Compatibilization of poly(styrene-acrylonitrile) (SAN) / poly(ethylene) blends via amine functionalization of SAN chain ends

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Abstract

Styrene/acrylonitrile (SAN) copolymers with excellent chain-end fidelity and low polydispersity M_w/M_n (1.10 – 1.30) were synthesized by nitroxide mediated polymerization (NMP) in dimethylformamide (DMF) solution with a succinimidyl ester (NHS) terminal group from the so-called SG1 nitroxide residue. These copolymers were thermally stabilized by removing the N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl) nitroxide] (SG1), and then modified to form primary amine end-functional SAN (SAN-NH_2). Homogeneous coupling reactions and Fourier-transform infrared spectroscopy (FTIR) indicated that the amine group was effectively placed at the chain end. SAN-NH_2 was reactively blended with maleic anhydride grafted poly(ethylene) (PE) at 20 wt.% loading at 180 °C and the resulting morphology was compared against the non-reactive blend. Scanning electron microscopy (SEM) indicated finer SAN domains ~ 1 μm which were thermally stable upon annealing in the reactive case. The dispersed SAN domains were reoriented using a channel die to impart elongated domains with aspect ratios ~ 14, which would be desirable for barrier materials.

Résumé

Les copolymères de styrène/acrylonitrile (SAN) avec des excellente fidélité en bout de chaîne et des faible polydispersité M_w/M_n (1,10 - 1,30) ont été synthétisés par polymérisation des nitroxydes (NMP) dans une solution de diméthylformamide (DMF) avec d'ester de succinimidyle (NHS) groupe terminal de l'soi-disant SG1 résidus nitroxyde. Ces copolymères ont été stabilisée thermiquement par élimination du groupe N-tert-butyl-N-[1-diéthylphosphono-(2,2-diméthylpropyl) nitroxyde] (SG1), et ensuite modifiée pour former une amine primaire à fonctionnalité en bout de chaine des copolymères (SAN-NH_2) . Réactions de couplage homogènes et transformée de Fourier spectroscopie infrarouge (FTIR) a indiqué que le groupe amine a effectivement été placé en bout de chaîne. SAN-NH_2 a été réactive mélangée avec l'anhydride maléique greffé poly(éthylène) (PE) au chargement de 20% en poids à 180 °C et la morphologie obtenue a été comparée à la mélange non réactif. Dans le cas réactif, microscopie électronique à balayage (MEB) ont indiqué plus fines domaines de SAN ~1 um qui étaient stables thermiquement après recuit. Les domaines dispersés SAN ont été réorientés en utilisant un dé canal pour donner domaines allongés avec des rapports d'aspect ~14, ce qui serait souhaitable pour des matériaux barrières.

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Contribution of Author

The following thesis is based on a manuscript which was submitted to "Macromolecular Reaction Engineering" (manuscript number: mren.201200081), where I, Keith James Oxby, am the first author. The manuscript provided in Section 2 is the pre-peer reviewed version of the article titled: "Compatibilization of Poly(styrene-acrylonitrile) (SAN)/ Poly(ethylene) Blends via Amine Functionalization of SAN Chain Ends". The supporting information submitted with this manuscript is shown in Section 3. As a contribution to this manuscript, I have performed all the polymer syntheses, modification, characterization, blending, morphology analysis and interpretation of the results. I have written the manuscript, which was revised and edited by my supervisor, Prof. Milan Marić.

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1 General Introduction

1.1 Background

Polymer Blends

Blending two types of polymers together can result in materials with desirable combinations of properties. This is a commercially attractive technique due to the ease of forming new customized materials at a low cost compared to new polymer creation.[1, 2]

The miscibility of polymer blends is based on the Gibbs free energy of mixing (ΔG_m) as shown in Equation 1.

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{1}$$

ΔH_m is the enthalpy of mixing, T is the temperature and ΔS_m is the entropy of mixing. Polymer blends are classified as miscible, homogenous blends when $\Delta G_m \leq 0$, or as immiscible, non-homogenous blends when $\Delta G_m > 0$. Miscibility is affected by the specific monomers present, the molecular weight of polymers, the fraction of each polymer in the blend and many other factors.[2] The Flory-Huggins theory can be used to model the miscibility of polymer blends as shown in Equation 2.

$$\frac{\Delta G_m}{(p_1N_1 + p_2N_2)} = kT\left(\frac{\phi_1}{p_1}\ln\phi_1 + \frac{\phi_2}{p_2}\ln\phi_2 + \phi_1\phi_2\chi_{12}\right) \tag{2}$$

N1 and N_2 are the number of molecules of the respective polymers, p_1 and p_2 are the degrees of polymerization of the respective polymers, k is the Boltzmann constant, Φ_1 and Φ_2 are the lattice volume fractions (i.e. the volume fractions of the respective monomers) and χ_{12} is the polymer-polymer interaction parameter. Polymer blends are nearly always immiscible due to a low entropy of mixing.[2] Unlike small molecules, polymers do not increase much their entropy when they are mixed together, since the long chains in the molecular structure restrict the possible configurations the molecules may take.[2] Unfortunately, immiscible blends usually have weak adhesion at the interface between polymer phases, which leads to poor mechanical properties and a lack of stability in the microstructure when heated above the glass transition temperatures or softening points.[2] Compatibilization is used to stabilize the interface between the immiscible polymer phases, which in turn creates a useful polymer blend.[3, 4] Compatibilization can be achieved using a block copolymer (two distinct polymer segments covalently attached to one another) in the same way that a surfactant can be used to stabilize an oil-water emulsion.[5] If one block of the copolymer is miscible with one of the homopolymers and the other block is miscible with the second homopolymer, a stable interface can be formed. This results in a prevention of coalescence and thus a finer dispersion of the phases in the blend and better material properties.[2] However, using pre-made block copolymers as compatibilizers has some problems associated with it. Sometimes, block copolymers have difficulty diffusing to the interface of the two homopolymers, or the block copolymers can form micelles within a single homopolymer. [5, 6] In either case, the pre-made block copolymer route does not achieve the desired compatibilization. To produce polymer blends industrially, compatibilization is usually achieved via reactive extrusion of functional polymers.[2, 7] Two functional homopolymers can react to form a block or graft copolymer at the interface of the two materials during melt blending which can stabilize the interface in the same way that a block copolymer would.[7] At the same time, diffusion and micelle formation issues are avoided.[2]

For the reactive extrusion to be effective in compatibilizing the immiscible polymer blend, a pair of cross-reactive functional groups must be used to covalently link the two polymers.[2] The pairing of functional groups used is limited by thermal stability, reaction rates, and the elimination of small molecule by-products.[4] Some commonly used compatibilizing reaction pairings are amine-anhydride, amine-carboxylic acid, amine-epoxy, isocyanate-hydroxyl, oxazoline-carboxylic acid, and epoxy-carboxylic acid.[4] The amine-anhydride coupling is especially effective since it provides very fast reactions – a useful feature for compatibilization and processing within an extruder with limited residence times.[4, 7, 8] An example of this reaction can be seen in Figure 1.

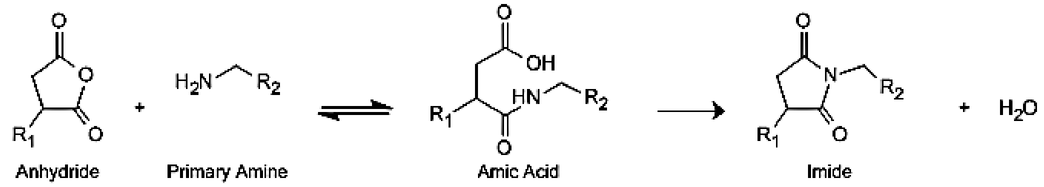

Figure 1 – Reaction between primary amine and maleic anhydride.

Barrier Polymers

Barrier polymers can be defined as macromolecules which have the ability to block the passage of certain other molecules such as gases or organic liquids.[9] There is a wide range of applications for barrier polymers, and the specific properties required in each application require specific barrier properties. The selection of a barrier polymer for a particular application typically involves trade-offs between permeation, mechanical, and aesthetic properties as well as economic and recycling considerations.[9] Usually, polymers with high barrier properties are either too expensive or do not have the mechanical properties needed for an application. For this reason barrier polymers are often layered[10-12] or blended[13] with one or more other polymers to achieve the desired material properties. Layering is used frequently for food-packaging films where up to 11 layers can be used including a barrier layer, adhesive layers, structural layers and impact resistance layers.[12] Another technique is to use inorganic composite fillers such as nanoclay to improve barrier properties of a material which is of low cost, or has desirable mechanical properties.[14-16]

Polymer blending has a main advantage over layering in that multiple polymers can be used together with a single processing step. Layering requires one extra extruder for each additional layer in a coextruded film, or extra processing steps to surface coat from a solvent or dispersion.[17] Multilayer coextrusion requires heavy capital investment, and it is often difficult to optimize and control the process.[18]

Xylene, gasoline or other hydrocarbons can easily permeate through a container made of poly(ethylene) (PE).[13] Therefore in fuel tanks – the targeted application for this research – the classical approach is to blend relatively hydrophilic poly(ethylene terephthalate) (PET) or a poly(amide) such as nylon which are immiscible with hydrophobic PE.[7, 13, 19] The inherent functionality at the chain end of these barrier polymers makes compatibilization possible when a functional PE is used, such as maleic anhydride grafted PE. When 20 wt.% nylon is dispersed as fine particles within a PE matrix, barrier properties are modestly increased by 20%.[17] However, under ideal processing conditions, a lamellar morphology of the dispersed nylon phase can be obtained. This change in morphology results in a higher tortuosity within the blend which significantly reduces the permeability, and almost achieves the permeability of a coextruded nylon sheet.[1, 20, 21]

Poly(styrene-*ran*-acrylonitrile), SAN, has excellent grease and chemical resistance as well as high gas barrier properties due to the polarity of the acrylonitrile monomer.[22] For this reason it would make an excellent barrier material within a PE blend. However, commercially available SAN made by conventional free radical polymerization does not have inherent functionality making reactive extrusion infeasible. In order to create compatible PE/SAN blends, a functional SAN must be synthesized.

Controlled Radical Polymerization

Free-radical polymerization (RP) is used in industry to synthesize the majority of commercial polymers.[23] It is an ideal polymerization method for industrial synthesis because it can easily be implemented on a large scale, it works on many monomer types, and it is not overly sensitive to water or trace oxygen in the system. However, it does have disadvantages. It is difficult to control molecular weight, the molecular weight distribution (polydispersity) is generally broad, and it is difficult to create block copolymers and other tailored microstructures.[24] Traditionally, living anionic polymerization (LAP) has been used to create polymers with controlled microstructures and molecular weights, and nearly monodisperse molecular weight distributions. 'Living' polymer chains are created in which termination does not occur and all chains grow simultaneously.[25] However, these methods require extremely pure monomers with protected functional groups, air-free transfers are necessary, and they are highly sensitive to oxygen and water.[25]

Controlled radical polymerization (CRP) techniques have been developed over the last 20 years to combine the best aspects of RP and LAP. The three main techniques are atom transfer radical polymerization (ATRP),[26-29] reversible addition-fragmentation-chain transfer (RAFT)[30-32] and nitroxide-mediated polymerization (NMP).[33-38] CRP techniques mimic the 'living' characteristics of LAP by attempting to eliminate or retard termination to some degree, and controlling molecular weight by increasing the rate of initiation relative to the rate of propagation.[34] The resulting polymers are 'living' in a sense, which allows for block copolymers to be made.[39] Similar to RP, CRP polymerizations are not extremely sensitive to oxygen or trace water in the system.[39]

CRP can be used to create useful SAN copolymers with low polydispersity and controlled structure, including block copolymers. SAN copolymers can easily be made using NMP,[40-42] ATRP[43-45] and RAFT.[46, 47] CRP techniques are also very useful in synthesizing functional polymers. This will be further explained in Section 2.1.

1.2 Research Objectives

The research presented in this thesis was based on applying NMP techniques to synthesize primary amine functional SAN which could be used to create compatibilized blends with maleic anhydride grafted PE (MA-PE) via reactive extrusion. The effectiveness of the amine functionality on the resulting SAN copolymers at compatibilizing a blend with MA-PE was studied by comparing to a blend of MA-PE with non-functional SAN. The microstructures of these blends were characterized to determine the level of compatibilization achieved with the functional SAN, and thermal stability of the microstructure was also tested. The final goal of the research was to study the effect of unidirectional shear flow on the blend microstructure in the attempt to create a lamellar SAN morphology within the PE matrix which could be suitable for barrier materials. Chapters 2 and 3 describe these objectives which constitute the manuscript submitted to Macromolecular Reaction Engineering.

2 Compatibilization of Poly(styrene-acrylonitrile) (SAN)/ Poly(ethylene) Blends via Amine Functionalization of SAN Chain Ends

2.1 Manuscript Introduction

Many barrier polymers are made of blends of polyolefins such as poly(ethylene) (PE) for structural support and hydrophobicity, and a hydrophilic barrier material such as polyamide (nylon) or polyester (poly(ethylene terephthalate)) as the dispersed phase.[13] This type of barrier material is common in fuel tank applications.[13, 17, 48, 49] If a lamellar morphology is obtained with the polymer blend, barrier properties approach those of a layered material made by coextrusion.[20, 21] However, most polymer blends are immiscible and must be compatibilized to form stable blend morphologies. The inherent amine functionality at the chain end of a polyamide makes it very easy to blend with maleic anhydride grafted PE to form a compatibilized polymer blend with a stable morphology.[20, 50] Similarly, most polyesters have carboxylic acid and hydroxyl functionality at the chain ends and can be blended with epoxy functional PE.[51] By requiring inherent functionality on the polymer chain, the range of available barrier materials to blend with PE is seemingly very narrow.

Poly(acrylonitrile) (PAN) has high chemical resistance and gas barrier properties relative to many other polymers.[22] However, due to its high melting point, high melt viscosity and thermal instability, poly(acrylonitrile) is seldom homopolymerized for practical applications and thus acrylonitrile is almost always copolymerized with another monomer.[22] Its most common comonomer is styrene. Poly(styrene-*ran*-acrylonitrile) (SAN) keeps many of the excellent barrier properties of PAN, but the styrene contributes to improved processability.[22] Conventional free radical polymerization of SAN gives polymers with broad polydispersities ~2, and poorly defined microstructure.[40, 52] Controlled radical polymerization (CRP) can be used to create useful SAN copolymers with low polydispersity and controlled microstructure, such as segmented block copolymers. SAN copolymers can easily be made using nitroxide mediated polymerization (NMP),[40-42] atom transfer radical polymerization (ATRP),[43, 45, 53] and reverse atom transfer radical polymerization (RAFT).[46, 47, 54] The ability to form SAN-containing block copolymers allows for additional tailoring of properties for the blend.

Although SAN copolymers would make an excellent substitute for nylon or polyester as the dispersed hydrophilic phase in PE blends for barrier applications, they have not been used in this application before. This is primarily due to a lack of compatibility between PE and SAN, which would require reactive blending. SAN must be functionalized appropriately in order to blend it with a functionalized PE resin to produce the desired, stable morphology.

NMP offers an excellent opportunity to create functionalized SAN copolymers with well-defined placement of functional groups, which can be melt-blended with functionalized PE. A suitable pairing would be an amine functionalized SAN copolymer and a maleic anhydride grafted PE as this is a fast reaction pairing used in many commercial blends and high conversions can be achieved in the short residence times within extruders.[4, 19, 55, 56] Maleic anhydride grafted PE is commercially available, and there are several possible routes for synthesizing a primary-amine functional SAN copolymer. One simple technique is to chemically modify the nitrile groups of SAN using a reduction/hydrogenation reaction to yield amine groups. However, this approach is not useful in keeping the barrier properties provided by the acrylonitrile groups and for this reason, was not investigated. The only example found for a SAN/polyolefin blend was a SAN/poly(ethylene propylene) (EP) rubber blend.[57] This study created primary amine random functional SAN by deriving primary amines from carbamate-containing comonomers in the SAN.[57] This functional SAN was then reacted with a maleic anhydride grafted EP at the interface between two separate sheets but reactive melt-blending to produce dispersed-phase type of morphologies was not performed.[57] Amine end-functional poly(styrene) (PS) has been synthesized using RAFT [58] and ATRP.[59, 60] Amine functional SAN polymers have been synthesized using conventional free radical polymerization as well.[61] However, there have not been any investigations into the amine end functionalization of PS or SAN using the commercially available BlocBuilder® unimolecular NMP initiator. NMP offers the advantage of resulting in metal-free polymers when compared to ATRP, and it also avoids the discolouration caused by RAFT polymerization. Our group has recently shown that SAN copolymerizations are effectively controlled by the N-succinimidyl ester terminated alkoxyamine derived from BlocBuilder (NHS-BlocBuilder).[62] The reactivity of the succinimidyl moiety gives the possibility of creating amine end-functional polymers.[63] The goal of this study was thus to synthesize amine end-functional SAN copolymers using NMP with NHS-BlocBuilder, to test the reactivity in various reactive blending applications, and to characterize and modify the microstructure of the blends to form the desired lamellar morphologies for application towards barrier materials.

2.2 Experimental Section

Materials

Acrylonitrile (AN, 99%) and styrene (S, 99%), were purchased from Sigma-Aldrich and purified by passing through a column of basic alumina (Brockmann, Type 1, 150 mesh) mixed with 5% calcium hydride (90– 95%, reagent grade), then sealed with a head of nitrogen and stored in a refrigerator until needed. Hexane (98.5%), methanol (99.8%), methylene chloride (99.5%), N, N-dimethylformamide (DMF, 99.8%) and tetrahydrofuran (THF, 99.9%) were obtained from Fisher and used as received. Ethylenediamine (≥99%), magnesium sulphate (97%+), butylated hydroxytoluene (BHT) and thiophenol (97%) were purchased from Sigma-Aldrich and used as received. Benzylamine (99%) was purchased from Acros Organics and used as received. N-(2-methylpropyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)-O-(2-carboxylprop-2-yl) hydroxylamine (BlocBuilder®, 99%), and maleic anhydride grafted linear low density poly(ethylene) (MA-PE) with the trade name Orevac 18302N were obtained from Arkema and used as received. The MA-PE has a melt flow index of 1.70 g/10 min (ASTM 1238/E), a melting temperature of 126 °C and a glass transition temperature of -42 °C. N-hydroxysuccinimide (98%) and N, N'-dicyclohexylcarbodiimide (DCC, 99%) were received from Sigma-Aldrich and used in conjunction with BlocBuilder® to synthesize the N-succinimidyl ester terminated alkoxyamine BlocBuilder (NHS-BlocBuilder) using the same procedure as Vinas et al.[63] PS; (number average molecular weight M_n = 13.0 kg/mol, polydispersity index M_w/M_n = 1.10) and PAN; (M_n = 60.6 kg/mol, M_w/M_n = 1.70) were used as standards for Fourier transform infrared spectroscopy (FTIR) to determine copolymer composition and were obtained from Scientific Polymer Products Inc.

Synthesis of poly(styrene-acrylonitrile) with NHS-BlocBuilder

A nitroxide mediated copolymerization of S/AN in 50wt% N, N-dimethylformamide (DMF) was conducted at 110 °C, using NHS-BlocBuilder. Properties of the resulting polymer (NHS-SAN) can be seen in Table 1. The polymerization was performed in a 50 mL three-neck round bottom glass flask equipped with a magnetic stir bar, condenser, and thermal well. The flask was set inside a heating mantle and placed on a magnetic stirrer. The central neck was connected to a condenser and capped with a rubber septum with a needle to relieve pressure applied by the nitrogen purge throughout the reaction. A thermocouple was connected to a controller and inserted into the second neck of the flask. NHS-BlocBuilder (0.189 g, 0.394 mmol), and the stirrer were added via the third neck of the flask, which was then sealed with a rubber septum. Previously purified S (7.105 g, 68.3 mmol), AN (2.419 g, 45.6 mmol), and DMF (9.530 g, 108 mmol) were each injected into the flask via syringe. As stirring began and the monomers were well mixed, the chilling unit using a glycol/water mixture that is connected to the condenser was set to 7 °C. A nitrogen flow was introduced to purge the solution for 30 min. The reactor was then heated to 110 °C at a rate of about 8.5 $°C \cdot min^{-1}$ while maintaining the purge. Once the reaction reached a temperature of 100 °C, this was taken as the initial point of the reaction and the reaction was left for 165 min. The reaction mixture was allowed to cool to room temperature. The final polymer was precipitated in methanol, vacuum filtered, and then dried overnight in a vacuum oven at 50 °C. The initial molar composition, $f_{AN,0}$, was 0.40, which is near the copolymer composition azeotropic point.[64] The target number average molecular weight ($M_{n,\ target}$) at complete conversion, calculated by the mass of monomer relative to the moles of NHS-BlocBuilder initiator, was set to 24 kg · mol^{-1}. The final yield of NHS-SAN after 165 min was 4.7 g (47% conversion of monomers based on gravimetry) with number-average molecular weight M_n = 17.2 kg · mol^{-1} and polydispersity index M_w/M_n= 1.12 determined by gel permeation chromatography (GPC) calibrated relative to linear PS standards in THF at 35 °C. The AN molar composition of the SAN copolymer using FTIR was F_{AN} = 0.43.

Table 1. Properties of the poly(styrene-acrylonitrile) polymers.

Sample	**End Group**	**SG1 Present?**	**M_n [kg · mol^{-1}]$^{a)}$**	**$M_w/M_n$$^{b)}$**	**$F_{AN}$$^{c)}$**	**Tg (°C)$^{d)}$**
NHS-SAN	NHS	Yes	17.2	1.12	0.43	-
NHS-SAN-D	NHS	No	16.7	1.13	0.43	109
NH_2-SAN	Primary amine	No	18.7	1.09	0.42	-
BzAm-SAN	Benzyl amide	No	18.6	1.08	0.42	-

[a] Number average molecular weight measured using gel permeation chromatography;
[b] Polydispersity index measured using gel permeation chromatography;
[c] Mole fraction of the polymer made up of acrylonitrile;
[d] Glass transition temperature measured using differential scanning calorimetry

Removal of the SG1 End-Group from SAN Copolymer for Chain-End Thermal Stability

Permanent removal of the N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl) nitroxide] (SG1) radical was performed as done previously.[65] With the same set-up as described in the previous section, NHS-SAN copolymer (4.506 g, 0.262 mmol, 17.2 kg · mol^{-1}, $M_w/M_n = 1.12$, $F_{AN} = 0.43$) and DMF (18.705 g, 212 mmol) were added to the 50 mL round bottom flask, and it was sealed as before. A nitrogen flow was introduced to purge the solution for 30 min. Thiophenol (0.37 g, 3.4 mmol) was injected into the reaction mixture via syringe. The reactor was heated to 110 °C at a rate of about 8.5 °C · min^{-1} while maintaining the purge. The reaction was left stirring at 110 °C for 270 min. The solution was allowed to cool to room temperature, and the polymer was precipitated in methanol, vacuum filtered, and dried overnight in a vacuum oven at 50 °C. The final yield after 270 min was 4.0 g (90% yield) with number-average molecular weight $M_n = 16.7$ kg/mol and polydispersity index $M_w/M_n = 1.13$ determined by GPC calibrated relative to linear PS standards in THF at 35 °C. The AN molar composition of the SAN copolymer using FTIR was $F_{AN} = 0.43$. As SG1 has phosphorous in its structure, the removal of the SG1 end-group was confirmed using ^{31}P NMR spectroscopy. Thermal stability was measured using thermal gravimetric analysis (TGA). Properties of the resulting deactivated NHS-SAN polymer (NHS-SAN-D) are summarized in Table 1.

End-modification of PS and SAN oligomers and deactivated SAN polymer

Both primary amine end-functional and non-functional SAN were synthesized by reacting amines with the n-hydroxysuccinimidyl ester group of the NHS-SAN-D copolymers as done previously using a poly(isoprene) polymer.[66] NHS-SAN-D precursor (1.999 g, 0.120 mmol, 16.7 kg · mol^{-1}, M_w/M_n = 1.13, F_{AN} = 0.43) was dissolved in dichloromethane (40 mL) in a 125 mL single-neck glass round bottom flask. The flask was sealed with a rubber septum, and was fitted with a needle to relieve pressure. The stirring, dissolved mixture was purged with a flow of nitrogen for 30 min, then the purge and vent needle were removed from the flask. Ethylenediamine (0.25 mL, 27 times molar excess) was added to the flask by syringe and was allowed to stir at room temperature for 300 minutes. A precipitate of N-hydroxysuccinimide could be seen after 30 min of stirring. Once the reaction was complete, the mixture was twice washed with deionized water and then washed with brine. The mixture was then dried using magnesium sulphate, filtered, and dried under vacuum. The remaining polymer (NH_2-SAN, Table 1) was dissolved in THF, precipitated in hexanes and vacuum filtered. It was left in a vacuum oven overnight at 50 °C. The disappearance of the peaks at 1742 cm^{-1} and 1676 cm^{-1} using FTIR indicated a disappearance of the ester linkage.

The remaining NHS-SAN-D (1.999 g, 0.120 mmol, 16.7 kg · mol^{-1}, M_w/M_n = 1.13, F_{AN} = 0.43) was modified in a similar reaction, but using benzylamine instead of ethylenediamine. This resulted in a non-functional benzylamide terminated SAN (BzAm-SAN, Table 1) for comparison against the reactive SAN.

Melt Rheology of SAN and MA-PE

Sample discs of MA-PE of 1 mm thickness and 25 mm diameter (~0.6 g) were prepared in a Carver model 3857 hot press at 190 °C and 12 tons clamping force between poly(tetrafluoroethylene) sheets. The discs were left at this force for 30 minutes, with quick pressure releases at ten minute intervals to remove any gas bubbles. The discs were cooled under 12 tons of clamping force by water-cooling the plates at a rate of 40 °C · min^{-1}. Sample discs of NHS-SAN (with 0.05 wt.% BHT as an antioxidant) of 1 mm thickness and 25 mm diameter (~0.6 g) were also prepared in a Carver model 3857 hot press at 160 °C and 10 tons clamping force between poly(tetrafluoroethylene) sheets. The discs were left at this force for 9 minutes, with quick pressure releases at three minute intervals to remove any gas bubbles. The discs were cooled under 10 tons of clamping force by water-cooling the plates at a rate of 40 °C · min^{-1}.

Rheology measurements were performed on the MA-PE and NHS-SAN polymers using an Anton Parr MCR302 parallel plate rheometer using a frequency sweep experiment at a temperature of 200 °C. The strain was kept below 10% to stay within the linear viscoelastic regime. Angular frequency was varied between 0.01 and 600 s^{-1}.

Melt blending of SAN copolymers and poly(styrene-maleic anhydride)

NH_2-SAN was melt blended with a previously made poly(styrene-maleic anhydride) (SMA) copolymer with 15 mol% maleic anhydride content.[67] There was a 5:1 molar ratio of maleic anhydride to primary amine groups. Amine functional SAN (0.50 g) and SMA (0.10 g) were mechanically blended at room temperature, and then were fed into a miniature conical co-rotating twin screw extruder (Haake Minilab) at 180 °C. The screw speed was set to 50 rpm. After 5 min of mixing in the extruder, the polymer was scraped off the screws, as the sample mass was not sufficient enough to be pushed out through the die. As a comparison, BzAm-SAN was also blended with SMA using the same procedure. Blended polymers were characterized using GPC against PS standards at 35 °C in THF.

Melt Blending of SAN copolymers and Maleic Anhydride Grafted Polyethylene

NH_2-SAN (0.71 g, 20 wt.%) and MA-PE (2.83 g, 80 wt.%) were mechanically mixed at room temperature, then fed into the same miniature twin screw extruder at 200 °C. The screw speed was set to 150 rpm. The material was in the extruder for 15 minutes and then quenched immediately (within 15 seconds) in liquid nitrogen to maintain the morphology of the blend. The same procedure was followed for the BzAm-SAN copolymer. Due to the insolubility of MA-PE in THF, GPC could not be used for characterization for any block copolymer formation, so electron microscopy was used to determine the microstructure of the blend that in turn could be used to infer whether any reaction occurred. Samples were also annealed under vacuum at 110 °C (above the glass transition temperatures of SAN and MA-PE) and 140 °C (above the melting point of MA-PE) for 18 hours to compare against the quenched samples to determine the stability of the microstructure.

Reorientation of SAN Domains Using a Channel Die

MA-PE/SAN blends were exposed to unidirectional reorientation within a channel die done using a method shown previously.[68] The channel was 6 mm wide by 15 mm deep by 60 mm long (Figure 2). MA-PE/SAN blend samples of 0.14 g each were first pressed into a rectangular shape 6 mm by 15 mm by 2 mm to ensure unidirectional flow within the channel die (Figure 3). The channel die was heated between the two platens of the hot press at 180 °C. The rectangular piece of MA-PE/SAN blend was put in the centre of the channel such that the 6 mm and 15 mm dimensions of the polymer fit tightly into the channel die, and the plunger was placed on top of the die. The assembly was placed between the hot press platens on top of a poly(tetrafluoroethylene) sheet. The platens were closed lightly to allow the assembly to heat up for 1 minute. Then the platens were pushed together at a constant rate until polymer ribbons were extruded from both ends of the channel (Figure 4). Applied clamping force did not exceed 4 tons. The polymer ribbons were removed gently with tweezers and immediately quenched in liquid nitrogen for several minutes to ensure that the morphology was frozen in.

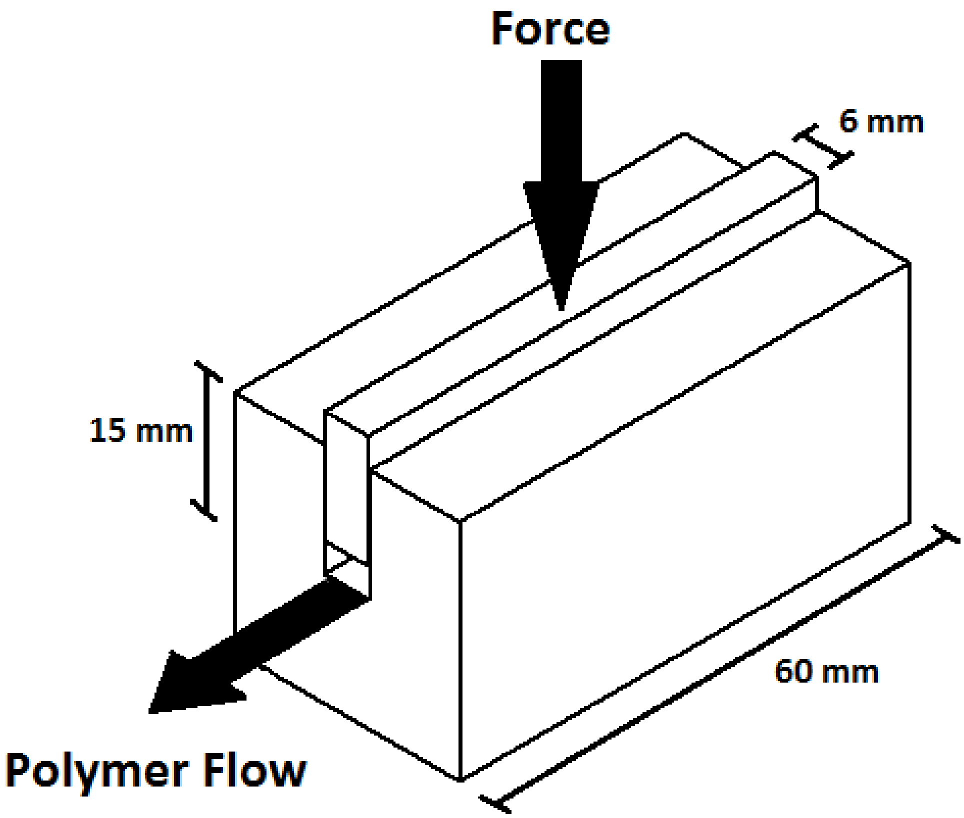

Figure 2. Direction of polymer flow in the channel die.

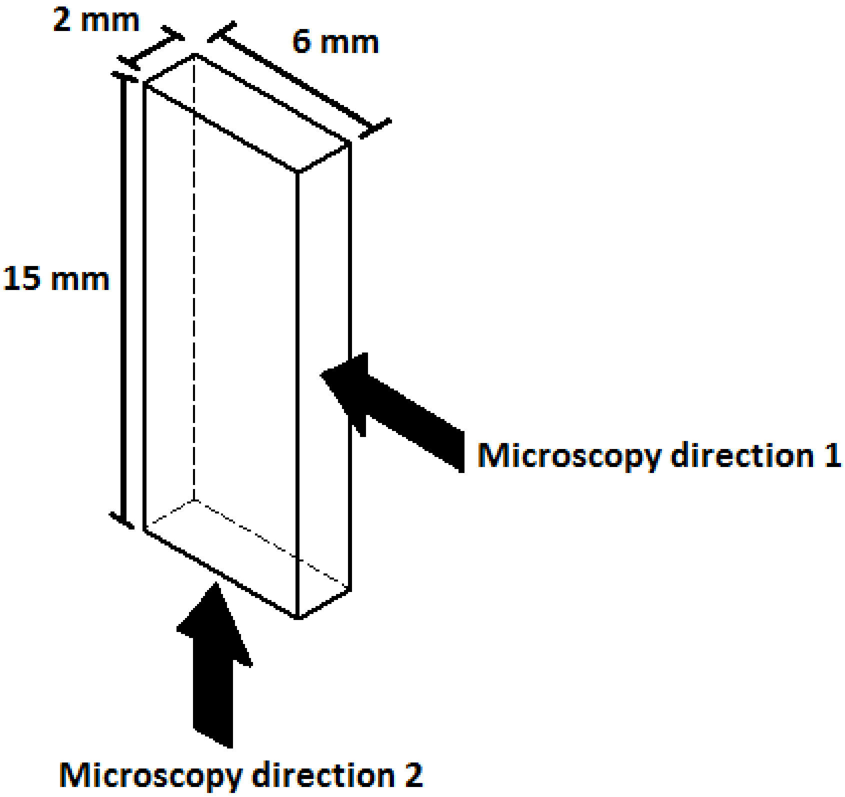

Figure 3. Diagram of polymer blends pressed into rectangles for reorientation.

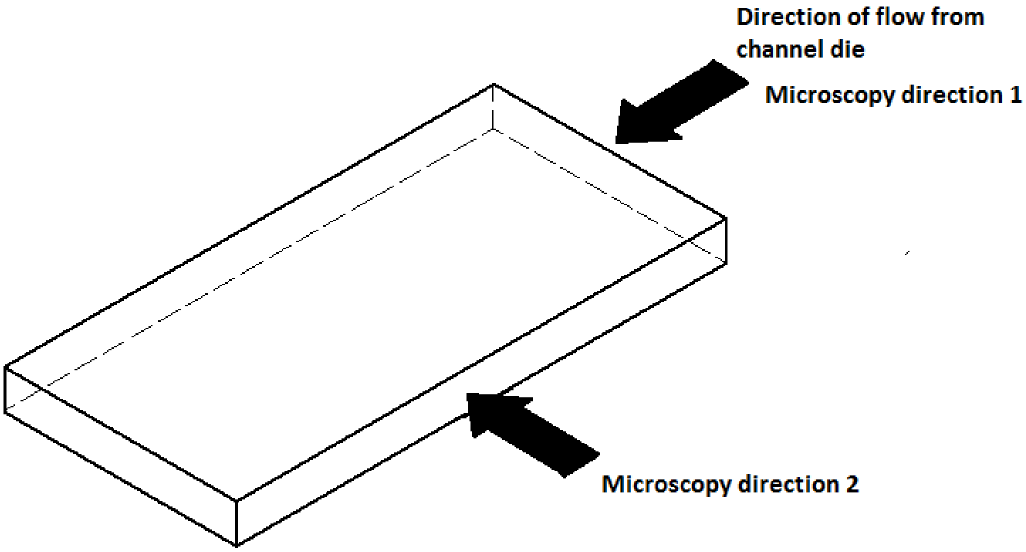

Figure 4. Representation of extrudate from channel die.

Sample Preparation for Microscopy

For the MA-PE/SAN blends, quenched samples were freeze fractured in liquid nitrogen and then glued onto aluminum stubs. After thorough drying, the samples were then placed in THF for 60 minutes to selectively remove the dispersed SAN phase. The samples were sputter-coated with 20 Å of Au-Pd to make the sample conductive, and then viewed with a Hitachi S-4700 Field Emission Scanning Electron Microscope (FE-SEM) at an accelerating voltage of 10 kV.

Image Analysis

To better resolve the minor phase drops from each other and the MA-PE matrix, the particles were traced onto a transparency and scanned at a resolution of 300 dpi. From the scanned transparency, the particle areas were measured using ImageJ Version 1.45s software. The areas were converted to an equivalent sphere diameter. At least 300 particles were counted from each sample to ensure reliable statistics. The size of the dispersed phase was characterized by the volume to surface average diameter, $\langle D \rangle_{VS}$. $\langle D \rangle_{VS}$ gives the average interfacial area per unit volume, which can be used to determine how much graft copolymer is formed at the polymer/polymer interface.[69] The error in particle size has been found to be small (10%), so stereological corrections were not used.[69]

Characterization

Molecular weights (number average molecular weight M_n, weight average molecular weight M_w) and polydispersity index M_w/M_n were estimated using gel permeation chromatography (Waters Breeze) with THF as the mobile phase at a flow rate of 0.3 mL · min^{-1}. The GPC was equipped with three Styragel® HR columns (HR1 with molecular weight measurement range of 10^2 to 5×10^2 g · mol^{-1}, HR2 with molecular weight measurement range of 5×10^2 to 2×10^4 g · mol^{-1} and HR4 with molecular weight measurement range of 5×10^3 to 6×10^5 g · mol^{-1}) and a guard column. The columns were kept at 35 °C during the analysis and the molecular weights were estimated relative to linear PS standards. The GPC was equipped with both differential refractive index (RI 2410) and ultraviolet (UV 2487) detectors for which the RI detector was used solely for the experiments described herein.

Attenuated total reflectance (ATR) FTIR (Spectrum BX, Perkin-Elmer) was used to determine the molar compositions of the SAN copolymers. An ATR correction was used on the spectra. The peak absorbances at 700 cm^{-1} and 2240 cm^{-1} were used as markers for S and AN, respectively. To precisely identify the copolymer compositions, 6-point calibration curves were constructed with mixtures of PS and PAN standards. This has been shown to be a relatively effective way to determine SAN copolymer composition [62].

Thermal gravimetric analysis (TGA; Q500 from TA Instruments) was used to determine the thermal stability of the SAN copolymers before and after SG1 removal. The temperature was increased at 20 °C · min^{-1} from 25 °C to 700 °C.

Differential scanning calorimetry (DSC; Q2000 from TA Instruments) was used to determine the glass transition temperature and the melting temperature of the polymers. A heat, cool, heat cycle was done with a temperature range of -90 °C to 200 °C, and measurements from the second heat were used as the first cycle was used to remove any thermal history. The DSC temperature was calibrated using Indium.

^{31}P NMR was done on a 200 MHz Varian Mercury instrument with 512 scans done on each sample to determine if the phosphorous group from the SG1 initiator was cleaved.

2.3 Results and Discussion

Thermal Stability of Polymers

At temperatures above 70 °C, the SG1 radical can easily dissociate from the polymer, forming free radicals which can lead to a depropogation process.[65] Since the SAN was to be blended in an extruder at 200 °C, it was important for it to be thermally stable. The SG1-terminated SAN polymers were deactivated using thiophenol, and TGA was performed on the SAN before and after SG1 removal. The results (Figure 5) agreed with those found by Nicolas et al who did the same experiment using poly(methyl methacrylate-*ran*-acrylonitrile) synthesized with BlocBuilder®.[65] At 200 °C, 97.0% of the living SAN polymer remained, and 99.5% of the deactivated SAN remained. TGA also showed that 100.0% of the PE remained at 200 °C.

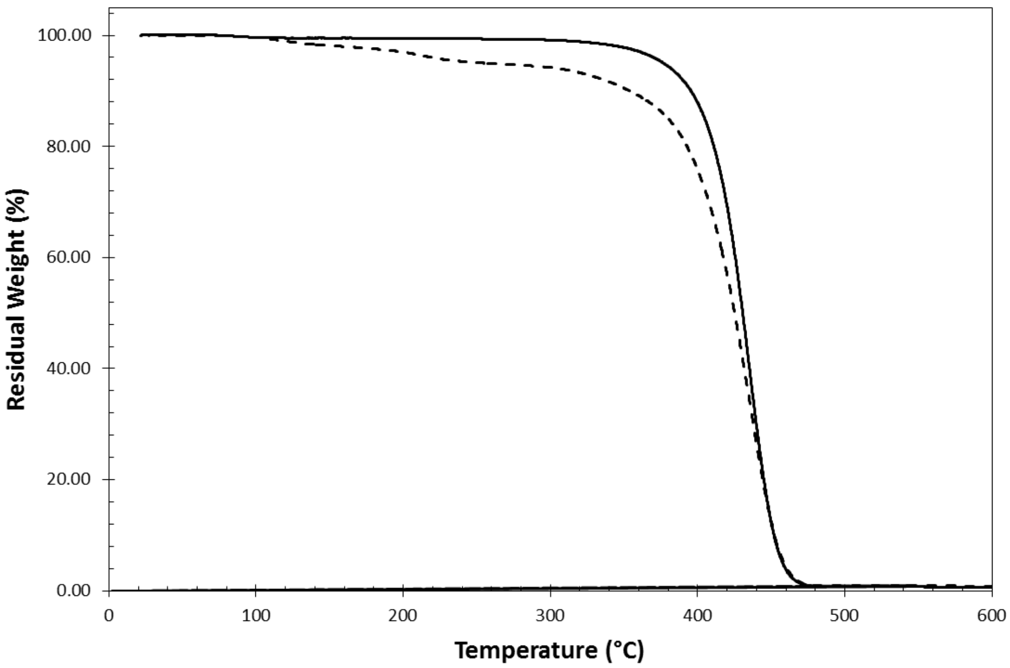

Figure 5. Thermal gravimetric analysis of NHS-SAN polymer before (dotted line) and after (solid line) SG1 removal.

End-group modification of SAN

Half of the NHS-SAN copolymer was reacted with ethylenediamine to form amine-terminated SAN (NH_2-SAN). The other half was reacted with benzylamine to form non-functional SAN (BzAm-SAN) for comparative purposes. Due to the size of the polymer chains, it was difficult to detect the appearance of primary amine end groups using the FTIR spectra, but the peaks at 1742 and 1676 cm^{-1} caused by the ester linkage of the NHS group (COO-NHS) clearly disappeared after both end-group reactions (Figure 6). The *Supporting Information* (Section 3) shows more evidence that this reaction went as expected by showing analysis of low molecular weight PS and SAN oligomers, which underwent the same chain end modification reactions.

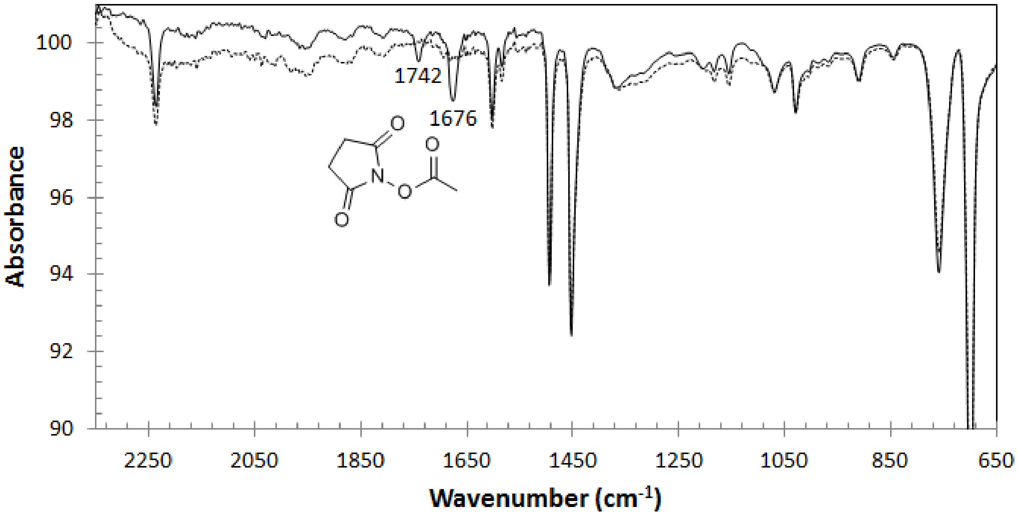

Figure 6. FTIR spectra of deactivated NHS-SAN polymer before (solid line) and after (dotted line) amine functionalization reaction. Disappearance of peaks at 1676 and 1742 cm^{-1} indicate the removal of the NHS ester linkage.

Reactive Blending of SAN and SMA

Non-functional and functional SAN polymers were melt blended with a previously made SMA copolymer to confirm the reactivity of the SAN in a way that could be characterized by GPC since PE does not have a common solvent with the SAN for GPC analysis. This homogeneous reaction also serves to show that the coupling reaction works in the absence of any interface between the two polymers to be blended. The GPC plot in Figure 7a shows the results of the BzAm-SAN blended with the SMA. The elution time peak of the blend shows no difference from the peaks of the individual polymers, indicating that no reaction occurred. Figure 7b shows the results from the blend of NH_2-SAN with SMA. The blend shows a peak formed at a lower elution time, indicating that a higher molecular weight graft copolymer was formed during the extrusion process. The majority of the blend still shows the same peak as the pure polymers, which can be explained by the molar excess of SMA functional groups relative to the NH_2-SAN amine groups.

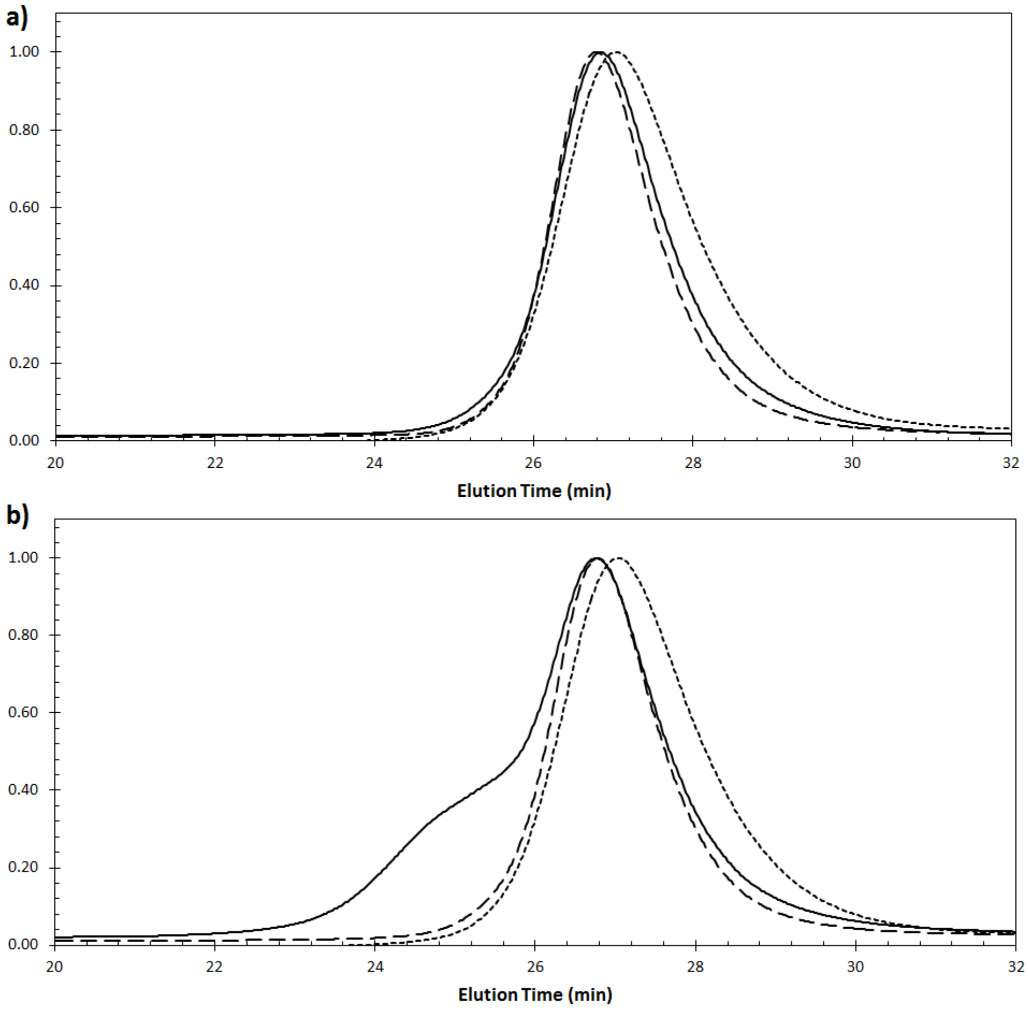

Figure 7. GPC results for a) poly(styrene-ran-maleic anhydride) (SMA; dotted line) and poly(styrene-ran-acrylonitrile) (BzAm-SAN, Table 1; dashed line) homopolymers and the blend consisting of SMA and BzAm-SAN. Blend is shown as the solid line. b) GPC results for SMA (dotted line), amine terminated SAN (NH_2-SAN, Table 1; dashed line), and the blend consisting of SMA and NH_2-SAN. Blend is shown as the solid line.

Rheology of SAN and MA-PE

Complex viscosity measurements for SAN and MA-PE are shown in Figure 8a against varying angular frequency. Storage modulus and loss modulus are shown in Figure 8b. Shear rate was estimated at both the top and bottom of the screws by dividing the linear screw speed by the gap distance. At the top, where the screws are widest and have the highest linear velocity, the shear rate is approximately 80 s^{-1}. At the bottom, where the screws are the narrowest, the shear rate is approximately 25 s^{-1}. By assuming the Cox-Merz rule applies, we tried to match the steady shear rates in the extruder to the oscillatory shear rates in the rheometer. Therefore, the viscosity conditions within the extruder were approximated using the rheology measurements at 200 °C and angular frequency of 64 s^{-1} which is the volume average shear rate within the extruder. At these conditions, the complex viscosity of the MA-PE was 1200 Pa · s, and the complex viscosity of the SAN was 26 Pa · s and thus the viscosity ratio was 0.02 at these conditions. For optimal blending, and to minimize the particle size of the dispersed phase, the viscosity ratio of the dispersed phase to the matrix phase should be as close to unity as possible.[70-75] Obviously, the viscosity ratio plays an important role in achieving the minimum particle size – however many blends still achieve sub-micron dispersions during reactive blending with low viscosity ratios.[6]

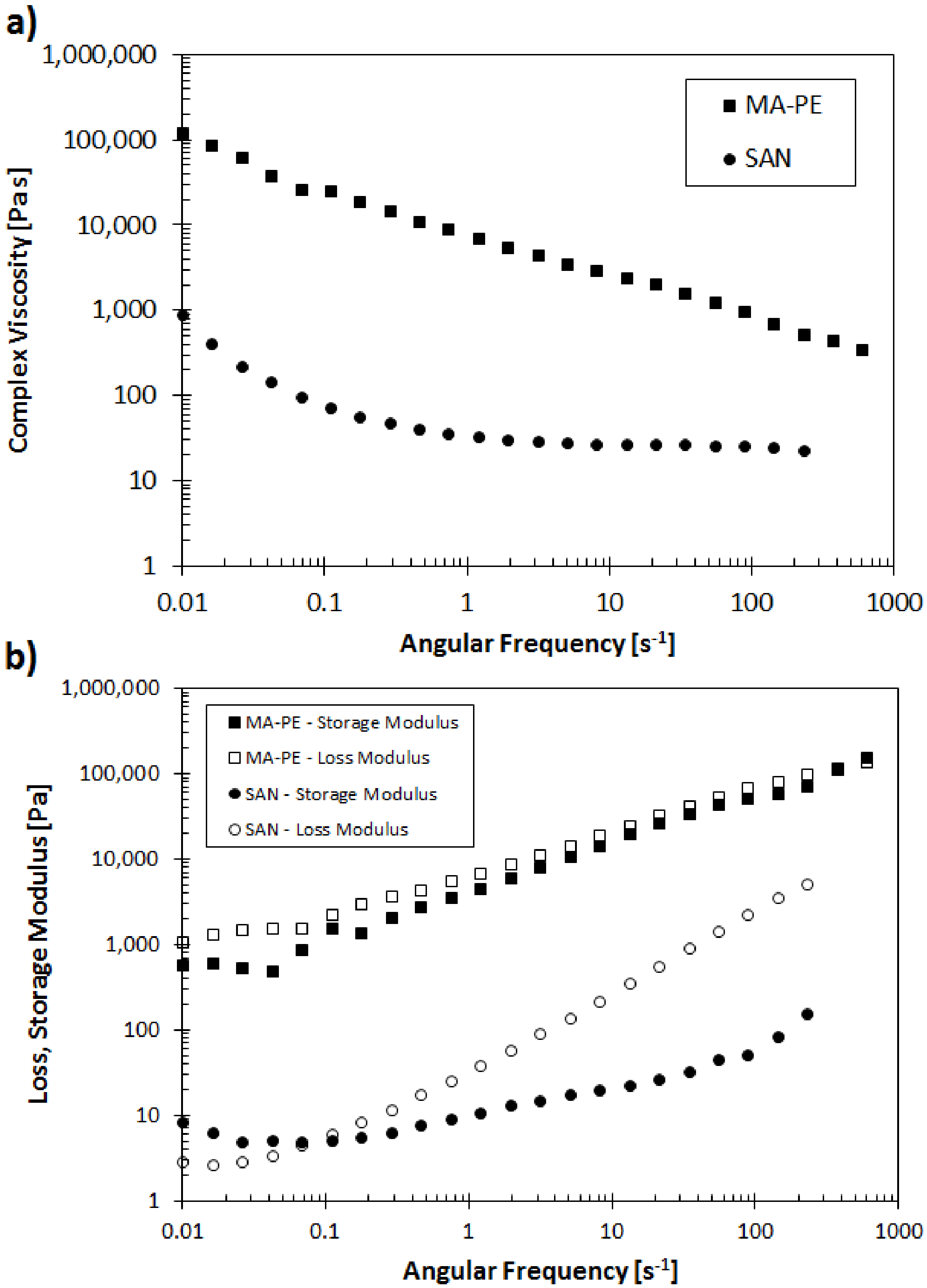

Figure 8. (a) Complex viscosity measurements of maleic anhydride grafted poly(ethylene) (MA-PE) and poly(styrene-acrylonitrile) (NHS-SAN, Table 1) at 200 °C. (b) Storage modulus and loss modulus of maleic anhydride grafted poly(ethylene) (MA-PE) and poly(styrene-acrylonitrile) (NHS-SAN, Table 1) at 200 °C

Reactive Blending of SAN and MA-PE

NH_2-SAN and BzAm-SAN polymers were separately melt blended with MA-PE at a 20 wt.% SAN loading which is typical for PE barrier blends.[17] It was expected to form imide bonds between the primary amine end group of the NH_2-SAN and the maleic anhydride groups, which are found randomly along the MA-PE backbone. This would form graft copolymers, which would stabilize the interface between the immiscible MA-PE and NH_2-SAN phases and prevent dispersed phase coalescence and thus a relatively small dispersed SAN phase domain size would result. The non-functional SAN does not have primary amine groups and would not have the opportunity to form stabilizing graft copolymers. This non-stable blend should result in large dispersed SAN domains that were unstable upon further annealing.

SEM images of the blends are shown in Figure 9 and blend morphology characterization in shown in Table 2. $\langle D \rangle_{VS}$ for the MA-PE/NH_2-SAN blend was 2.6 µm, while $\langle D \rangle_{VS}$ for the MA-PE/BzAm-SAN blend was 9.7 µm. This indicates that the MA-PE/NH_2-SAN blend was able to prevent dynamic coalescence much better compared to the MA-PE/BzAm-SAN blend, as was expected. The amine functionalized SAN successfully reacted with the MA-PE to form a stabilizing graft copolymer at the interface between the NH_2-SAN and MA-PE. Some studies have reported sub-micron dispersed phase domain sizes when blending primary amine functional polymers with anhydride functional polymers,[57, 69] indicating that the blends presented here have not achieved the smallest possible dispersed particle size for this reactive pairing. However, the larger particle sizes presented here can be explained by the low viscosity ratio of the SAN to the MA-PE. With a viscosity ratio closer to unity, better dispersion would be achieved, and smaller SAN domains would be present. However, this study was limited to using a high viscosity MA-PE, which was obtained commercially. Higher molecular weight SAN polymers approaching 100,000 g · mol^{-1} are attainable by NMP,[76] and these will be investigated in the future in the form of acrylonitrile-containing block copolymers.

Table 2. Summary of blend microstructure for extruded blends and annealed blends

Sample	**SAN Used**	**SAN/PE (wt.%)**	**Annealing Conditions**	**$(D)_{vs}$ (μm)[a)]**
f-SAN	NH_2-SAN	20 / 80	None	2.6
f-SAN-110	NH_2-SAN	20 / 80	18 h at 110 °C	3.2
f-SAN-140	NH_2-SAN	20 / 80	18 h at 140 °C	2.1
nf-SAN	BzAm-SAN	20 / 80	None	9.7
nf-SAN-110	BzAm-SAN	20 / 80	18 h at 110 °C	11.4
nf-SAN-140	BzAm-SAN	20 / 80	18 h at 140 °C	8.8

a)Volume to surface area average diameter

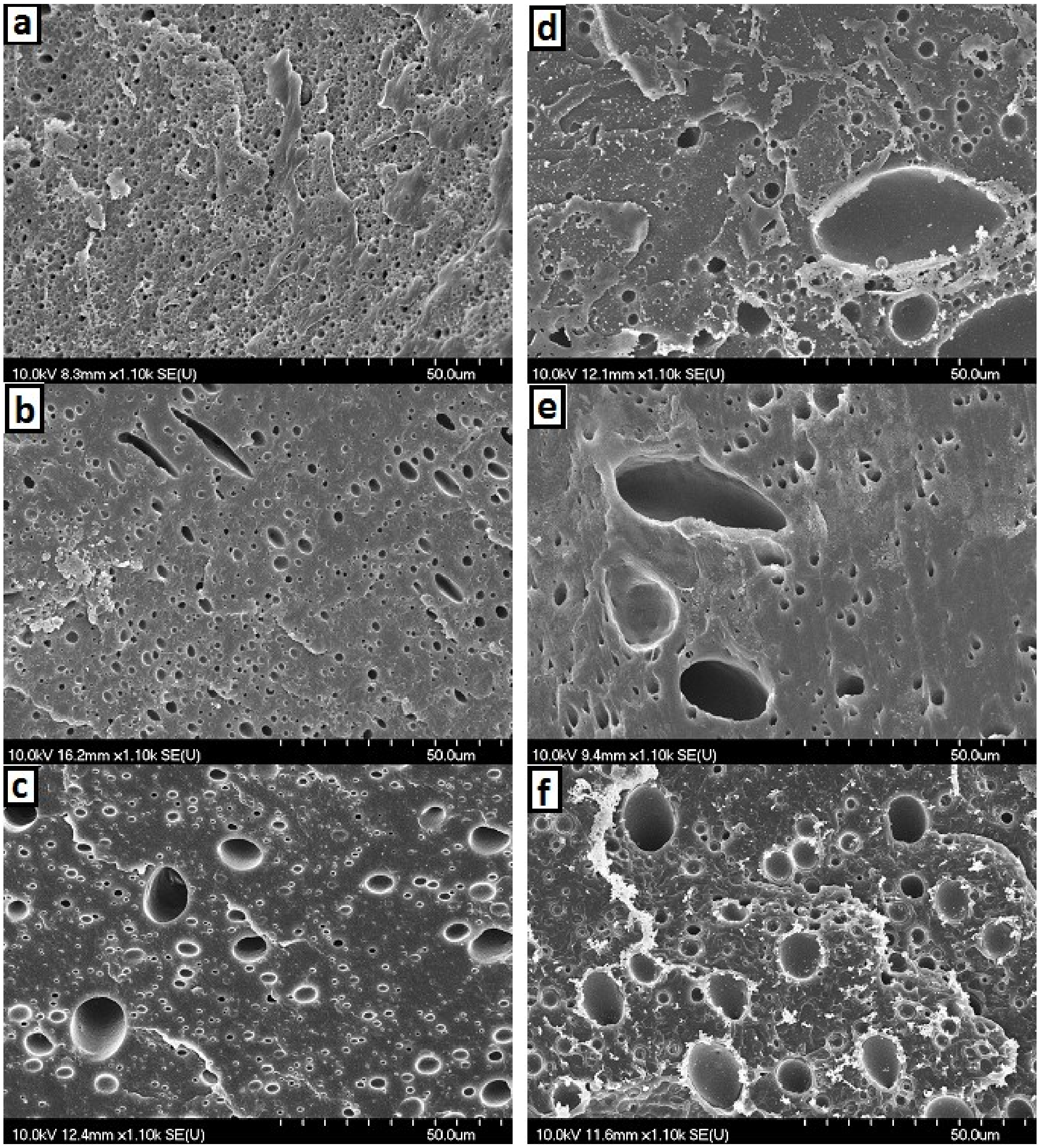

Figure 9. SEM images of a) MA-PE/NH$_2$-SAN (80/20) after extrusion and freeze-fracturing, b) MA-PE/NH$_2$-SAN (80/20), annealed at 110 °C, c) MA-PE/NH$_2$-SAN (80/20), annealed at 140 °C, d) MA-PE/BzAm-SAN (80/20), e) MA-PE/BzAm-SAN (80/20), annealed at 110 °C for 18 h, f) MA-PE/BzAm-SAN (80/20), annealed at 140 °C for 18 h. SAN phase was removed using THF before microscopy to show contrast between phases.

To test the stability of the blends, thermal annealing was done on the samples at both 110 °C and 140 °C. The first temperature was above the glass transition temperature of both the MA-PE and SAN, but below the crystalline melting temperature of the MA-PE. The second temperature was above the melting point of the MA-PE. In both cases, the annealing was done for 18 h, which should have been long enough to observe any static coalescence effects. $\langle D \rangle_{VS}$ of the annealed blends are also shown in Table 2. At 110 °C, there was a slight coarsening of the particles, but at 140 °C, there was not a significant difference in the particle size for either the functional or non-functional blends. This seems to indicate that static coalescence is slow. However, since the functional SAN blend consistently gives a smaller $\langle D \rangle_{VS}$ than the non-functional SAN blend, it can be firmly concluded that the reactive blending contributed to the prevention of dynamic coalescence.

Reorientation of SAN Domains

A channel die was used to modify the morphology of the SAN domains within the MA-PE matrix (Figure 2). The goal was to stretch the SAN droplets into lamellar structures, which would provide better barrier properties due to higher tortuosity within the blend. A narrow channel die was used to achieve unidirectional flow similar to what is found inside a blow molding machine. To ensure unidirectional flow within the channel die, the extruded MA-PE/SAN blend samples were pressed into a rectangular shape that would fit the dimensions of the die well (Figure 3). However, this also added an extra application of heat and shear to the molten blend. For this reason, SEM micrographs were taken to quantify if any changes in SAN domain size occurred (Figure 10a,b,d,e). Images were taken on two perpendicular planes of the rectangles to ensure spherical SAN domains. $\boldsymbol{\langle D \rangle_{VS}}$ for the functional and non-functional blends are shown in

Table 3. The SAN domains are smaller in these samples than in the extruded samples. It is possible that by adding the compression force on the molten blends, further particle break-up was achieved. It cannot be concluded that further interfacial reaction occurred with the functional SAN blend, because the non-functional SAN blend also reduced the SAN domain size and thus the particle size reduction must be due to additional deformation.

The rectangular polymer blend samples were pressed from a length of 2 mm to a length of 60 mm within the channel die. The height of the sample started at 15 mm and ended up at 0.5 mm. This gives an extension ratio of 30. The width of the sample was constant at 6 mm. Uni-dimensional flow was confirmed by taking SEM images of the reoriented samples in the cross direction (microscopy direction 1 in Figure 4) and verifying that the SAN domain surfaces remained circular. The SEM images (Figure 10c,f) of the perpendicular face (microscopy direction 2 in Figure 4) show that the droplets did stretch and coalesce into longer domains. These elongated domains of the NH_2-SAN phase had an average aspect ratio of 14.5 (length divided by diameter), with average length of 14.7 μm and diameter of 1.0 μm. If the lamellar domains are assumed to be cylinders, the average volume is 18.1 μm^3. Given the average volume of the original SAN particles was only 0.8 μm^3, several particles must have coalesced during the shear flow to form the elongated domains. The BzAm-SAN blends did not possess sufficiently elongated domains to calculate average dimensions. Since the interface of these materials is not compatibilized, it is likely that the SAN domains coalesced into large domains. Consequently, the NH_2-SAN/PE blends were more amenable to SAN domain reorientation as coalescence could be prevented and allow for better stability of the resulting structures.

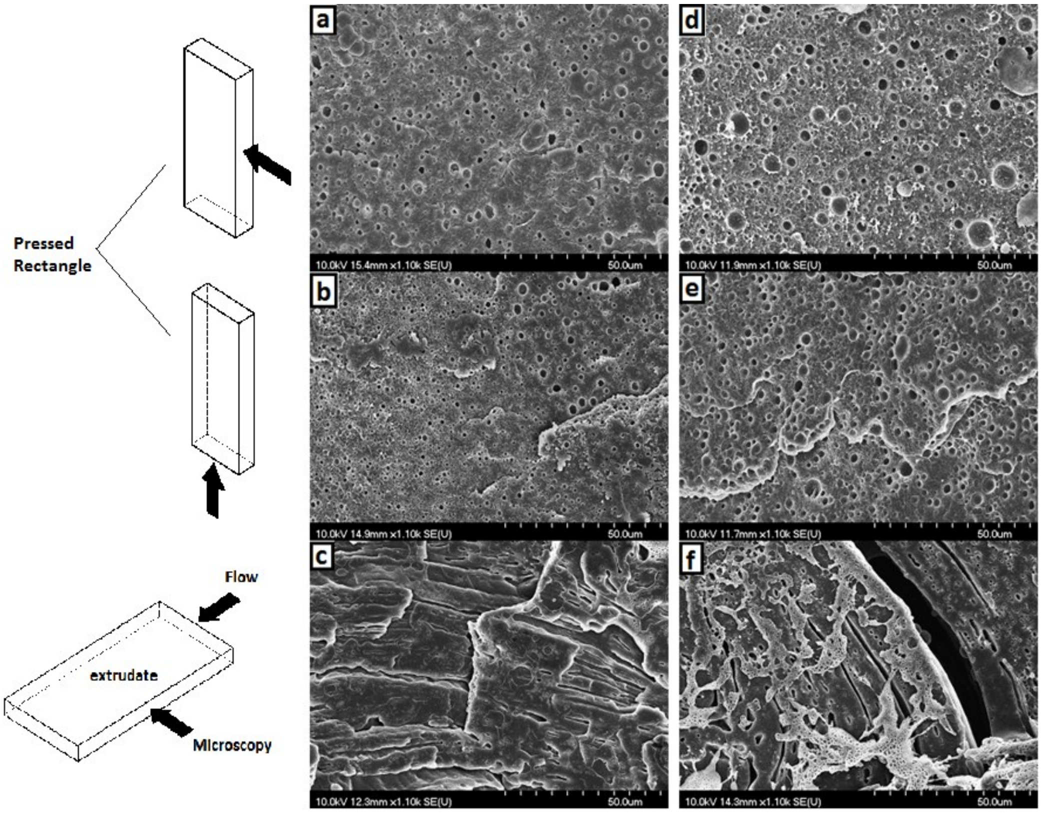

Figure 10. SEM images of a) MA-PE/NH_2-SAN (80/20) pressed into rectangle, b) MA-PE/NH_2-SAN (80/20) pressed into rectangle, c) MA-PE/NH_2-SAN (80/20) pressed in channel die d) MA-PE/BzAm-SAN (80/20), pressed into rectangle, e) MA-PE/BzAm-SAN (80/20), pressed into rectangle, f) MA-PE/BzAm-SAN (80/20), pressed in channel die.

Table 3. Summary of dispersed SAN particle size for blends pressed into rectangles (Figure 3)

Sample	$\langle D \rangle_{VS}$ **(μm)**
f-SAN blend (direction 1)	1.7
f-SAN blend (direction 2)	1.0
nf-SAN blend (direction 1)	4.4
nf-SAN blend (direction 2)	2.6

2.4 Conclusions

In this study, acrylonitrile-containing copolymers with primary amine end groups at the chain end were successfully synthesized in a controlled manner by nitroxide mediated polymerization and subsequent chain end transformation. These functional SAN polymers were melt blended with maleic anhydride functionalized poly(ethylene) (MA-PE). The blend morphology of the dispersed SAN phase was finer (~2 μm) when the functional NH_2-SAN was used instead of the non-functional BzAm-SAN (~10 μm), showing that the amine-functional polymers were enabling compatibilization of the blend by prevention of dynamic coalescence. Finally, using a channel die, the spherical SAN domains were stretched out to form a lamellar blend structure, which is desirable for barrier applications. Non-reactive blends could not form stable, elongated SAN domains within the PE matrix. These copolymers represent an initial iteration to make tailored acrylonitrile barrier polymers for poly(olefins) and future work will be directed towards tailoring of the dispersed phase morphology.

3 Supporting Information to the Manuscript

3.1 Experimental

Materials

Acrylonitrile (AN, 99%) and styrene (S, 99%), were purchased from Sigma-Aldrich and purified by passing through a column of basic alumina (Brockmann, Type 1, 150 mesh) mixed with 5% calcium hydride (90– 95%, reagent grade), then sealed under a head of nitrogen and stored in a refrigerator until needed.

Hexane (98.5%), methanol (99.8%), methylene chloride (99.5%), N, N-dimethylformamide (DMF, 99.8%) and tetrahydrofuran (THF, 99.9%) were obtained from Fisher and used as received. Ethylenediamine (≥99%), 1,4-Dioxane (99%) and magnesium sulphate (97%+) were purchased from Sigma-Aldrich and used as received. N-(2-methylpropyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)-O-(2-carboxylprop-2-yl) hydroxylamine (BlocBuilder® , 99%) was obtained from Arkema and used as received. N-hydroxysuccinimide (98%) and N, N'-dicyclohexylcarbodiimide (DCC, 99%) were received from Sigma-Aldrich and used in conjunction with BlocBuilder® to synthesize the N-succinimidyl ester terminated alkoxyamine BlocBuilder (NHS-BlocBuilder) using the same procedure as Vinas et al.[63] PS; (number average molecular weight M_n = 13.0 kg/mol, polydispersity index M_w/M_n = 1.10) and PAN; (M_n = 60.6 kg/mol, M_w/M_n = 1.70) were used as standards for Fourier transform infrared spectroscopy (FTIR) to determine copolymer composition and were obtained from Scientific Polymer Products Inc.

Synthesis of Poly(styrene) and poly(styrene-acrylonitrile) oligomers with NHS-BlocBuilder

A nitroxide mediated polymerization (NMP) of styrene (S), in 50 wt.% 1,4-dioxane was conducted at 110 °C using NHS-BlocBuilder to test the functionalization procedure without any acrylonitrile (AN). NMP S/AN copolymerizations in 50 wt.% *N, N*-dimethylformamide (DMF) were conducted at 110 °C, also using NHS-BlocBuilder. The polymerizations were performed in a 50 mL three-neck round bottom glass flask equipped with a magnetic stir bar, condenser, and thermal well. The flask was set inside a heating mantle and placed on a magnetic stirrer. The central neck was connected to a condenser and capped with a rubber septum with a needle to relieve pressure applied by the nitrogen purge throughout the reaction. A thermocouple was connected to a controller and inserted into the second neck of the flask. Table 4 describes the properties of the oligomers synthesized.

Table 4. Properties of the poly(styrene-acrylonitrile) oligomers.

Sample	$f_{St,0}$	$f_{AN,0}$	Polymerization time [min]	M_n [kg · mol^{-1}]$^{a)}$	$M_w/M_n$$^{b)}$	$F_{AN}$$^{c)}$
PS - oligomer	1.00	0	35	3.0	1.13	0
SAN-oligomer	0.60	0.40	29	2.9	1.30	0.29

a)Number average molecular weight measured using gel permeation chromatography;
b)Polydispersity index measured using gel permeation chromatography;
c)Mole fraction of the polymer made up of acrylonitrile.

For the S polymerization, 0.920 g of NHS-BlocBuilder, 28.870 g of 1,4-dioxane, and 28.855 g of S were added to the reactor. A nitrogen flow was introduced to purge the solution for 30 min. The reactor was then heated to 110 °C at a rate of about 8.5 °C · min^{-1} while maintaining the purge. Once the reaction reached a temperature of 100 °C, this was taken as the initial point of the reaction and the reaction was left for 35 min. The reaction mixture was allowed to cool to room temperature. The final polymer was precipitated in methanol, vacuum filtered, and then dried overnight in a vacuum oven at 50 °C. The target number average molecular weight ($M_{n,\ target}$) at complete conversion, calculated by the mass of monomer relative to the moles of NHS-BlocBuilder initiator, was set to 15 kg ·

mol^{-1}. The final yield of NHS-SAN after 35 min was 5.1 g (18% conversion of monomers based on gravimetry).

For the SAN copolymerization, 0.559 g of NHS-BlocBuilder, 14.040 g of DMF, 10.493 g of S and 3.555 g of AN were added to the reactor. A nitrogen flow was introduced to purge the solution for 30 min. The reactor was then heated to 110 °C at a rate of about 8.5 °C · min^{-1} while maintaining the purge. Once the reaction reached a temperature of 100 °C, this was taken as the initial point of the reaction and the reaction was left for 29 min. The reaction mixture was allowed to cool to room temperature. The final polymer was precipitated in methanol, vacuum filtered, and then dried overnight in a vacuum oven at 50 °C. The target number average molecular weight ($M_{n,\ target}$) at complete conversion, calculated by the mass of monomer relative to the moles of NHS-BlocBuilder initiator, was set to 12 kg · mol^{-1}. The final yield of NHS-SAN after 35 min was 3.0 g (21% conversion of monomers based on gravimetry).

End-modification of PS and SAN oligomers

Primary amine end-functional PS and SAN oligomers were synthesized by reacting ethylenediamine with the n-hydroxysuccinimidyl ester group of the oligomers as done previously.[66] The oligomer was dissolved in dichloromethane in a single-neck glass round bottom flask. The flask was sealed with a rubber septum, and was fitted with a needle to relieve pressure. The stirring, dissolved mixture was purged with a flow of nitrogen for 30 min, and then the purge and vent needle were removed from the flask. Ethylenediamine (27 times molar excess) was added to the flask by syringe and was allowed to stir at room temperature for 300 minutes. A precipitate of N-hydroxysuccinimide could be seen after 30 min of stirring. Once the reaction was complete, the mixture was twice washed with deionized water and then washed with brine. The mixture was then dried using magnesium sulphate, filtered, and dried under vacuum. The remaining polymer was dissolved in THF, precipitated in hexanes and vacuum filtered. It was left in a vacuum oven overnight at 50 °C.

3.2 Results and Discussion

Low molecular weight NHS-PS was reacted with ethylene diamine to form amine-terminated PS (NH_2-PS). Pure PS was investigated first since it was not clear if the ethylene diamine would react with the acrylonitrile.[77] An oligomer was used to get a better resolution for characterizing the end group of the polymer. It was attempted to verify this reaction by proton nuclear magnetic resonance spectroscopy (^{1}H NMR). There were new peaks formed, but proof was not obtained by this method for PS or SAN due to overlapping peaks. However, FTIR was performed on the polymers before and after the modification. Figure 11a shows a section of the spectra comparing the NHS-PS to the NH_2-PS in the relevant wavenumber range. There was a distinct disappearance of the absorbances at 1742, 1784, and 1810 cm^{-1} caused by the ester linkage of the NHS group (COO-NHS).[78] There was also disappearance of the peaks at 1204 and 1064 cm^{-1}, which represent the NHS moiety.[78] New stretches were formed at 1662 and 1522 cm^{-1} which correspond to amide I and amide II bands, respectively, for a primary amide.[78] This indicates that the amide bond was formed as planned, and these polymers possess primary amine functionalization at one chain end.

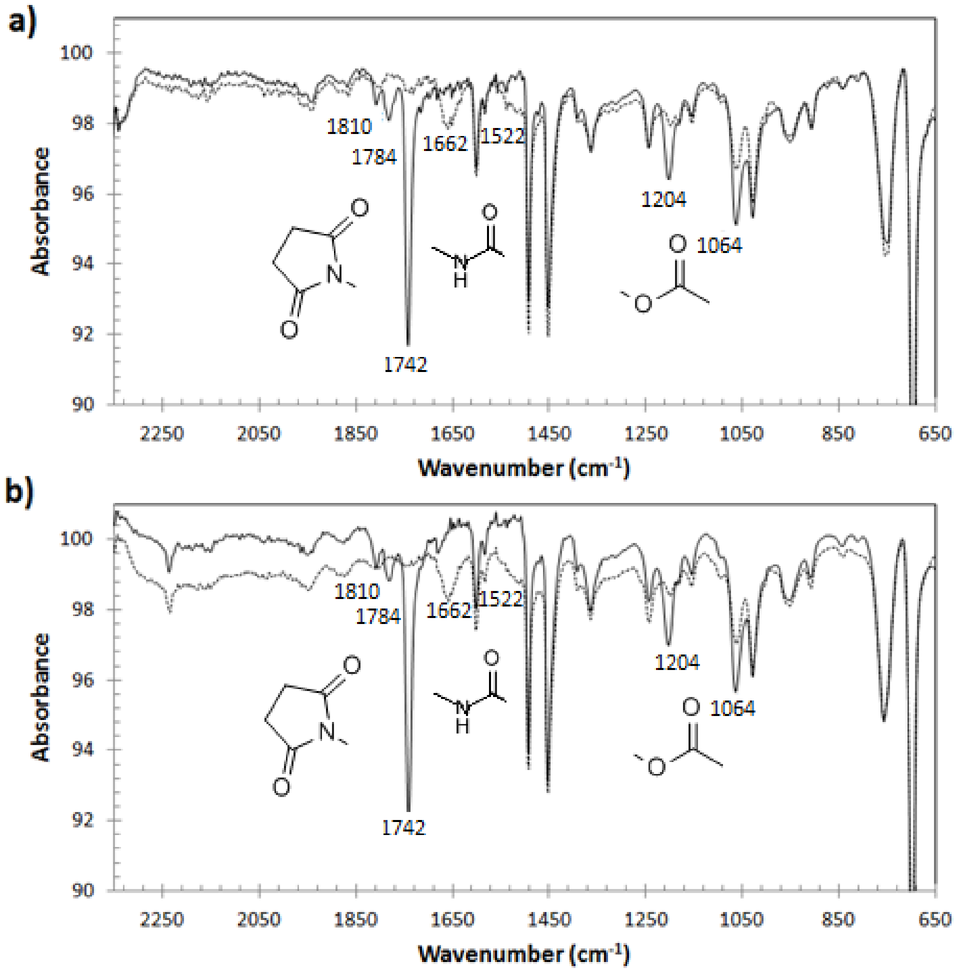

Figure 11. FTIR spectra of a) PS oligomer before (solid line) and after (dotted line) amine functionalization reaction. b) SAN oligomer before (solid line) and after (dotted line) amine functionalization reaction.

Similarly, NHS-SAN oligomer was reacted with ethylene diamine to form amine-terminated SAN (NH$_2$-SAN). As expected, the NH$_2$-SAN had nearly the same composition of acrylonitrile as the NHS-SAN it was made from (F$_{AN}$ = 30%). The same FTIR observations were made for the SAN oligomer (Figure 11b) as was the case for the PS oligomer, showing that there was not an interaction between the ethylenediamine and the acrylonitrile monomers.

4 Considerations for Future Work

It would be beneficial to study the effect of having multiple amine functional groups per SAN polymer chain on the ability to form compatible blends with MA-PE. This could be achieved via terpolymerization of styrene, acrylonitrile and a primary amine containing monomer. Amine pendant functional poly(styrene) and poly(methyl methacrylate) block copolymers have been synthesized using 4-aminostyrene as a comonomer using NMP.[79] A cheaper alternative that may prove to be more feasible for large scale synthesis is 3-isopropenyl-α,α-dimethylbenzylamine which has been copolymerized with styrene and with methyl methacrylate (MMA) using conventional radical polymerization.[80] This could be a suitable monomer to impart pendant amine functionality into a SAN copolymer, and may lead to higher levels of compatibility within the MA-PE/SAN blends. Since a single molecule of random functional SAN could theoretically react with MA-PE at multiple locations during melt blending, or even to multiple MA-PE molecules, interesting morphologies may result. It may be possible that the interface would be 'stitched' so extensively that the morphology would not be altered by any further processing or re-orientation. Future work should also include the testing of mechanical and barrier properties of the reoriented MA-PE/SAN blends in order to determine their usefulness for the end application as fuel tank barrier materials. It is possible that the level of acrylonitrile in the polymers needs to be increased in order to offer sufficient barrier properties. In this case, a SAN copolymer would need to be synthesized with copolymer concentrations greater than 40 mol%. Commercially available SAN for barrier applications can have up to 75 mol% acrylonitrile content.[22] However, this high content of acrylonitrile is difficult to achieve in SAN, since the copolymer composition azeotropic point of SAN is close to 40 mol% acrylonitrile.[64] Even with a monomer feed composition of acrylonitrile at 70 mol%, the copolymer composition was found to be only 52 mol%.[64] It may be possible to incorporate higher acrylonitrile levels into the polymers by making a block copolymer with the second block consisting of pure PAN.

5 General Conclusions

The work contained in this thesis showed an initial step towards the creation of barrier materials for fuel tanks formed by polymer blends of functional PE and functional, acrylonitrile containing barrier polymers. It was shown that primary amine end functional SAN (NH_2-SAN) can be synthesized using NMP and post-synthesis chemical modification. NH_2-SAN was melt blended with maleic anhydride grafted PE (MA-PE) in a miniature twin screw extruder at a level of 20 wt.% NH_2-SAN and 80 wt.% MA-PE and shown to form a compatible blend when compared to blends made with non-functional SAN (BzAm-SAN) and MA-PE. The finer particle dispersion obtained with the NH_2-SAN blend showed that dynamic coalescence was prevented by the formation of covalent bonds formed between the functional polymers. The MA-PE/ NH_2-SAN blend was subjected to unidirectional shear flow within a channel die, and a lamellar structure was obtained. The next steps required for the design of the fuel tank barrier materials will involve mechanical property testing as well as permeation testing.

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