solvent in a three necked 50ml reactor with a nitrogen purge, thermocouple/thermowell and, reflux condenser. The reactor sat on top of a stirring plate and heating mantle. Appropriate amounts of AIBN, S, AN, AA, and, 1,4- dioxane, were weighed and poured into the reactor, with the formulation for S AN AA 1 (see Table 2) shown as an example. For this particular experiment, 0.10537 g (0.64 mmol) AIBN, 5.4704 g (52.52 mmol) S, 2.0955 g (39.49 mmol) AN, 1.945 g (26.99 mmol) AA, and, 10.0471 g (114.03 mmol) 1,4-dioxane were poured into the reactor. The reactor solution was purged with nitrogen for at least 30 minutes prior to starting the reaction. The set point of the reaction was set to 70°C. The chiller was set to 4°C. After heating at 70 °C for 2-3 hours, the polymer was precipitated the first time in about 200 ml of hexane, redissolved in a minimum amount of solvent and, precipitated a second time in about 50 ml of hexane to remove unreacted monomers. Finally, the polymer was vacuum dried in the oven at 50-60°C overnight. This particular copolymer had a  $M_n$  of 42.5 kg mol<sup>-1</sup> and  $\tilde{D}$  of 1.65 relative to PMMA standards at 40 °C in THF. The terpolymer had S and AN molar composition of 0.26 and 0.67 respectively, which was determined by <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 6.9-7.5 (m, 5H, Ar H), 0.8-2 (m, 3H, CH-CH<sub>2</sub>), 3.7 (s, 3H, O-CH<sub>3</sub>).

#### 3.3.2.3 Synthesis of SAN Copolymers by NMP

S and AN were copolymerized via NMP using 1,4-dioxane as the solvent in a three necked 50ml reactor with a nitrogen purge, thermocouple/thermowell and, reflux condenser. The reactor sat on top of a stirring plate and heating mantle. Appropriate amounts of NHS-BB, S, AN, and, 1,4-dioxane were measured out and poured into the reactor, with the formulation for S\_AN\_NHS-BB-1 (see Table 5) shown as an example. For this particular experiment, 0.1805g (0.38mmol) NHS-BB, 9.4527g (90.76 mmol) S, 0.5698g (10.74mmol) AN, and 10.1038g (114.67mmol) 1,4-dioxane were measured and poured into the reactor. The reactor solution was purged with nitrogen for at least 30 minutes prior to starting the reaction and maintained throughout the reaction. The set point of the reaction was set to 115°C. The chiller was set to 4°C. Once the reaction was

complete after 4-5 hours, the polymer was precipitated the first time in about 200ml of hexane, re-dissolved in a minimum amount of solvent, and precipitated a second time in about 50ml of hexane to remove unreacted monomers. Finally, the polymer was vacuum dried in the oven at 50-60°C overnight. This particular copolymer had  $M_n$  of 7.0 kg mol<sup>-1</sup> and  $\tilde{D}$  of 1.18 relative to PMMA standards at 40°C. The copolymer had S composition of 0.93 and a conversion of 0.38, which were both determined by <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 6.9-7.5 (m, 5H, Ar H), 1.2-2 (m, 2H, CH<sub>2</sub>).

## 3.3.2.4 Chain Extension with Styrene/Tert-butyl acrylate by NMP

Chain extension was done on the final SAN copolymer synthesized (with a S molar composition of 0.62, see Table 6) in 1,4-dioxane with the same setup described for the other NMP experiments. A S/t-BA mixture at a mol ratio of 50/50 was mixed in with the SAN copolymer and 1,4-dioxane. The macro-initiator (SAN) was rich in AN to give the first block significant barrier properties (typical barrier materials have 40-50mol% AN).<sup>[37]</sup> The chain extension was done at 100°C. Once the product was purified by air drying (due to difficulty in precipitation) and vacuum dried at 60°C, the t-BA groups were converted to acid groups (SAN-b-SAA) using a previously used protocol with trifluoroacetic acid.<sup>[87]</sup> The SAN copolymer had a  $M_n$  of 10 kg mol<sup>-1</sup> and Đ of 1.23, and the block copolymer had a  $M_n$  of 36.6kg mol<sup>-1</sup> and Đ of 1.34 relative to PMMA standards at 40°C in THF.

#### **3.3.3. Characterization**

# 3.3.3.1. Proton Nuclear Magnetic Resonance (<sup>1</sup>H NMR)

A Varian 300MHz was used to characterize the composition of all polymers by <sup>1</sup>H NMR. The peaks of interest for SAN copolymers were at ~ $\delta$ =6.5-7ppm for the five styrenic protons and  $\delta$ =1.2-2ppm for the backbone protons. The peaks of interest for the S/AN/AA terpolymers and SAN-b-SAA were at  $\delta$  = 6.5-7ppm for the five styrenic protons,  $\delta$  = 0.8-2ppm for the backbone protons, and  $\delta$  = 3.6ppm for methyl protons of AA which had been previously methylated with a trimethylsilyldiazomethane solution.<sup>[87]</sup> For all polymers, the AN content was calculated using the backbone CH<sub>2</sub> protons rather than solely the proton on the alpha carbon.<sup>[40, 41]</sup> For kinetic studies, conversion was calculated using <sup>1</sup>H NMR. Specifically, the vinyl protons were used for each monomer, none of which overlapped. DMSO-d<sub>6</sub> was used as the solvent for <sup>1</sup>H NMR to calculate conversion for the kinetic studies. It was used instead of CDCl<sub>3</sub> to avoid interference with the signal due to S. CDCl<sub>3</sub> was used to determine polymer compositions.

### 3.3.3.2. Gel Permeation Chromatography (GPC)

All polymers were analyzed using a Waters Breeze system equipped with three Styragel columns (molecular weight ranges: HR1:  $10^2$ - $5x10^3$  g mol<sup>-1</sup>, HR2:  $5x10^2$ - $2x10^4$  g mol<sup>-1</sup>, HR3:  $5x10^3$ - $6x10^5$  g mol<sup>-1</sup>) and a guard column. The flow rate was 0.3 ml min<sup>-1</sup>. The GPC was equipped with a differential refractive index (RI 2410) detector. All polymers were analyzed with THF as the mobile phase at a column temperature of 40°C. The molecular weights were measured relative to PMMA standards. Prior to analysis, polymer samples containing AA were methylated with a trimethylsilyldiazomethane solution (2M in hexanes) to prevent sticking of the acid groups onto the column.<sup>[87]</sup>

#### 3.3.3.3. <u>Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy</u>

A Perkin-Elmer spectrum TWO with UATR accessory (also from Perkin-Elmer) and diamond as the ATR crystal was used to qualitatively analyze SAN copolymers, S/AN/AA terpolymers, and the chain extension. The peak of interest for SAN copolymers was v = 2200 cm<sup>-1</sup> for the nitrile stretch for AN.<sup>[42]</sup> The peaks of interest for S/AN/AA terpolymers and SAN-b-SAA were at v = 1600-1800 cm<sup>-1</sup> for the carbonyl stretch of AA, v = 2200 cm<sup>-1</sup> for the nitrile stretch for AN and v = 3000 cm<sup>-1</sup> for the O-H stretch of the acid to ensure that the carbonyl peak did not represent unconverted/unreacted t-BA (further evidence of this was obtained from the <sup>1</sup>H NMR spectrum).<sup>[42]</sup>

## 3.3.3.4. Thermal Gravimetric Analysis (TGA)

A TGA Q500 from TA Instruments was used to determine the minimum degradation temperature and degradation profiles of the S/AN/AA terpolymers. The analysis began at ambient temperature (35-40°C) and went to 550°C at a heating rate of 10°C min<sup>-1</sup>. The analysis was done under oxygen rather than nitrogen to simulate the environment in an extruder.

#### 3.3.3.5. Differential Scanning Calorimetry (DSC)

A DSC Q2000 from TA Instruments was used to approximate the  $T_g$  of the S/AN/AA terpolymers. The analysis for S/AN/AA terpolymers was comprised of two heating cycles and one cooling cycle. Heating began at -20°C and went to 160°C at a rate of 20°C min<sup>-1</sup>. The cooling cycle began at 160°C and went to -20°C at a rate of 20°C min<sup>-1</sup>. The measurements were done in an aluminium *t-zero* pan and were calibrated with an empty aluminium *t-zero* pan.

#### 3.3.3.6. Extrusion and Scanning Electron Microscopy (SEM)

SAN copolymers and SAN-b-SAA were each melt blended with PE-g-GMA in a Haake MiniLab II twin screw extruder in counter-rotating mode. A 70:30 mass ratio of PE-g-GMA:polymer was used. The mixture was manually mixed with a spatula prior to feeding it to the extruder. The operating conditions for the extruder were 160°C at 50 rpm. The material was passed through the extruder a total of three time before the product was collected (a total residence time of 2-3 minutes). The product was quenched in liquid nitrogen within the first 10-20 seconds as it exited on the third pass to preserve the morphology. A sample of the product was freeze-fractured and was put into a beaker of THF (and stirred) for a minimum of a 24 hours to ensure the dispersed phase was etched out. The samples were dried and glued onto aluminium stubs with cyanoacrylate glue. They were then coated with a 2 nm layer of platinum to make the sample conductive for SEM analysis. A FEI Inspect F-50 FE SEM was used to analyze the surfaces of the extruded polymers at 1-2kV (significant charging occurred at higher settings). Finally, ImageJ was used to analyze the dispersed phase size. A minimum of 350 particles were used in determining the average volume to surface area diameter  $\langle D \rangle_{\rm s}$ . The particles were manually picked out using the ROI manager rather than letting the software automatically detect particles. The background was subtracted before adjusting the threshold.  $\langle D \rangle_{s}$  of each blend before and after annealing was calculated.  $\langle D \rangle_{s}$  was calculated by using the Equation 5 found in the literature.<sup>[5]</sup>

$$< D >_{VS} = \frac{\sum_{i=1}^{k} n_i D_i^3}{\sum_{i=1}^{k} n_i D_i^2}$$
 (5)

33

where *n* is the number of particles and *D* is the diameter of the assumed spherical particle.  $\langle D \rangle_{vs}$  was calculated by assuming that the particles were spherical (in 3-D) and circular (in 2-D) so that their diameter could be extracted from their area.

# 3.3.3.7. <u>Rheology</u>

Sample discs (~0.7 g) of PE-g-GMA, SAN copolymer and SAN-b-SAA were prepared in a Carver Model 3857 hot press at 200°C. The discs were 1 mm in thickness and 25 mm in diameter. The discs were prepared between poly(tetrafluoroethylene) plates at a clamping force of 12 tons. The pressing time was 30 minutes for PE-g-GMA with quick releases at 10 minute intervals to remove any air bubbles. The pressing time for the remaining samples was 10 minutes with quick releases at 3 minute intervals. The discs were cooled to room temperature at a rate of about 35 °C min<sup>-1</sup>. Rheology measurements were performed on the prepared discs using an Anton Parr MCR 302 parallel plate rheometer using a frequency sweep at 160°C under nitrogen. The strain was kept below 10% to stay within the linear viscoelastic regime and the angular frequency was varied between 0.01 and 300 s<sup>-1</sup>.

# **3.4. Results & Discussion**

### 3.4.1. Synthesis of Styrene/Acrylonitrile Copolymers

S was copolymerized with AN using conventional radical polymerization with AIBN as the initiator. The objective was to make copolymers with a sufficiently high AN content for barrier applications so feed compositions were varied to cover a broad range and characterize its incorporation into the copolymers. The data is presented in Table 1 with Figure 1 as a typical example of the <sup>1</sup>H NMR spectra.

	Feed Composition					Characterizat	ion
Experiment I.D	[AIBN] x10 <sup>2</sup> (M)	[S] (M) <sup>a</sup>	[AN] (M) <sup>a</sup>	fs,0 <sup>b</sup>	Fs <sup>c</sup>	Mn (kg mol <sup>-1</sup> ) <sup>d</sup>	Ðď
S_AN_Exp1	5.40	3.39	2.06	0.62	0.62	62.7	1.76
S_AN_Exp2	4.48	3.93	1.40	0.74	0.76	34.5	1.80
S_AN_Exp3	3.32	4.03	0.59	0.87	0.85	35.2	1.72
S_AN_Exp4	3.64	2.08	4.58	0.31	0.52		

*Table 1*: Characterization of non-reactive SAN copolymers synthesized by conventional radical polymerization

<sup>a</sup> 50:50 wt% monomers to solvent ratio; <sup>b</sup> initial composition of styrene in the monomer mixture; <sup>c</sup> Styrene mol fraction in the copolymer (calculated using <sup>1</sup>H NMR); <sup>d</sup> Obtained by GPC using THF as the mobile phase with respect to PMMA standards at 40°C



*Figure 1*: <sup>1</sup>H NMR spectrum of S\_AN\_Exp1.

The compositions were calculated by examining the peak areas for the styrenic protons of S labelled in Figure 1 as "B", and the backbone protons labelled as "A" and using the following previously published method:<sup>[41]</sup>

n=moles of S present in copolymer= $\frac{B}{5}$ m=moles of AN present in copolymer= $\frac{A}{2} - n$ 

 $F_{S}$  and  $F_{AN}$  were calculated using:

$$F_S = \frac{n}{n+m}$$

Table 1 shows that the azeotropic composition (i.e. when initial monomer feed composition is equal to copolymer composition) for this system was approximately  $f_s=0.62$ , which is very similar to previous studies.<sup>[31, 32, 88]</sup> Furthermore, previous studies have pointed out that as  $f_{AN}$  approaches unity,  $F_s$  approaches approximately 0.5 (an alternating copolymer), which can also be seen from the data.<sup>[31,32,88]</sup>. Table 1 also shows that varying the feed composition still results in significant AN incorporation, which is in agreement with earlier studies.<sup>[32, 66]</sup> With the confirmation that AN can be incorporated over a wide compositional range, the incorporation of a reactive functionality (carboxylic acid) was attempted via terpolymerization of S, AN and AA.

# 3.4.2. Synthesis of Styrene/Acrylonitrile/Acrylic Acid Terpolymers

With the incorporation of AN confirmed, further investigations were done to try to incorporate a carboxylic acid in a terpolymer. Initially, methacrylic acid was attempted to be incorporated with S and AN, but its incorporation was extremely low (<1% mol). It was hypothesized that the methyl group on the vinyl group decreased its reactivity due to steric hinderance<sup>[89]</sup> AA was instead attempted. AA was incorporated into a terpolymer previously with S and AN.<sup>[90]</sup> Table 2 and 3 show the different feed compositions that were tested to assess how to obtain a significant AN content while at the same time to obtain a significant acid content to aid in reactive compatibilization (~ 5-10 mol%). Figure 2 shows a typical <sup>1</sup>H NMR spectrum of these terpolymers.

Experiment	[AIBN] x10 <sup>2</sup>	[S]	[AN]	[AA]	fs,0	faa,0
I.D.	( <b>M</b> )	<b>(M)</b> <sup>a</sup>	( <b>M</b> ) <sup>a</sup>	( <b>M</b> ) <sup>a</sup>		
S_AN_AA_1	3.18	2.60	1.96	1.34	0.44	0.23
S_AN_AA_2	3.03	3.41	0.90	1.16	0.62	0.21
S_AN_AA_3	3.22	2.68	2.20	1.20	0.44	0.20
S_AN_AA_4	3.23	3.51	0.84	1.09	0.65	0.20
S_AN_AA_5	3.42	3.82	0.30	1.03	0.74	0.20
S_AN_AA_6	3.23	3.45	0.77	1.23	0.41	0.25
S_AN_AA_7	3.33	3.49	0.83	1.08	0.65	0.20
S_AN_AA_8	3.27	3.81	0.39	0.91	0.75	0.18
S_AN_AA_9	3.60	2.61	0.92	2.36	0.44	0.40
S_AN_AA_10	3.78	3.10	0.93	1.66	0.55	0.30

*Table* 2: Formulations for the Synthesis of Styrene/Acrylonitrile/Acrylic Acid Terpolymers by Conventional Radical Polymerization.

<sup>a</sup> 50:50 wt% monomers to solvent ratio

	Feed Cor	nposition	Terpolymer Composition		TerpolymerMoleculaCompositionDistri		Molecular V Distribut	Veight ion
Experiment I.D.	f <sub>s,0</sub>	f <sub>AA,0</sub>	Fs <sup>a</sup>	FAA <sup>a</sup>	Mn (kg mol <sup>-1</sup> ) <sup>b</sup>	Đb		
S_AN_AA_1	0.44	0.23	0.26	0.07	42.5	1.65		
S_AN_AA_2	0.62	0.21	0.44	0.04	34.7	1.43		
S_AN_AA_3	0.44	0.20	0.21	0.04	52.0	1.58		
S_AN_AA_4	0.65	0.20	0.44	0.04	63.0	1.92		
S_AN_AA_5	0.74	0.20	0.43	0.04	55.4	1.71		
S_AN_AA_6	0.41	0.25	0.49	0.18	70.0	1.92		
S_AN_AA_7	0.65	0.20	0.35	0.08	15.6	1.56		
S_AN_AA_8	0.75	0.18	0.67	0.25	60.1	1.84		
S_AN_AA_9	0.44	0.40	0.67	0.26	19.4	1.37		
S_AN_AA_10	0.55	0.30	0.75	0.04	74.6	1.81		

*Table* 3: Characterization of Styrene/Acrylonitrile/Acrylic Acid Terpolymers Synthesized by Conventional Radical Polymerization

<sup>a</sup> Copolymer composition calculated using <sup>1</sup>H NMR; <sup>b</sup> Obtained by GPC using THF as the mobile with respect to PMMA standards at 40°C



Figure 2: <sup>1</sup>H NMR spectrum of S\_AN\_AA\_9

The polymer compositions were determined by examining the peak for the styrenic protons (B), along with the peak for the methyl protons of AA (after methylation) (A),

and the backbone protons (D). The approach is outlined below to determine the mole fractions of the monomers in the terpolymer.

X=moles of S in terpolymer =  $\frac{B}{5}$ 

Y=moles of AA in terpolymer =  $\frac{A}{3}$ 

Z=moles of AN in terpolymer =  $\frac{D}{3} - X - Y$ 

The initial experiments (S\_AN\_AA\_1 & 3) resulted in an acid incorporation in the desired range of 5-10mol%. While this was encouraging, a challenge became prevalent. As can be seen from Table 3, while the acid content was desirable, the corresponding AN content was > 60 mol%. The desired AN content was approximately 40-50% mol, typical of barrier materials even though a higher AN content can be used as long as the material can be processed. Therefore, a study of the ternary system was conducted to determine a qualitative trend to slightly lower the AN content while maintaining the desired AA content. It seems from the small sample set that rather than decreasing the AN feed content and increasing the S feed content, decreasing the AN feed content and increasing the AA feed content as can be seen by S\_AN\_AA\_ 6 & 9, can result in high acid terpolymer compositions. However, S\_AN\_AA\_4, 5 & 7, were satisfactory in controlling both the AA and achieving sufficient AN content in the terpolymer (4-8% mol and 52-57% mol respectively).

Thermal properties of the terpolymers were characterized via TGA and DSC. A typical example of the spectra obtained from DSC analysis is shown in Figure 3. From Figure 3, it can be seen that the  $T_g$  is a little bit above 100°C. The  $T_g$  of the terpolymers are listed in Table 4.



*Figure 3*: DSC analysis of S\_AN\_AA\_1.

Experiment I.D.	Fs	FAA	Tg (°C)
S_AN_AA_1	0.26	0.07	113.9
S_AN_AA_2	0.44	0.04	
S_AN_AA_3	0.21	0.04	
S_AN_AA_4	0.44	0.04	100.3
S_AN_AA_5	0.43	0.04	82.2
S_AN_AA_6	0.49	0.18	
S_AN_AA_7	0.35	0.08	76.5
S_AN_AA_8	0.67	0.25	87.5
S_AN_AA_9	0.67	0.26	105.1
S_AN_AA_10	0.75	0.04	98.6

The  $T_gs$  of PAN, poly(styrene) and poly(acrylic acid) are approximately 90-100°C,+ as can be suggested by the terpolymers listed in Table 4. There is some variation in  $T_g$  as it

is not only a function of molecular weight and composition, but of monomer sequencing due to possible interactions and/or steric hinderance between adjacent monomer units.<sup>[92-94]</sup> This, along with the different molecular weight distributions explain the variation in  $T_g$  in the synthesized terpolymers. DSC provided relevant information regarding the  $T_g$  (and therefore, extrusion temperature), but TGA was also performed to understand the degradation process of the terpolymers with Figure 4 as a typical example.



*Figure 4*: TGA analysis of S\_AN\_AA\_1.

The expected degradation profile of S\_AN\_AA terpolymers matches Figure 4. Moisture and residual solvent evaporated at about 100°C. Afterwards, AA began to transform to anhydrides (up to 150°C) and then to smaller volatilized organic compounds beyond 150°C.<sup>[95]</sup> S and AN decomposed after 250°C.<sup>[96]</sup> It was important to see the early degradation of AA, as this puts a constraint on the temperatures that the terpolymers could be extruded.

### 3.4.3. Synthesis of Styrene/Acrylonitrile Copolymers by NMP

After confirming that AN could be incorporated into a copolymer with S and into a terpolymer with S and AA, controlled radical polymerization, specifically NMP, was used to synthesize SAN copolymers with a narrower Đ along with chain-end fidelity

(possibility of chain extension) to incorporate further properties and/or functional groups. Also, placing functional groups near one end of the chain should improve their accessibility to react with complementary functional groups from the other polymer during blending.<sup>[85]</sup> Table 5 shows the reaction formulations and the characterization of the copolymers that were synthesized.

	Feed Composition				Characterization		
Experiment I.D.	NHS-BB	S	AN	fs,0	Fs <sup>b</sup>	Mn	Т
	( <b>M</b> )	(M) <sup>a</sup>	( <b>M</b> ) <sup>a</sup>			(kg mol <sup>-1</sup> ) <sup>c</sup>	
S_AN_NHS-BB-1	0.018	4.34	0.51	0.89	0.93	10.0	1.18
S_AN_NHS-BB-2	0.018	4.04	1.09	0.79	0.86	13.5	1.20
S_AN_NHS-BB-3	0.018	3.77	1.60	0.70	0.72	10.6	1.17
S_AN_NHS-BB-4	0.018	3.38	2.22	0.60	0.64	20.0	1.25

Table 5: Characterization of SAN Copolymers Synthesized by NMP.

<sup>a</sup> 50:50 wt% monomers to solvent ratio<sup>; b</sup> Calculated using <sup>1</sup>HNMR; <sup>c</sup> Obtained by GPC using THF as the mobile phase with respect to PMMA standards at 40°C

It can be immediately noticed from Table 5 that the  $\tilde{D}$  of the copolymers synthesized is significantly lower than the ones synthesized by conventional radical polymerization. Furthermore, the copolymer compositions matched well to those previously reported<sup>[18]</sup> and our earlier results by conventional radical polymerization. Kinetic studies were also performed for each polymerization to see how well the polymerization mimicked the expected behaviour for a controlled mechanism (i.e. linear  $M_n$  versus conversion). The kinetic plots for the polymerizations are shown in Figure 5 and 6. It is worth noting that the beginning of the reaction was arbitrarily chosen to be when the temperature reached 100°C.



*Figure 5*: Kinetic plots (scaled conversion of  $\ln[(1-x)^{-1}]$  (x = conversion) versus time) for SAN copolymers with feed composition S:AN (in mol%) of: a) 89:11, b) 79:21, c) 70:30, d) 60:40.

It can be seen from Figure 5 that over the course of the 5 hour reaction period, the kinetic plots are relatively linear and show a steady consumption of monomers over time, with no indication of a plateau that would imply dead chains.<sup>[13, 17, 65, 87]</sup>



*Figure 6*: Number average molecular weight  $(M_n)$  vs conversion relative to PMMA standards in THF at 40 °C for SAN copolymers with feed compositions S:AN (in mol %) of a) 89:11, b) 79:21, c) 70:30, d) 60:40.

Furthermore,  $M_n$  versus conversion plots show that the chains are growing linearly over time, which is also an indicator that the polymerization was reasonably controlled with no overt chain termination or transfer suggested.<sup>[13,17,65,87]</sup> Figure 5c and 6c show the possibility of dead chains as the conversion and  $M_n$  seem to plateau slightly, or perhaps, some chain transfer to solvent that becomes noticeable after 3-4 h. Otherwise, the kinetic plots demonstrate a linear trend and give an apparent rate constant ( $k_pK$ , the slope of the  $ln(\frac{1}{1-x})$  versus time plot) of 3.2-5.8 x 10<sup>-5</sup> s<sup>-1</sup> where  $k_p$  is the propagation rate constant and K is the equilibrium constant.  $k_p$  for AN is reported to be  $1.5x10^4$  L mol<sup>-1</sup> while for S,  $k_p$  is reported as  $1.8x10^3$  L mol<sup>-1</sup>.<sup>[18]</sup> K for S and AN is  $2.2x10^{-9}$  mol L<sup>-1</sup> and  $1x10^{-10}$  mol L<sup>-1</sup> respectively.<sup>[18]</sup> It is not surprising that even though the feed composition was varied, the apparent rate constant ( $k_p$ ) and equilibrium constants (K) for both S and AN are approximately equal.<sup>[18]</sup> Acid functionality was then attempted to be incorporated now that well defined SAN copolymers were synthesized.

### 3.4.4. Synthesis of Block Copolymers using SAN copolymers

The ideal goal was to synthesize S/AN/AA terpolymers by NMP so that the acid groups could be randomly distributed in the terpolymer like with conventional radical polymerization, but the terpolymerization yielded little to no acid (<0.5% AA). Based on the reactivity ratios published in the literature for this ternary system, AA should have been incorporated readily into the polymer.<sup>[90]</sup> Literature suggests that the MEHQ inhibitor plays a key role in retarding the polymerization of AA.<sup>[62]</sup> It was not removed prior to use however, and the same unpurified AA was successfully used previously with NMP.<sup>[87]</sup> AA is known to attack SG1, so it is possible that AA preferred to attack SG1 and caused irreversible chain termination rather than incorporate into the terpolymer. Consequently we chose to use the block copolymer so that the SAN segment is ensured and then the second block consists of the AA needed for the reactive blending. The formulation and its characterization is listed in Table 6 and 7. The first block was a SAN block at the azeotropic feed composition  $\sim f_s = 0.6$ . The second block was a S/t-BA block at a mol ratio of 50/50. Due to AA's tendency to attack the SG1 groups of BB, the acid functionality was incorporated indirectly in the form of a protected version of AA, t-BA. The *tert*-butyl group can be easily removed by the use of an acid resulting in a carboxylic acid functionality.

	Feed Composition				С	haracterizati	on
Experiment	[NHS-BB]	[S]	[AN]	fs,0	Fsb	Mn	Т
I.D.	( <b>M</b> ) <sup>a</sup>	( <b>M</b> ) <sup>a</sup>	(M) <sup>a</sup>			(kg mol <sup>-1c</sup>	

Table 6: Formulation and characterization of SAN macro-initiator

<sup>a</sup> 50/50 wt% ratio of monomers to solvent; <sup>b</sup> Calculated <sup>1</sup>H NMR; <sup>c</sup> Measured with respect to PMMA standards at 40°C using THF as the mobile phase

	Feed Composition					Cha	racterization	
Experiment	[S/AN initiator]	[S]	[t-BA]	fs,0	Fsb	FAN <sup>b</sup>	Mn	Т
I.D.	( <b>M</b> ) <sup>a</sup>	( <b>M</b> ) <sup>a</sup>	(M) <sup>a</sup>				(kg mol <sup>-1</sup> ) <sup>c</sup>	
S/AN-b-S/t-BA	0.002	2.02	2.02	0.50	0.74	0.16	36.6	1.34

Table 7: Formulation and characterization of SAN-b-S/t-BA

<sup>a</sup> 50/50 wt% ratio of monomers to solvent; <sup>b</sup> Calculated <sup>1</sup>H NMR; <sup>c</sup> Measured with respect to PMMA standards at 40°C using THF as the mobile phase

During the kinetic studies, evidence pointed toward a controlled radical mechanism and the ability to chain extend is the last criterion for it.<sup>[13, 17, 65, 87]</sup> The increase in  $M_n$  is a good indicator of a successful chain extension and a living polymer, but further evidence can be seen from the GPC chromatograph in Figure 7.





A clear shift to the left in the GPC chromatograph, indicative of higher molecular weight chains, indicates that chain extension was successful. There was not excessive skewness, indicative of a low molecular tail, implying that there was not a significant amount of dead chains in the SAN macrointiator. The t-BA groups were converted to carboxylic acid groups using trifluoroacetic acid, which gave the block copolymer the necessary acid functionality for extrusion. The first block had a composition (S:AN) of 62:38 mol%.

With the second block, the total polymer had an AA composition of 10 mol% (approximately 40 AA groups per chain) and an AN composition of about 16 mol%. It seems that the AN loading is low to be an effective barrier material, but recall that the AN is contained within a single block and if desired can be manipulated by the feed content for first block and the size of the second block.

#### **3.4.5. Extrusion & SEM analysis**

Prior to extrusion, the SG1 group of the SAN copolymers and SAN-b-SAA used in extrusion was cleaved using a literature method to increase the thermal stability<sup>[10]</sup> The reactive and non-reactive polymers made by NMP were extruded with PE-g-GMA at 160°C. Blend miscibility can be determined theoretically by evaluating a blend pair's interaction parameter ( $\chi_{blend}$ ), which can be calculated by Equation 6.<sup>[56]</sup>

$$\chi_{blend} = \chi_{A/B} = \frac{v}{RT} * (\delta_A - \delta_B)^2$$
(6)

where,  $\chi_{blend}$  is the interaction parameter between PE-g-GMA (A) and the co/block copolymer (B), R is the gas constant, T is absolute temperature of the blend, v is the molar volume and  $\delta$  is the Hildebrand solubility parameter.  $\chi_{blend}$  for the reactive and nonreactive blends are listed in Table 8.

Blend	δΑ	δв	Xblend
	$(cal^{1/2}cm^{-3/2})$	$(cal^{1/2}cm^{-3/2})$	
PE-g-GMA & SAN	7.90	9.92	0.45
PE-g-GMA & SAN-b-S/AA	7.90	9.93	0.47

Table 8: Interaction Parameters of the Blending Pairs

 $\chi_{\text{blend}}$  for both the non-reactive and reactive blends is quite high indicating that the blends are indeed immiscible.<sup>[57]</sup> The molar mass of the polymer repeat unit was calculated using the polymer compositions as the weights) approximately to be 84 g mol<sup>-1</sup> and 86 g mol<sup>-1</sup> for the non-reactive and reactive blends respectively. The density was also calculated using the polymer composition as weights and was 0.87 g ml<sup>-1</sup> and 0.91 g ml<sup>-1</sup> for the non-reactive and reactive blends respectively. The molar volumes were calculated from the mass of the repeat units and the densities. Furthermore,  $\delta$  was determined by using a weighted average (using the polymer compositions as the weights) of the solubility parameters found in the literature for the homopolymers.<sup>[57]</sup> The *in situ* reaction between the complementary functional groups will result in the formation of a graft copolymer at the interface, which will reduce the coalescence significantly.<sup>[10]</sup> The non-reactive blend does not possess complementary functional groups so the blend should show signs of significant coalescence. Therefore, SEM images post-extrusion and post-annealing were used to verify the effect of compatibilization. The SEM images are shown in Figure 8 and the quantitative analysis is shown in Table 9.



*Figure 8*: SEM images of a) 70wt% PE-g-GMA, 30wt% SAN after extrusion and freeze fracturing, b) 70wt% PE-g-GMA, 30wt% SAN-b-S/AA after, extrusion and freeze fracturing, c) 70wt% PE-g-GMA, 30wt% SAN post annealing, d) 70wt% PE-g-GMA, 30wt% SAN-b-S/AA post annealing.

		<b>Blend Ratio</b>			Characterization
SEM Image	PE-g-GMA (wt%)	SAN-b-S/AA (wt%)	SAN (wt%)	Annealing Conditions	$\left< D \right>_{vs}$ ( $\mu$ m)
а	70	0	30	None	3.0
b	70	30	0	None	1.7
с	70	0	30	18 hrs at 150°C	12.6
d	70	30	0	18 hrs at 150°C	1.6

Table 9: Particle Analysis of SEM Images

 $\langle D \rangle_{is}$  estimates the ratio of volume to interfacial area.  $\langle D \rangle_{is}$  vs is used as it relates easily to the interfacial coverage of the compatibilizing block copolymer around the dispersed phase particle. For example,  $\langle D \rangle_{u^{S}}$  can be used to estimate how much graft copolymer is formed at the interface if a common solvent exists between the polymers for GPC analysis. The quantitative analysis shows that the reactive blend and the non-reactive blend yield similar  $\langle D \rangle_{vs} = 1.7 \ \mu m$  and 3.0  $\mu m$  respectively. It was expected that the acidepoxy reaction would reduce the interfacial tension enough to see a more drastic difference in the domain sizes. A possible explanation could be that the two polymers have similar interfacial tensions. Coupling this with the known slow kinetics (<10% conversion within the first 2 minutes) of the acid-epoxy reaction,<sup>[11]</sup> it may suggest little reaction during extrusion. However, annealing showed that the reactive blend was sufficiently stable whereas the non-reactive blend dramatically coalesced (domain size increased by a factor of 4). Longer extrusion times or addition of a catalyst might have helped. A previous study was able to achieve a 30% conversion with this reaction coupling with a residence time of 10 minutes.<sup>[97]</sup> To further improve the kinetics, a catalyst was used to improve the conversion to 80%.[97]

# 3.4.6 Rheology

The complex viscosity of the SAN copolymer, SAN-b-SAA and PE-g-GMA was measured at 160°C and is shown below in Figure 9.



*Figure 9*: Complex viscosity vs. angular frequency measurements for PE-g-GMA (blue), SAN (orange), and SAN-b- SAA (grey).

For the particular extruder used, the shear rate was approximated using the largest and smallest diameter of the screws at a rotational speed of 50 rpm. The shear rates were approximated as 27 and 9 s<sup>-1</sup>. In this interval, the viscosity ratio ( $\eta$ ) of the co/block copolymer to PE-g-GMA is approximately 0.03-0.04. For the best dispersion,  $\eta$  of 1 should result in the smallest domain sizes.<sup>[10, 59-62]</sup> Obviously mixing could have improved with a higher  $\eta$  and this is likely due to the relatively low molecular weight SAN-b-S/AA copolymer used. Our previous study with SAN/PE blends (using an amine/anhydride reaction where the SAN was terminated with a single amine group and the PE was grafted with maleic anhydride (MA)) had similar  $\eta \sim 0.04$  at shear rates ~ 10-100 s<sup>-1</sup> and the SAN particle size was stable and  $\langle D \rangle_{\nu s} \sim 2 \ \mu m.^{[10]}$  In another study, using the same extruder, we blended a MA/AN/PAS terpolymer made by conventional radical polymerization containing several pendant amine groups into PE-g-MA, and we obtained sub-micron particle sizes. Here,  $\eta \sim 0.5$  at the shear rates of interest (the terpolymer had a much higher molecular weight compared to the polymers used here). There are obvious several factors at play in compatibilization/mixing of polymer blends: interfacial tension (and hence interfacial thickness which can limit the amount of

copolymer formed), type of reaction and the rheology of the individual components. Here, we showed that the epoxy/acid reaction (which is easy to functionalize the respective homopolymers) is effective at producing stable morphologies of SAN/PE blends with relatively small particle sizes. The next steps would be to orient the SAN domains in an elongated manner in the PE matrix to provide a more effective barrier morphology.

# **3.5.** Conclusion

In this study, AN-containing polymers with and without an acid functionality were synthesized by NMP. They were melt each blended with PE-g-GMA, poly(ethylene) grafted with glycidyl methacrylate, at  $160^{\circ}$ C at 50 rpm. The domain size of the dispersed phase was 1.7 µm and 3.0 µm when functional (via AA copolymerization) and non-functional SAN was used respectively. Upon annealing, evidence of significant coalescence was seen for the non-reactive blend as its domain size increased to 12.6 µm. The domain size for the reactive blend did not increase indicating that enough of the acid-epoxy coupling reaction occurred to keep a stable morphology.

# 4. Future Considerations

While the S/AN-b-S/AA block copolymers yielded a stable morphology due to the acidepoxy reaction, it would be interesting to disperse the acid functionality by the means of a terpolymer rather than a block copolymer. This proved to be difficult in the few trials ran with NMP. Even indirect attempts with t-BA or a silane-protected version of AA did not incorporate significantly in a terpolymer with S and AN. Therefore, before any efforts go into this, a blend of S/AN/AA terpolymer synthesized by conventional radical polymerization (which polymerized successfully) with PE-g-GMA can be attempted to see if the dispersed acid functionality reduces the domain size of the blend any further compared to the block copolymer.

The next step for the amine-maleic anhydride blend would be to use controlled polymerization techniques to yield a well-defined terpolymer. Cheaper monomers such as 3-isopropenyl- $\alpha$ , $\alpha$ -dibenzyl isocyanate can be transformed to an amine functionality.<sup>[98]</sup> Alternatively, if deemed cheaper, some AN can be sacrificed and transformed into amine groups by an SN<sub>2</sub> reaction with lithium aluminium hydride as a reducing agent.

Given that radical polymerization has the ability to synthesize long chain polymers,  $M_n$  could be increased in an attempt to increase the viscosity ratio closer to unity. It may prove to be worthwhile as the domain sizes should theoretically decrease by increasing the viscosity ratio for both systems.

Finally, the operating conditions should be carefully looked at. Research groups use blending equipment with residence times that vary between 2-20 minutes<sup>[5, 6, 9, 10, 60, 63, 74, 78, 99]</sup> While the residence time for the amine-maleic anhydride coupling is not a significant factor due to its extremely fast kinetics, the same cannot be said for the acidepoxy coupling.<sup>[97]</sup>

# 5. Conclusions

The work contained in this thesis is the continuation of the work previous colleagues began in the investigation of compatibilizing blends with AN containing polymers for barrier applications. The work showed that AN could be polymerized with different monomers using both conventional radical polymerization and NMP in the form of copolymers, terpolymers and block copolymers. More importantly, compatible functional groups were inserted as pendant groups in the polymers rather than just at the terminal ends, giving the polymers more reactivity and versatility. Specifically, amine groups were inserted into MA/AN copolymers in the form of PAS and carboxylic acid groups were inserted into SAN copolymers in the form of t-BA. PE. MA/AN/PAS terpolymers were melt blended with PE-g-MA at 200° C and SAN-b-S/AA was melt blended with PE-g-GMA at 160°C. The domain sizes were 1.2µm and 1.7µm respectively. The respective non-reactive blends yielded domain sizes of 12.5µm and 3.0µm. The non-reactive blends showed signs of coarsening upon annealing and so it was concluded that the coupling reactions not only occurred, but were responsible for the stable morphology.

These results are significant as they show that AN can be used for its barrier properties even though PAN cannot be processed easily. Previous barrier materials containing polyesters, polyamides, and nylon while being effective, lack the ability to form complex architectures because they are synthesized by a condensation reaction. Furthermore, compatibilization can be more difficult as they only have a single terminal functional group. Additionally, the level of polarity (and therefore, barrier properties) cannot be manipulated.

However, because AN based polymers were synthesized by radical polymerization, complex architectures and other properties (toughness, elasticity etc...) can be added in the form of other monomers all the while manipulating the AN content (and therefore, barrier properties) in the final co/terpolymer. Furthermore, the research illustrates the effectiveness of compatibilizing polymer blends over adding fillers and simply blending. The reduced domain sizes not only improve mechanical (and barrier properties) of the material, but the physical bonds formed ensure that the material will be stable during downstream processing steps. The one step extrusion followed by a channel die to create the brick like morphology can be much more economical over multilayer extrusion because multilayer extrusion possibly uses multiple extruders and dies.

53

# **References**

- 1. Dhoot, S.N., B.D. Freeman, and M.E. Stewart, *Barrier Polymers*, in *Encyclopedia* of *Polymer Science and Technology*. 2002, John Wiley & Sons, Inc.
- 2. Subramanian, P.M., *Permeability barriers by controlled morphology of polymer blends*. Polymer Engineering & Science, 1985. **25**(8): p. 483-487.
- 3. Horák, Z., et al., *Polymer Blends*, in *Encyclopedia of Polymer Science and Technology*. 2002, John Wiley & Sons, Inc.
- 4. Utracki, L.A., *Compatibilization of Polymer Blends*. The Canadian Journal of Chemical Engineering, 2002. **80**(6): p. 1008-1016.
- 5. Marić, M. and C.W. Macosko, *Improving polymer blend dispersion in minimixers*. Polymer Engineering & Science, 2001. **41**(1): p. 118-130.
- 6. Marić, M. and C.W. Macosko, *Block copolymer compatibilizers for polystyrene/poly(dimethylsiloxane) blends*. Journal of Polymer Science Part B: Polymer Physics, 2002. **40**(4): p. 346-357.
- Sundararaj, U. and C.W. Macosko, Drop Breakup and Coalescence in Polymer Blends: The Effects of Concentration and Compatibilization. Macromolecules, 1995. 28(8): p. 2647-2657.
- Tao, Y., A.H. Lebovitz, and J.M. Torkelson, *Compatibilizing effects of block* copolymer mixed with immiscible polymer blends by solid-state shear pulverization: stabilizing the dispersed phase to static coarsening. Polymer, 2005. 46(13): p. 4753-4761.
- 9. Marić, M., N. Ashurov, and C.W. Macosko, *Reactive blending of poly* (*dimethylsiloxane*) with nylon 6 and poly (styrene):Effect of reactivity on morphology. Polymer Engineering & Science, 2001. **41**(4): p. 631-642.
- Oxby, K.J. and M. Marić, Compatibilization of Poly(styrene-acrylonitrile) (SAN)/Poly(ethylene) Blends via Amine Functionalization of SAN Chain Ends. Macromolecular Reaction Engineering, 2014. 8(2): p. 160-169.
- 11. Orr, C.A., et al., *Homogeneous reactive coupling of terminally functional polymers*. Polymer, 2001. **42**(19): p. 8171-8178.
- 12. Moon, B., T.R. Hoye, and C.W. Macosko, *Synthesis of end- and mid-Phthalic Anhydride Functional Polymers by Atom Transfer Radical Polymerization*. Macromolecules, 2001. **34**(23): p. 7941-7951.
- 13. Matyjaszewski, K. and J. Spanswick, *Controlled/living radical polymerization*. Materials Today, 2005. **8**(3): p. 26-33.
- 14. Nicolas, J., et al., *Nitroxide-mediated polymerization*. Progress in Polymer Science, 2013. **38**(1): p. 63-235.
- 15. Nicolas, J. and Y. Guillaneuf, *Living Radical Polymerization: Nitroxide-Mediated Polymerization*, in *Encyclopedia of Polymeric Nanomaterials*, S. Kobayashi and K. Müllen, Editors. 2014, Springer Berlin Heidelberg. p. 1-16.
- Nicolas, J., et al., Nitroxide-Mediated Controlled Free-Radical Emulsion Polymerization Using a Difunctional Water-Soluble Alkoxyamine Initiator. Toward the Control of Particle Size, Particle Size Distribution, and the Synthesis of Triblock Copolymers. Macromolecules, 2005. 38(24): p. 9963-9973.
- 17. Lessard, B. and M. Marić, *Effect of an Acid Protecting Group on the "Livingness" of Poly(acrylic acid-ran-styrene) Random Copolymer*

*Macroinitiators for Nitroxide-Mediated Polymerization of Styrene.* Macromolecules, 2008. **41**(21): p. 7881-7891.

- 18. Maric, M. and V. Consolante, *Versatility of a succinimidyl-ester functional alkoxyamine for controlling acrylonitrile copolymerizations*. Journal of Applied Polymer Science, 2013. **127**(5): p. 3645-3656.
- 19. DeLassus, P., *Barrier Polymers*, in *Kirk-Othmer Encyclopedia of Chemical Technology*. 2000, John Wiley & Sons, Inc.
- 20. Jones, T.D., et al., *Synthesis and reactive blending of amine and anhydride endfunctional polyolefins*. Polymer, 2004. **45**(12): p. 4189-4201.
- 21. Améduri, B., B. Boutevin, and P. Gramain, *Synthesis of block copolymers by radical polymerization and telomerization*, in *Polymer Synthesis/Polymer Catalysis*. 1997, Springer Berlin Heidelberg. p. 87-142.
- 22. Baumann, M., et al., Synthesis of polystyrene-block-poly(styrene-co-acrylonitrile) block copolymers and thermoanalytical studies of nitroxide-terminated poly(styrene-co-acrylonitrile) copolymers. Macromolecular Materials and Engineering, 2000. **280-281**(1): p. 1-6.
- 23. Ceresa, R.J., *The block copolymerization of methyl methacrylate and acrylonitrile: II. Characterization and structure.* Polymer, 1960. **1**(0): p. 488-498.
- El-Sabee, M.Z., A.H. Ahmed, and S. Mawaziny, *Copolymerization of acrylonitrile with ethyl methacrylate—I*. European Polymer Journal, 1974. 10(12): p. 1149-1152.
- Fan, D., et al., Synthesis of SAN-containing block copolymers using RAFT polymerization. Journal of Polymer Science Part A: Polymer Chemistry, 2006. 44(7): p. 2260-2269.
- 26. Fukuda, T., et al., *Well-Defined Block Copolymers Comprising Styrene–Acrylonitrile Random Copolymer Sequences Synthesized by "Living" Radical Polymerization.* Macromolecules, 1996. **29**(8): p. 3050-3052.
- 27. Iwakura, Y., et al., *Copolymerization of acrylonitrile and vinyl pyridine*. Journal of Polymer Science, 1959. **39**(135): p. 203-209.
- 28. Köken, N., et al., *Block copolymers of acrylonitrile and poly(dimethylsiloxane)s*. Journal of Applied Polymer Science, 2013. **127**(5): p. 3790-3797.
- 29. Mahato, B. and S. Maiti, *New block copolymers V. Synthesis, characterization and morphological studies of poly(pentamethylene terephthalate)-b-(acrylonitrile butadiene rubber)*. Colloid and Polymer Science, 1988. **266**(7): p. 601-607.
- 30. Mazzucco, M.L., et al., *Nanocomposites of acrylonitrile-butadienestyrene/montmorillonite/styrene block copolymers: structural, rheological, mechanical and flammability studies on the effect of organoclays and compatibilizers using statistically designed experiments.* Journal of Composite Materials, 2015.
- 31. Ritchey, W.M. and L.E. Ball, *Measurement of copolymerization reactivity ratios by NMR*. Journal of Polymer Science Part B: Polymer Letters, 1966. **4**(8): p. 557-566.
- 32. Sanghvi, P.G., et al., *Reactivity ratios and sequence distribution of styrene– acrylonitrile copolymers synthesized in microemulsion medium.* European Polymer Journal, 2000. **36**(10): p. 2275-2283.

- 33. Tsarevsky, N.V., et al., Synthesis of Styrene–Acrylonitrile Copolymers and Related Block Copolymers by Atom Transfer Radical Polymerization. Macromolecules, 2002. **35**(16): p. 6142-6148.
- 34. Yin, Z., et al., *Dependence of the Morphology Development on the Kinetics of Reactive Melt Blending of Immiscible Polymers*. The Canadian Journal of Chemical Engineering, 2002. **80**(6): p. 1044-1050.
- 35. Allen, S.M., et al., *The barrier properties of polyacrylonitrile*. Journal of Membrane Science, 1977. **2**(0): p. 153-163.
- 36. Park, H.C. and C.R. Ashcraft, *The Use of Polyacrylonitrile Film in Barrier Food Packaging*. Journal of Plastic Film and Sheeting, 1985. **1**(2): p. 95-103.
- 37. Liesl, K.M., *Permeability Properties of Plastics and Elastomers*. 2003: William Andrew. 615.
- 38. Hann, N.D., *Effects of lithium bromide on the gel-permeation chromatography of polyester-based polyurethanes in dimethylformamide*. Journal of Polymer Science: Polymer Chemistry Edition, 1977. **15**(6): p. 1331-1339.
- 39. Li, X.-R., X.-L. Wang, and H. Koseki, *Study on thermal decomposition characteristics of AIBN*. Journal of Hazardous Materials, 2008. **159**(1): p. 13-18.
- 40. Bhanu, V.A., et al., *Synthesis and characterization of acrylonitrile methyl acrylate statistical copolymers as melt processable carbon fiber precursors*. Polymer, 2002. **43**(18): p. 4841-4850.
- Zengeni, E., et al., *Poly(acrylonitrile-co-methyl acrylate) copolymers: Correlation between copolymer composition, morphology and positron annihilation lifetime parameters.* Journal of Applied Polymer Science, 2011. 119(2): p. 1060-1066.
- 42. Smith, B., *Fundamentals of Fourier Transform Infared Spectroscopy*. 2nd ed. 2011: CRC Press. 207.
- 43. Gottlieb, H.E., V. Kotlyar, and A. Nudelman, *NMR Chemical Shifts of Common Laboratory Solvents as Trace Impurities.* The Journal of Organic Chemistry, 1997. **62**(21): p. 7512-7515.
- 44. Covolan, V.L., G. Ruggeri, and E. Chiellini, *Synthesis and characterization of styrene/Boc-p-amino styrene copolymers*. Journal of Polymer Science Part A: Polymer Chemistry, 2000. **38**(16): p. 2910-2918.
- 45. Goikhman, M.Y., et al., *Synthesis and optical properties of copolymers of 4aminostyrene with the side styrylquinoline chromophore groups*. Russian Chemical Bulletin, 2011. **60**(2): p. 295-303.
- 46. Yamaguchi, K., et al., Anionic living polymerization of p-N,N-bis(trimethylsilyl)aminostyrene. Synthesis of linear poly(p-aminostyrene) with a narrow molecular weight distribution. Journal of Polymer Science: Polymer Letters Edition, 1983.
  21(5): p. 395-401.
- 47. Marić, M., et al., *Incorporating primary amine pendant groups into copolymers via nitroxide mediated polymerization*. Reactive and Functional Polymers, 2011.
   **71**(12): p. 1137-1147.
- 48. Dunn, P. and B.C. Ennis, *Thermal analysis of polyacrylonitrile. Part I. The melting of polyacrylonitrile.* Journal of Applied Polymer Science, 1970. **14**(7): p. 1795-1798.

- 49. Frushour, B., *Melting behavior of polyacrylonitrile copolymers*. Polymer Bulletin, 1984. **11**(4): p. 375-382.
- 50. Krigbaum, W.R. and N. Tokita, *Melting point depression study of polyacrylonitrile*. Journal of Polymer Science, 1960. **43**(142): p. 467-488.
- 51. Rangarajan, P., et al., *Effect of comonomers on melt processability of polyacrylonitrile*. Journal of Applied Polymer Science, 2002. **85**(1): p. 69-83.
- 52. Cameron, G.G., *The Odidative Thermal Degradation of Poly(Methyl Acrylate)*. Chemical Papers, 1972. **26**(3): p. 200-207.
- 53. Strauss, S., *Thermal Degradation fo Polyacrylonitrile, Polybutadiene, and Copolymers of Butdadiene With Acyrlonitrile and Styrene.* Journal of Research of the National Bureau of Standards, 1958. **61**(2): p. 5.
- 54. Still, R.H. and P.B. Jones, *Thermal degradation of polymers. part IV. Vacuum pyrolysis of poly(m-aminostyrene). The residue and the fraction volatile at pyrolysis temperature involatile at room temperature.* Journal of Applied Polymer Science, 1969. **13**(7): p. 1555-1567.
- 55. Katritzky, A.R., et al., *Quantitative Structure–Property Relationship (QSPR)* Correlation of Glass Transition Temperatures of High Molecular Weight Polymers. Journal of Chemical Information and Computer Sciences, 1998. 38(2): p. 300-304.
- 56. Barton, A., *Handbook of Poylmer-Liquid Interaction Parameters and Solubility Parameters*. 1990: CRC Press.
- 57. Emerson, J.A., et al., *Determination of Solvent–Polymer and Polymer–Polymer Flory–Huggins Interaction Parameters for Poly(3-hexylthiophene) via Solvent Vapor Swelling.* Macromolecules, 2013. **46**(16): p. 6533-6540.
- 58. van Krevelen, D.W., *Properties of Polymers*. 2012: Elsevier Science.
- 59. Favis, B.D. and J.P. Chalifoux, *The effect of viscosity ratio on the morphology of polypropylene/polycarbonate blends during processing*. Polymer Engineering & Science, 1987. **27**(21): p. 1591-1600.
- 60. Grace<sup>†</sup>, H.P., DISPERSION PHENOMENA IN HIGH VISCOSITY IMMISCIBLE FLUID SYSTEMS AND APPLICATION OF STATIC MIXERS AS DISPERSION DEVICES IN SUCH SYSTEMS. Chemical Engineering Communications, 1982. 14(3-6): p. 225-277.
- 61. Taylor, G.I., *The Transport of Vorticity and Heat through Fluids in Turbulent Motion*. Vol. 135. 1932. 685-702.
- 62. Wu, S., *Chain entanglement and melt viscosity of compatible polymer blends: poly(methyl methacrylate) and poly(styrene-acrylonitrile).* Polymer, 1987. **28**(7): p. 1144-1148.
- 63. Pagnoulle, C. and R. Jérôme, *Reactive Compatibilization of SAN/EPR Blends.* 2. *Effect of Type and Content of Reactive Groups Randomly Attached to SAN.* Macromolecules, 2001. **34**(4): p. 965-975.
- 64. Lewis, F.M., F.R. Mayo, and W.F. Hulse, *Copolymerization. II. The Copolymerization of Acrylonitrile, Methyl Methacrylate, Styrene and Vinylidene Chloride.* Journal of the American Chemical Society, 1945. **67**(10): p. 1701-1705.
- 65. Nicolas, J., S. Brusseau, and B. Charleux, A minimal amount of acrylonitrile turns the nitroxide-mediated polymerization of methyl methacrylate into an almost ideal

*controlled/living system.* Journal of Polymer Science Part A: Polymer Chemistry, 2010. **48**(1): p. 34-47.

- 66. Pichot, C., E. Zaganiaris, and A. Guyot, *Acrylonitrile copolymerization*. *VII Solvents effects in styrene copolymerization*. Journal of Polymer Science: Polymer Symposia, 1975. **52**(1): p. 55-66.
- 67. Climie, I.E. and E.F.T. White, *The aggregation of random and block copolymers containing acrylonitrile in mixed solvents*. Journal of Polymer Science, 1960.
  47(149): p. 149-156.
- Penfold, H.V., S.J. Holder, and B.E. M Kenzie, Octadecyl acrylate Methyl methacrylate block and gradient copolymers from ATRP: Comb-like stabilizers for the preparation of micro- and nano-particles of poly(methyl methacrylate) and poly(acrylonitrile) by non-aqueous dispersion polymerization. Polymer, 2010. 51(9): p. 1904-1913.
- 69. Tang, C., T. Kowalewski, and K. Matyjaszewski, *RAFT Polymerization of Acrylonitrile and Preparation of Block Copolymers Using 2-Cyanoethyl Dithiobenzoate as the Transfer Agent.* Macromolecules, 2003. **36**(23): p. 8587-8589.
- 70. Leal, L.G., *Droplet coalescence and breakup with application to polymer blending*. Journal of Central South University of Technology, 2007. **14**(1): p. 1-5.
- 71. Lyu, S.-P., F.S. Bates, and C.W. Macosko, *Coalescence in polymer blends during shearing*. AIChE Journal, 2000. **46**(2): p. 229-238.
- 72. Zou, Z.-m., Z.-y. Sun, and L.-j. An, *Studies on droplet size distributions during coalescence in immiscible polymer blends filled with silica nanoparticles.* Chinese Journal of Polymer Science, 2014. **32**(3): p. 255-267.
- Bell, J.R., et al., Annealing of Cocontinuous Polymer Blends: Effect of Block Copolymer Molecular Weight and Architecture. Macromolecules, 2010. 43(11): p. 5024-5032.
- 74. Galloway, J.A., et al., *Block copolymer compatibilization of cocontinuous polymer blends*. Polymer, 2005. **46**(1): p. 183-191.
- 75. Kipp, D. and V. Ganesan, *Influence of Block Copolymer Compatibilizers on the Morphologies of Semiflexible Polymer/Solvent Blends*. The Journal of Physical Chemistry B, 2014. **118**(16): p. 4425-4441.
- Lee, C.M., E.S. Kim, and J.-S. Yoon, *Reactive blending of poly(L-lactic acid) with poly(ethylene-co-vinyl alcohol)*. Journal of Applied Polymer Science, 2005.
   98(2): p. 886-890.
- T. Leibler, L., *Emulsifying effects of block copolymers in incompatible polymer blends*. Makromolekulare Chemie. Macromolecular Symposia, 1988. 16(1): p. 1-17.
- 78. Pospiech, D., *Influencing the Interface in Polymer Blends by Compatibilization with Block Copolymers*, in *Polymer Surfaces and Interfaces*, M. Stamm, Editor. 2008, Springer Berlin Heidelberg. p. 275-298.
- 79. Wacharawichanant, S., P. Amorncharoen, and R. Wannasirichoke, *Effects of Compatibilizers on Morphology and Properties of Polyoxymethylene/Polypropylene Blends*. Polymer-Plastics Technology and Engineering, 2015: p. null-null.

- 80. Fina, A., O. Monticelli, and G. Camino, *POSS-based hybrids by melt/reactive blending*. Journal of Materials Chemistry, 2010. **20**(42): p. 9297-9305.
- 81. Oyama, H.T., *Super-tough poly(lactic acid) materials: Reactive blending with ethylene copolymer*. Polymer, 2009. **50**(3): p. 747-751.
- 82. Pernot, H., et al., *Design and properties of co-continuous nanostructured polymers by reactive blending*. Nat Mater, 2002. **1**(1): p. 54-58.
- 83. Spinella, S., et al., Polylactide/Poly(ω-hydroxytetradecanoic acid) Reactive Blending: A Green Renewable Approach to Improving Polylactide Properties. Biomacromolecules, 2015. 16(6): p. 1818-1826.
- 84. Yang, H., et al., *Reactive blending of poly(ethylene terephthalate)(pet)/ poly(ethylene 2,6-naphthalate)(pen). I: Effect of mixing conditions on chain structure.* Polymer Engineering & Science, 2002. **42**(8): p. 1629-1641.
- 85. Jeon, H.K., et al., *Coupling Reactions of End- vs Mid-Functional Polymers*. Macromolecules, 2004. **37**(7): p. 2563-2571.
- 86. Vinas, J., et al., *SG1-based alkoxyamine bearing a N-succinimidyl ester: A versatile tool for advanced polymer synthesis.* Polymer, 2008. **49**(17): p. 3639-3647.
- Lessard, B., S.C. Schmidt, and M. Marić, *Styrene/Acrylic Acid Random Copolymers Synthesized by Nitroxide-Mediated Polymerization: Effect of Free Nitroxide on Kinetics and Copolymer Composition.* Macromolecules, 2008.
   41(10): p. 3446-3454.
- 88. Hill, D.J.T., et al., *Determination of reactivity ratios from analysis of triad fractions—analysis of the copolymerization of styrene and acrylonitrile as evidence for the penultimate model.* European Polymer Journal, 1989. **25**(9): p. 911-915.
- Otsu, T., *Reactivities of acrylic monomers and their radicals in radical polymerization*. Makromolekulare Chemie. Macromolecular Symposia, 1987. 10-11(1): p. 235-254.
- 90. Florjańczyk, Z., *Determination of the Reactivity Ratios in Terpolymerization on The Exmaple of Acrylic Acid-Styrene-Acrylonitrile System* Polymers Marcomolecular Plastics, 1991. **36**(5): p. 4.
- 91. Minagawa, M., et al., *Glass-Transition Temperature (Tg) of Free-Radically Prepared Polyacrylonitrile by Inverse Gas Chromatography, 2. Molecular-Weight Dependence of Tg of Two Different Types of Aqueous Polymers.* Macromolecular Chemistry and Physics, 2002. **203**(17): p. 2481-2487.
- 92. Rieger, J., *The glass transition temperature of polystyrene*. Journal of thermal analysis, 1996. **46**(3-4): p. 965-972.
- Beevers, R.B., Dependence of the glass transition temperature of polyacrylonitrile on molecular weight. Journal of Polymer Science Part A: General Papers, 1964. 2(12): p. 5257-5265.
- 94. Bonardelli, P., G. Moggi, and A. Turturro, *Glass transition temperatures of copolymer and terpolymer fluoroelastomers*. Polymer, 1986. **27**(6): p. 905-909.
- 95. McGaugh, M.C. and S. Kottle, *The thermal degradation of poly(acrylic acid)*. Journal of Polymer Science Part B: Polymer Letters, 1967. **5**(9): p. 817-820.

- 96. PfÄFfli, P., A. Zitting, and H. Vainio, *Thermal degradation products of homopolymer polystyrene in air*. Scandinavian Journal of Work, Environment & Health, 1978. **4**: p. 22-27.
- 97. Taha, M., et al., *Synthesis, by reactive extrusion, of high molar mass epoxy prepolymers containing rubber preformed particles.* Journal of Applied Polymer Science, 1997. **65**(12): p. 2447-2456.
- Trumbo, D.L., et al., *Copolymerization behavior of 3-isopropenyl-α,αdimethylbenzylamine and a preliminary evaluation of the copolymers in thermoset coatings*. Journal of Applied Polymer Science, 2001. 82(4): p. 1030-1039.
- 99. Martin, J.D. and S.S. Velankar, *Effects of compatibilizer on immiscible polymer blends near phase inversion.* Journal of Rheology (1978-present), 2007. **51**(4): p. 669-692.