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Synthesis of Pendant Amine Functional Methyl Acrylate/Acrylonitrile Copolymers and Reactively Compatibilized Blends with Poly(Ethylene)

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Abstract

Acrylonitrile (AN)-containing copolymers have not been widely considered as barrier dispersed phases in blends with poly(ethylene) (PE), despite the versatility in their synthesis (i.e. controlled radical radical polymerization). To use such copolymers in PE, compatibilization is essential to obtain the desired morphology and thus we made a primary amine functional monomer, IDBA (3-isopropenyl-α,α–dimethylbenzylamine), with minimal purification steps, high yield (up to 76%) and high conversion (98%) in multi-gram batches from a cheap, commercially available precursor m-TMI (3-isopropenyl-α,α–dimethylbenzyl isocyanate). Terpolymers of AN, IDBA, MA (methyl acrylate) and AN (acrylonitrile) were then synthesized in DMF solution by conventional radical polymerization (number average molecular weight $\overline{M}_n$ = 26 – 28 kg mol^{-1}). These polymers are reactively blended with maleic anhydride grafted PE(PE-MAn) at 20 and 40 wt% loadings at 140 °C and compared with non-reactive PE-MAn/MA-AN-AMS (AMS = α–methyl styrene). Scanning electron microscopy (SEM) indicates smaller, sub-micron, thermally stable dispersed phase particle size (volume to surface area diameter $\langle D \rangle_{VS}$) for the reactive blend ($\langle D \rangle_{VS}$ = 0.6 μm). The reactive blending of the high-AN containing terpolymers with PE is thus promising as a barrier material agains hydrocarbons.

Keywords

Compatibilization; Reactive Blending; Copolymerization; Functionalization of Polymers; Radical Polymerization

Introduction

The market for value-added commodity polymers based on poly(ethylene) (PE) is lucrative and appealing as a wide variety of properties can be accessed by simple modification and blending. By blending PE with other polymers, a diverse set of materials can be synthesized, possessing its own particular and advantageous qualities. For example, PE containers for hydrocarbons must be modified with non-polar polymers that would decrease the permeability to hydrocarbons [1]. This was shown previously by blending polyesters or polyamides into PE as elongated domains [1]. Here, a candidate barrier material where the dispersed phase polymer is equipped with grease resistance and oxygen barrier properties (a methyl acrylate (MA)/acrylonitrile (AN) copolymer) was synthesized and blended into PE. AN copolymers are considered as alternatives as they have extra latitude in design as they can be made by controlled polymerization schemes, which permit more control over microstructure and ultimately tailoring of properties [2-5].

AN in the copolymer offers excellent gas barrier properties (against oxygen and water vapor) as well as grease resistance [6-7]. MA, in contrast, provides the barrier material with high tensile strength and processability [8-9]. However, due to the relatively polar nature of the MA-AN copolymer, it is immiscible with PE and thus melt blending will not be effective, resulting in unstable morphologies. To obtain stable, fine morphologies are required to obtain desirable mechanical properties, and compatibilization via reactive blending was done. The amine-anhydride reaction for compatibilization has been documented as the fastest and most effective and is used in commercial blends (e.g. rubber toughened nylon such as DuPont's Nylon ST) [10], and thus it was selected in this case [11]. Thus, incorporation of an amine functional group into the MA-AN copolymer would be highly desirable for reactive blending, particularly with the availability of commercial maleic anhydride-grafted PE.

We previously made styrene/acrylonitrile (SAN) copolymers where we placed a single reactive amine group at the chain end [12]. The primary amine-terminated SAN was effective in compatibilization with maleic anhydride grafted poly (ethylene) (PE-MAn) and we were able to form elongated SAN domains in the PE. However, the dispersed phase particle size was limited to about 2-3 μm. We expected further modulation of particle size could potentially be accessed by making the acrylonitrile-containing copolymer with many pendant functional groups. Previous work using 4-aminostyrene (PAS) as the amine functional monomer has shown that primary amine incorporation as pendant groups into MA-AN copolymers can be successfully done with sub-micron particle sizes [13].

However, commercially available amine functional monomers (protected or unprotected) are generally expensive (CAD $43.01/gram of PAS [14] and CAD $144.50/gram of the carbamate protected methacrylamide N-tBOC-Mam [15]) and larger-scale synthesis requires cheaper functional monomers. We desired to make a more economical terpolymer by producing an amino-functional monomer from cheaper precursors. Such a monomer was obtained in high yield from the isocyanate precursor, 3-isopropenyl-α,α−dimethylbenzyl isocyanate (m-TMI) [16]. The precursor isocyanate monomer was considerably cheaper compared with the other amine-containing monomers (CAD $0.45/gram) [17]. The amino-functional monomer produced was 3-isopropenyl- α, α −dimethylbenzylamine (IDBA). We adopted the synthesis of IDBA with some modification from the literature to produce it in higher yields with fewer impurities. Then, conventional radical polymerization of IDBA with MA and AN was performed to give pendant amino functionality into the polymer. This terpolymer was then reactively blended with PE-MAn and compared to the non-functional analog blend of MA, AN, and α−methyl styrene (MA-AN-AMS) with PE-MAn. Phase morphology and stability were then examined as a function of blend composition.

Experimental Section

Materials

3-Isopropenyl-α,α-dimethylbenzyl isocyanate (*m*-TMI, 95%, containing ≤200 ppm BHT as inhibitor), ethylene glycol butyl ether (butyl cellosolve, ≥99%), dichloromethane (DCM, ≥99.8%), dibutyltin dilaurate (DBTL, 95%), monoethanol amine (≥98%), ethylene diamine (≥99%), ethanol (96%), dimethyl sulfoxide-d$_6$ (DMSO-d$_6$, 99.9 atom %) and 2,2-azobis(2-methylpropionitrile) (AIBN, 99%) were purchased from Sigma–Aldrich and used as received. Acrylonitrile (AN, ≥99%, contains 35-45 ppm monomethyl ether hydroquinone as inhibitor), Methyl acrylate (MA, 99%, containing ≤100 ppm monomethyl ether hydroquinone as inhibitor) and α-Methyl styrene (AMS, 99%, contains 15 ppm p-*tert*-butylcatechol as inhibitor) were also 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. *N,N*-dimethylformamide (DMF, 99.8%), tetrahydrofuran (THF, 99.9%), methanol (99.8%), 1, 2-dichloroethane (≥99%), acetone (99.5 %), anhydrous ethyl ether (≥99 %) and anhydrous magnesium sulfate (certified) were purchased from Fisher and used as received. Anhydrous sodium sulfate (≥99.0%) was purchased from EMD BioSciences Inc. and used as received. Potassium hydroxide (85%) was purchased from Acros Organics and used as received. Chloroform-d ($CDCl_3$, 99.8 atom %) was purchased from Cambridge Isotope Laboratories and used as received. Hydrochloric acid (37%, 12 M) was purchased from ACP chemicals and diluted with water to get dilute hydrochloric acid (5%, 1 M). Maleic anhydride grafted linear low density poly (ethylene) (PE – MAn) (1.70 wt% grafted maleic anhydride) with a melt flow index (MFI) of 1.5 g $(10\ \mathrm{min})^{-1}$ at 190 ^{o}C, density of 0.91g ml^{-1}, melting point of 123^{o}C (with the trade name Orevac 18302N) and a glass transition temperature of -42 °C was obtained from Arkema and used as received.

Methods

1) Synthesis of 3-isopropenyl-α, α-dimethylbenzylamine (IDBA) Monomer

First, the synthesis of IDBA was investigated by replicating the procedure outlined by Trumbo *et al* [16]. The details of this process can be found in the *Supporting Information* section. IDBA was then synthesized using a procedure via a carbamate intermediate as shown in Figure 1 [18].

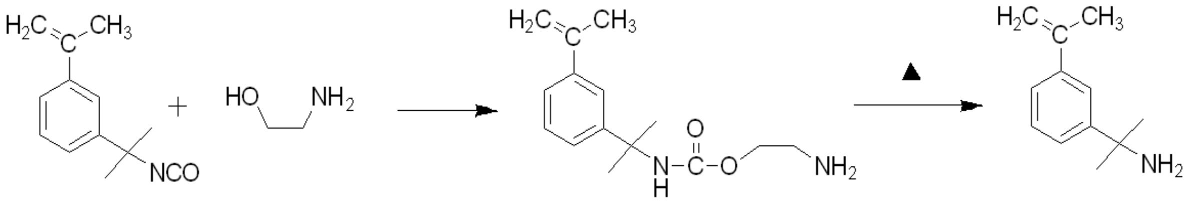

FIG. 1 SYNTHESIS OF IDBA VIA CARBAMATE INTERMEDIATE REACTION [18].

A 100 mL three neck round bottom flask equipped with a thermal well and magnetic stir bar was charged with monoethanol amine (24.28 g, 397.5 mmol, 2 times molar excess compared to the *m*-TMI used) and ethanol (~ 64.0 g, the solvent is added in a 1:1 ratio with the reaction mixture) and placed on a magnetic stirrer. A thermocouple was inserted in the thermal well and attached to a temperature controller. The other two necks of the flask were sealed with rubber septa. Over the course of 3 hours, *m*-TMI (40.0 g, 198.7 mmol) was added drop wise to the flask, using a syringe, with vigorous stirring at room temperature. This slow addition prevented a highly exothermic reaction. The temperature of the reaction mixture was allowed to subside for 15 – 20 minutes after which a sample was taken for FTIR analysis. The infrared spectra showed no isocyanate (N=C=O) absorbance peak around 2700 cm^{-1}. Then, the reaction mixture was added to a beaker equipped with a magnetic stir bar, containing anhydrous ethyl ether (30 mL) and dilute hydrochloric acid (20 mL, 1M ~ 5%). The mixture was left to stir at room temperature for 12 hours on a magnetic stirrer. Then, the organic layer (ethyl ether) was isolated using a separatory funnel and washed with water (2 x 200 mL). The resultant material was dried with anhydrous sodium sulfate and left to dry in the fume hood for 24 hours. The carbamate (37.8 g, 144. 3 mmol) was transferred to a 50 mL three-neck round bottom glass flask equipped with a magnetic stir bar, reflux condenser, thermal well and vacuum distillation column. The condenser was connected to an ethylene glycol/water mixture recirculating chiller, set at 2 ° C, and attached to the central neck of the flask to prevent the evaporation of the mixture components. The condenser was capped with a rubber septum containing an exhaust needle to relieve any pressure built up during the reaction. The flask was set inside a heating mantle and placed on a magnetic stirrer. A thermocouple was situated inside the thermal well, inserted in the second neck of the flask, and connected to a temperature controller. The carbamate was heated at 120 °C for 24 hours under reflux and simultaneous vacuum distillation was conducted at 80-100 mbar to push the equilibrium from the carbamate to the IDBA product by constant removal of the product as it is formed. The IDBA was washed with deionized water/5% water in sodium chloride to remove water-soluble impurities. The compound was then dried in a vacuum oven at 50 °C for 3 hours. The final yield of 3-isopropenyl-α,α-dimethylbenzylamine (IDBA) monomer was 18.7 g (73.9 %). The final product was characterized using ^{1}H NMR (in $CDCl_3$) and FTIR. The data for the experiments carried out are summarized in Table 1.

TABLE 1. SYNTHESIS OF IDBA VIA CARBAMATE INTERMEDIATE: SUMMARY OF EXPERIMENTAL ROUTES

	Solvent	**Reactant 1**	**Reactant 2**	**Temp [°C]**	**Time [h]**	**Final product**	**Yield [%]**
Exp 1(a)	Ethanol	Monoethanol amine	*m*-TMI	20	3	Carbamate	76.1
Exp 1(b)	None	Carbamate	None	120	24	IDBA	76.3
Exp 2(a)	Ethanol	Monoethanol amine	*m*-TMI	20	3	Carbamate	72.6
Exp 2(b)	None	Carbamate	None	120	24	IDBA	73.9

2) Synthesis of MA-AN-IDBA and MA-AN-AMS Terpolymers

A conventional free-radical polymerization, of MA-AN-IDBA, with the initial molar composition, $f_{MA,0}$ = 0.50,

$f_{AN,0}$ = 0.40, in 50wt% *N, N* dimethylformamide (DMF) was conducted at 70 ° C for 3 hours and is given as an example. 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. The initiator (AIBN, 0.11 g, 0.7 mmol), and the stirrer were added via the third neck of the flask, which was then sealed with a rubber septum. Previously purified MA (6.14 g, 70.6 mmol), AN (3.02 g, 56.5 mmol), IDBA (2.75 g, 14.1 mmol) and DMF (11.56 g, 158.1 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 4 °C. A nitrogen flow was introduced to purge the solution for 30 min. The reactor was then heated to 70 °C while maintaining the purge. The reaction was left for 3 hours, after which the mixture was allowed to cool to room temperature. The final polymer was precipitated in methanol and water, vacuum filtered, and then dried for 120 minutes in a vacuum oven at 50 °C. The target number average molecular weight $\overline{M}_{n,target}$) at complete conversion, calculated by the mass of monomer relative to the moles of initiator, was set to 17.3 kg mol^{-1}. The final yield of the copolymer after 3 hours was 9.2 g (80% conversion of monomers based on ^{1}H NMR analysis) with number-average molecular weight $\overline{M}_n$= 27.7 kg mol^{-1} and dispersity (Đ) = 3.59 (determined by gel permeation chromatography (GPC) calibrated relative to linear PMMA standards in DMF at 50 °C). A few drops of phenyl isocyanate were added to the vial before being introduced into the GPC column, to prevent the amine groups from attaching to the column. The MA and AN molar composition of the terpolymer was F_{MA} = 0.47 and F_{AN} = 0.39. They were calculated by ^{1}H NMR analysis (300 MHz, $CDCl_3$, δ): 6.9-7.5 (m, 4H, Ar H), 0.8-2 (m, 3H, $CH\text{-}CH_2$), 3.6 (s, 3H, $O\text{-}CH_3$). The same procedure was repeated for MA-AN-AMS to make a non-functional terpolymer for comparison with the amine functional IDBA terpolymer.

3) Reactive Blending of MA-AN-IDBA and MA-AN-AMS Terpolymers with PE – MAn

MA-AN-IDBA (0.71 g, 20 wt.%) and PE – MAn (2.83 g, 80 wt.%) were mechanically mixed at room temperature (the amine functional terpolymer was sticky and viscous so a spatula had to be used for proper mixing), then fed into a miniature conical counter rotating twin screw extruder (Haake Minilab) at 140 °C. The screw speed was set to 50 rpm. The material was in the extruder for 30 minutes (each extrude took approximately 3 minutes, so it was recycled 10 times) and then quenched immediately (within 15 seconds) in liquid nitrogen to freeze the morphology of the blend. The same procedure was followed for the MA-AN-AMS/PE-MAn blend under the same conditions. 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 at 130 °C (above the glass transition temperatures of MA-AN-IDBA and PE – MAn as well as the melting point of PE – MAn) for 18 hours to compare against the quenched samples to determine the stability of the microstructure. This was repeated for a 40 wt. %/60 wt. % ratio of MA-AN-IDBA/PE – MAn. The procedure was also repeated using the same extrusion and annealing conditions for the non – functional MA-AN-AMS polymer and PE – MAn blend to analyze the effects of reactive compatibilization on the microstructure of the polymer.

4) Sample Preparation for Microscopy

The blend samples were freeze fractured in liquid nitrogen and a portion of the sample was annealed at 130 °C as described in above section. The annealed and non-annealed samples were placed in DMF for a period of 6 hours to selectively remove the dispersed terpolymer phase. The samples were then thoroughly air-dried at room temperature and glued onto aluminum stubs. The samples were then sputter-coated with 3 nm of platinum in preparation for scanning electron microscopy (SEM) to make the sample conductive. Then, the microstructure of the blends was viewed with a Hitachi S-4700 Field Emission Scanning Electron Microscope (FE-SEM) at an accelerating voltage of 10 kV.

5) Image Analysis

From the scanned transparency, the areas A_i of n_i particles were measured using ImageJ Version 1.45s software.

The A_i were converted to an equivalent sphere diameter D_i. 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, $\langle D \rangle_{VS}$, which gives the average interfacial area per unit volume that can be used to estimate copolymer coverage at the interface [19]. $\langle D \rangle_{VS}$ was calculated by using Equation (1) [20].

$$\langle D \rangle_{vs} = \frac{\sum_{i=1}^{k} n_i D_i^3}{\sum_{i=1}^{k} n_i D_i^2} \tag{1}$$

Characterization

1) Gel Permeation Chromatography

Molecular weights (number average molecular weight $\overline{M}_n$, weight average molecular weight $\overline{M}_w$) and dispersity Đ were estimated using gel permeation chromatography (Waters Breeze) with DMF 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 50 °C during the analysis and the molecular weights were estimated relative to linear poly(methyl methacrylate) (PMMA) 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. Prior to analysis, polymer samples containing amine functional groups were quenched with phenyl isocyanate to prevent sticking of the amine groups onto the column.

2) Proton Nuclear Magnetic Resonance

A Varian Mercury-300 NMR (Nuclear Magnetic Resonance) spectrometer was used to determine the molar composition and conversion of the terpolymers. MestreNova® software was used to analyze the ^1H NMR spectra. The terpolymers were dissolved in deuterated chloroform ($CDCl_3$) and the chemical shifts were reported in parts per million (ppm) using tetramethylsilane (TMS) as a reference. The compositions were calculated using the method published in literature [8] using the formulae listed below.

$$l_{AN} = \frac{z}{2} - \frac{x}{3};\ n_{MA} = \frac{x}{3};\ m_{IDBA} = \frac{y}{4},\ m_{AMS} = \frac{y}{5}$$

In this case, the methylene protons for MA and AN overlapped and l = AN content in the terpolymer, m = IDBA/AMS content in the terpolymer, and n = MA content in the terpolymer. The other values are defined as follows: x = the integrated area to the peak corresponding to the methyl proton from the MA monomer only, δ: 3.6 ppm (s, 3H, $O\text{-}CH_3$), y = the integrated area associated to the peak of the aromatic protons from IDBA/AMS 6.9 – 7.5 ppm (m, 4H/5H, Ar H) and z = the integrated area corresponding to the methylene protons from MA and AN that overlap from 1.6 – 2.2 ppm (m, 2H, $CH\text{-}CH_2$).

The conversion of the monomers in the reactor was also calculated using ^1H NMR analysis, by tracking the vinyl peaks of each of the monomers. These peaks were distinguished by superimposing the pure monomer spectra(s) onto the polymer spectra. For MA, the vinyl peaks were δ: 5.8 ppm (1 H, m), 6.2 ppm (1 H, m) and 6.4 ppm (1 H, m). For AN, the vinyl peaks were δ: 5.6 ppm (1 H, m), 6.1 (1 H, m) and 6.2 (1 H, m). For IDBA, the vinyl peaks were δ: 5.1 ppm (1 H, s) and 5.4 ppm (1 H, s). For AMS, the vinyl peaks were 5.0 ppm (1 H, s) and 5.3 ppm (1 H, s). ^1H NMR analysis was done for samples taken every 60 minutes and the peaks on the ^1H NMR spectra were integrated. The decrease in the size of the peaks was noted. For molecules with multiple vinyl peaks, the average integrated area (I_i) was taken in order to represent the presence of the respective monomer. The individual monomer conversion was calculated using Equation (2).

$$X_i = 1 - \left(\frac{I_i}{f_i} \right) \tag{2}$$

In Equation (2), X_i = conversion of monomer i, I_i = average integrated area of monomer i, and f_i = Initial mole feed ratio of monomer i.

The overall conversion of the reaction was calculated using Equation (3) where X is the overall conversion.

$$X = \sum_i X_i f_i \tag{3}$$

3) Thermal Properties

The thermal properties of the polymers were measured using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). A TGA Q500 (TA Instruments) was used to measure the decomposition temperature of the polymer to set an upper temperature limit for blending. The analysis was done under oxygen rather than nitrogen to simulate the environment in an extruder. The DSC Q2000 (TA Instruments) was used to measure the melting/softening temperature of polymers to set the lower limit for blending. The measurements were done in an aluminum t-zero pan and were calibrated to an empty aluminum t-zero pan.

Results and Discussion

Synthesis of 3-Isopropenyl-α, α-Dimethylbenzylamine (IDBA) Monomer

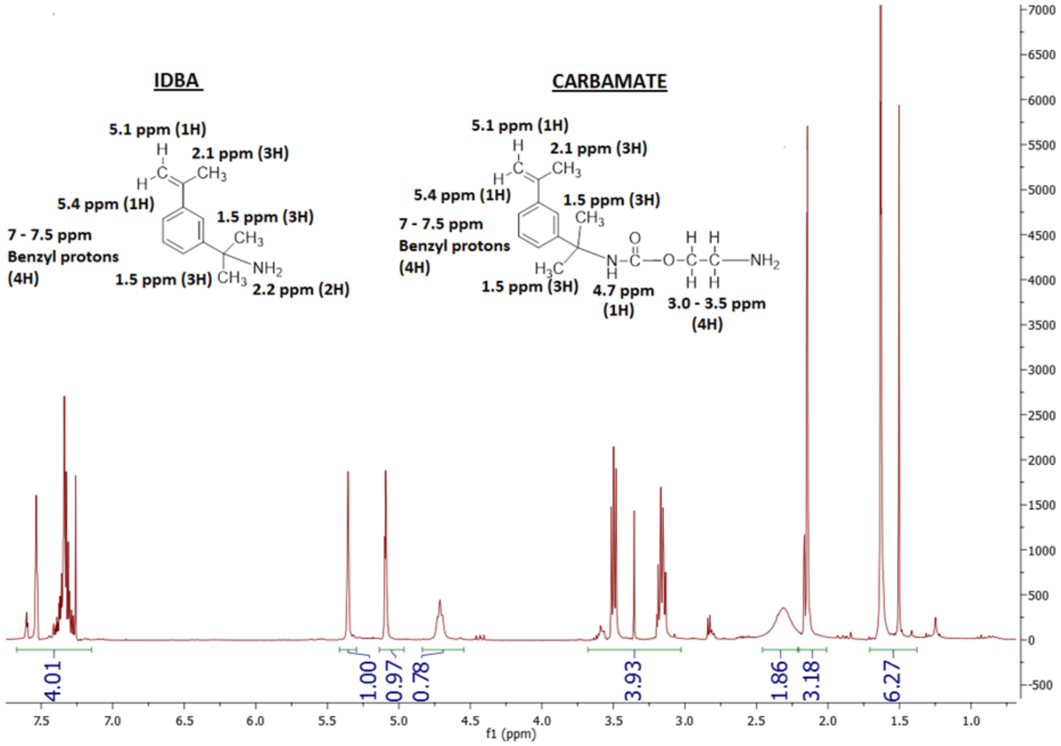

FIG. 2 ^{1}H NMR ($CDCl_3$) OF IDBA SYNTHESIZED BY CARBAMATE INTERMEDIATE.

This procedure (adapted from Charles et al. [18]) aimed to react an isocyanate with an alkanolamine to form a carbamate, which was then thermally decomposed to form the primary amine product (IDBA) as shown in Figure 1. The equilibrium of the decomposition reaction is known to predominantly favour the carbamate rather than the amine product [18]. As a result, it was necessary to continuously remove the resultant amine product as it is formed via vacuum distillation. The final structure of the IDBA was confirmed using ^{1}H NMR as shown in Figure 2. Conversion based on ^{1}H NMR from carbamate to IDBA was found to be 98%. The progression of the reaction to convert m-TMI to the carbamate was confirmed using FTIR spectrometry. The peaks used to identify the compounds were the isocyanate peak in m-TMI (2200 cm^{-1}), the carbonyl peak in the carbamate (1700 cm^{-1}) and the primary amine peak in the IDBA (3300 cm^{-1}) ***as shown in Figure 3.***

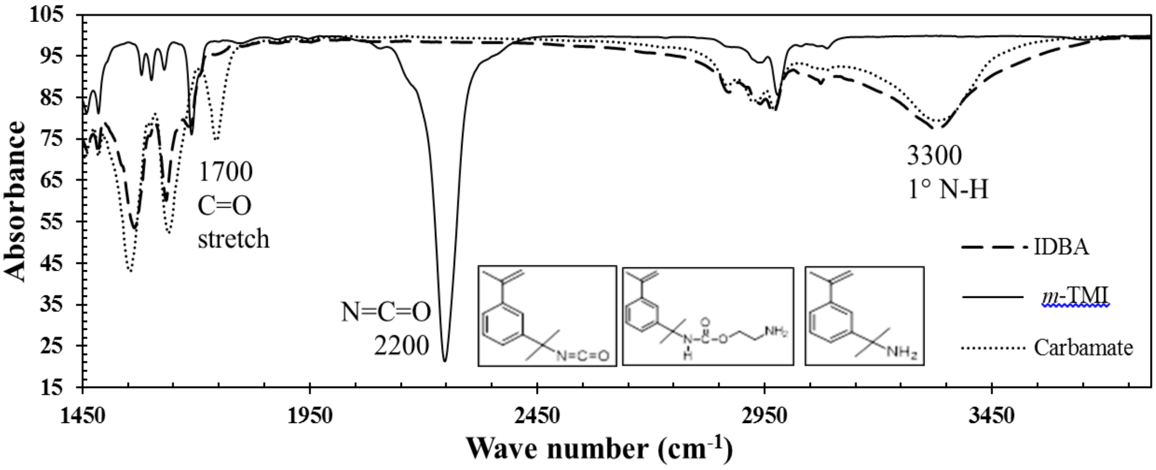

FIG. 3 FTIR SPECTRA OF m-TMI, CARBAMATE AND IDBA WITH INSET CHEMICAL STRUCTURES OF EACH SHOWN IN THAT ORDER.

This procedure had minimal purification steps, high yield and good conversion. Charles et al. [18] obtained yields up to about 50%. The yield was affected by the choice and amount of alcohol, as well as the amine used. In our procedure, we were able to get yields up to nearly 76% using ethanol and monoethanol amine. The monoethanol amine was used in a 2 times molar excess of the m–TMI precursor. The final yield was also influenced by the extraction process using ethyl ether and dilute hydrochloric acid. The ethyl ether organic layer dissolves the carbamate intermediate and separates it from the water-soluble impurities. In our procedure, the extraction was carried out for a period of 24 hours, allowing a higher concentration of intermediate to be dissolved in the organic layer, thus providing higher yield of final product. However, one of the most essential steps towards obtaining high yield was the continuous removal of IDBA product as it was formed, via vacuum distillation. This procedure was a significant improvement compared with the procedure suggested by Trumbo et al [16] since the decomposition of the carbamate to IDBA requires no solvent whereas, for methyl urethane (the intermediate described by Trumbo et al. [16]), butyl cellusolve was used (which was difficult to separate). Further, a strong basic catalyst such as KOH was not required. Thus, we can use the commercially available isocyanate functional TMI as a precursor to the IDBA, which can be synthesized in high yields and scaled-up quite easily to multi-gram quantities.

Synthesis of Terpolymers MA-AN-IDBA and MA-AN-AMS

TABLE 2. MA-AN-IDBA TERPOLYMERIZATION FORMULATIONS AND MOLECULAR PROPERTIES

Exp no.	Initial composition (mole fraction)			a)Copolymer composition (mole fraction)			a)Conv. [%]	b)$\overline{M}_n$ [kg mol^{-1}]	b)Đ	Time [h]	Temp [°C]
	$f_{MA,0}$	$f_{AN,0}$	$f_{IDBA,0}$	F_{MA}	F_{AN}	F_{IDBA}					
1	0.50	0.40	0.10	0.47	0.39	0.14	80.0	27.7	3.59	3	70
2	0.40	0.50	0.10	0.38	0.50	0.12	83.5	25.9	2.24	4	70
3	0.30	0.60	0.10	0.28	0.59	0.13	72.5	27.0	2.98	4	70
4	0.10	0.80	0.10	0.10	0.78	0.12	81.0	27.4	2.50	4	70

a)Values were determined using ^1H NMR spectroscopy in DMSO-d_6; b)Values were determined through GPC using linear poly(methyl methacrylate) (PMMA) standards in DMF at 50 °C

The amino – functional terpolymer of MA, AN and IDBA was synthesized with various initial feed compositions to obtain a material with satisfactory barrier properties (reasonably high acrylonitrile loading ~ 50 mol% with no higher than 80 mol% to not be detrimental to processing [6]) and sufficient IDBA incorporation required for reactive blending/compatibilization (~ 5-10 mol%). Table 2 lists the various terpolymers synthesized. The first set of experiments were done for 3 hours, but then reaction time was increased to 4 hours to increase the final conversion. As shown in Table 2, the final copolymer composition was similar to the initial monomer feed of each monomer.

This showed that IDBA could be incorporated into the MA-AN copolymer at the desired relatively low concentrations. The non–functional terpolymer of MA, AN, and AMS was synthesized under the same conditions as the functional polymer containing the amine groups using various monomer feed mole fractions. These non-functional terpolymers would serve as a control for subsequent blending experiments. The results are summarized in Table 3. ^{1}H NMR (in DMSO-d_6) was then used to quantitatively estimate the terpolymer composition.

TABLE 3. MA-AN-AMS TERPOLYMERIZATION FORMULATIONS AND MOLECULAR PROPERTIES

Exp no.	*Initial composition (mole fractions)*[a)]			*Copolymer Composition (mole fractions)*			[a)]*Conv [%]*	[b)] $\overline{M}_n$ *[kg mol^{-1}]*	[b)] *Đ*	*Time [h]*	*Temp [°C]*
	$f_{MA,0}$	$f_{AN,0}$	$f_{AMS,0}$	F_{MA}	F_{AN}	F_{AMS}					
1	0.50	0.40	0.10	0.38	0.45	0.17	42.5	15.4	1.56	4	70
2	0.30	0.60	0.10	0.28	0.58	0.14	58.5	24.8	1.72	4	70
3	0.10	0.80	0.10	0.08	0.77	0.15	61.5	17.4	1.64	4	70

[a)]Conversions were determined using ^{1}H NMR spectroscopy; [b)]Molecular weight data were determined by GPC relative to linear poly(methyl methacrylate) (PMMA) standards in DMF at 50 °C

Thermal Stability of Polymers

Thermal properties of MA-AN-AMS and MA-AN-IDBA polymers are required to determine the upper limit for the extrusion temperature. Table 4 and Table 5 summarize the TGA and DSC data for the MA-AN-IDBA and MA-AN-AMS terpolymers with various compositions. Thus, the extrusion temperature selected was based on the polymer's thermal properties. The decomposition temperature of MA-AN-AMS and MA-AN-IDBA polymers in the f_{MA} = 0.50, f_{AN} = 0.40 compositions were 150 °C and 160 °C respectively, so the temperature of extrusion was set at 140 °C for both in order to keep the experimental procedure uniform for the amine functional and non-functional polymers (these compositions were the only ones blended in this paper).

TABLE 4. THERMAL PROPERTIES OF MA-AN-IDBA TERPOLYMERS

[a)]*Mole Fraction in Copolymer (F_i)*			*Glass Transition Temperature T_g [°C]*	[b)]*Decomposition Temperature [°C]*	[c)] $\overline{M}_n$ *[kg mol^{-1}]*
F_{MA}	F_{AN}	F_{IDBA}			
[d)] 0.47	0.39	0.14	-2	160	27.7
[d)] 0.38	0.50	0.12	-2	130	25.9
[d)] 0.28	0.59	0.13	-30	140	27.0
[d)] 0.10	0.78	0.12	16	140	27.4

[a)] F_i = mole fraction of monomer final copolymer

[b)] Decomposition temperature determined using TGA

[c)] Molecular weights determined by GPC relative to linear PMMA standards in THF at 40 °C

[d)] The copolymer details are completely found in Table 2 as Experiments 1, 2, 3, and 4 respectively.

TABLE 5. THERMAL PROPERTIES OF MA-AN-AMS TERPOLYMERS

[a)]*Mole Fraction in Copolymer (F_i)*			*Glass Transition Temperature T_g [°C]*	[b)]*Decomposition Temperature [°C]*	$\overline{M}_n$ *[kg mol^{-1}]*
F_{MA}	F_{AN}	F_{AMS}			
[d)] 0.38	0.45	0.17	30	150	15.4
[d)] 0.28	0.58	0.14	32	140	24.8
[d)] 0.08	0.77	0.15	35	130	17.4

[a)]F = mole fraction of monomer in the final copolymer

[b)]Decomposition temperature determined from TGA

[c)]Number average molecular weight determined from GPC relative to linear PMMA samples in THF at 40 °C

[d)]Entries refer to samples in Table 3 as Expt. No. 1, 2, 3, respectively.

Reactive Blending of MA-AN-IDBA and MA-AN-AMS terpolymers with PE – MAn

The amine – functional terpolymer (Expt. #1 in Table 2: $F_{MA} = 0.47$, $F_{AN} = 0.39$, $F_{IDBA} = 0.14$) was blended with maleic anhydride grafted poly (ethylene) (PE - MAn) via reactive extrusion. The effectiveness of the amine functionality in the terpolymers in the reactive blends was assessed by comparison of the morphology after melt blending and annealing with the non-reactive analog (PE - MAn with non-functional MA-AN-AMS terpolymer, $F_{MA} = 0.38$, $F_{AN} = 0.45$, $F_{AMS} = 0.17$ (Expt. 1 in Table 3)). The blend morphologies were characterized to determine the level of compatibilization achieved, as witnessed by the dispersed phase particle size (i.e. coalescence was prevented by reactive compatibilization, which should result in smaller dispersed phase sizes). Further, thermal annealing was used to test morphological stability. The results are summarized in Table 6.

MA-AN-IDBA and MA-AN-AMS polymers were separately melt blended with PE – MAn at a 20 wt.% terpolymer loading with 80 wt.% PE – MAn, which is typical for PE barrier blends [22]. It was expected that the primary amine in the MA-AN-IDBA polymer would form imide bonds with the maleic anhydride groups, which are found randomly along the PE - MAn backbone. This would form graft copolymers, which would stabilize the interface between the immiscible PE – MAn and MA-AN-IDBA phases, preventing dispersed phase coalescence and thus a relatively small, dispersed MA-AN-IDBA phase domain size would result. The non-functional MA-AN-AMS does not have primary amine groups and thus no copolymer is expected to form at the interface. This non-reactive blend should result in large dispersed phase domains that would coalesce upon annealing [12].

TABLE 6. SUMMARY OF PARTICLE SIZE AND MORPHOLOGICAL STABILITY OF REACTIVE VERSUS NON-REACTIVE METHYL ACRYLATE/ACRYLONITRILE BLENDS WITH MALEIC ANHYDRIDE GRAFTED POLY(ETHYLENE)

Terpolymer sample	*Blend Ratio by Wt% (PE-MAn:Terpolymer)*	*Etching Time [h]*	*Annealing Conditions [˚C]*	*${}^{a)}\langle D\rangle_{VS}$ [μm]*
Expt. #1, Table 2 (reactive)	*80:20*	*2*	*None*	*0.60*
	80:20	*6*	*None*	*0.33*
	60:40	*6*	*None*	*1.11*
Expt. #1, Table 2 (reactive)	*80:20*	*2*	*68 h at 130 °C*	*0.77*
	80:20	*6*	*18 h at 130 °C*	*0.78*
	60:40	*6*	*18 h at 130 °C*	*1.17*
Expt. #1, Table 3 (non-reactive)	*80:20*	*2*	*None*	*2.90*
	80:20	*6*	*None*	*2.59*
	60:40	*6*	*None*	*14.9*
Expt. #1, Table 3 (non-reactive)	*80:20*	*2*	*68 h at 130 °C*	*3.12*
	80:20	*6*	*18 h at 130 °C*	*15.4*
	60:40	*6*	*18 h at 130 °C*	*25.5*

a)Volume to surface area average diameter

SEM images of the PE–MAn/MA-AN-IDBA and PE–MAn/MA-AN-AMS 80/20 blends are shown in Figure 5 and images of the 60/40 blends are shown in Figure 6. According to the blend morphology characterization shown in Table 6, the amine functional blends (MA-AN-IDBA) had smaller particle sizes ~ 1 μm and upon annealing, the particle size did not change significantly and hence, the blends appeared to be thermally stable. For the non – functional blends (MA-AN-AMS), the particle size found was 2-3 times larger compared with the reactive blend, and upon annealing the particle size increased significantly. The smaller particle size for the reactive blends relative to the non-reactive blends along with the particle size stability suggests the amine-anhydride coupling reaction was effective [12, 23]. The smaller $\langle D\rangle_{VS}$ for the PE–MAn/MA-AN-IDBA blend compared with the PE–MAn/MA-AN-AMS blend indicated that the functional blend was able to prevent dynamic coalescence much better compared with the non - functional blend, as expected. The 80/20 and 60/40 blends for the amine functional terpolymers were also found to be thermally stabile, unlike the non–functional blend. The annealing was done for at least 18 h in all cases, which should have been long enough to observe any static coalescence effects.

A study done by our group earlier used amine end–functional SAN copolymers for blending and reported particle sizes around 2 – 3 μm for 80/20 non–annealed blends of PE–MAn/SAN (styrene-acrylonitrile copolymer) [12]. The dispersed phase particle size was larger because the amine functional groups were only present at the ends. However, in this study we investigated pendant amine functionalization with more functional groups that could react with the PE–MAn. It has been found that the number and type of reactive groups attached onto the dispersed polymer affect the extent of the compatibilization reaction as well as the compatibilization capability of the graft copolymer in situ formed in a strong dependence on molecular weight and molecular architecture [22]. However, even smaller dispersed phase domain sizes have been reported in literature, when blending primary amine functional polymers with anhydride functional polymers [19, 22]. One possible reason for the slightly larger particle sizes obtained in this study could be explained by the viscosity ratio between the dispersed phase and the matrix (h_r). Rheological measurements of the reactive and non – reactive terpolymers were not parts of this study; previous work by our group using similar MA/AN copolymers [13] and the identical PE-MAn can provide some insight, however. Earlier, we determined h_r using complex viscosities from oscillatory measurements at 200 °C at an estimated shear rate for extrusion $\dot{\gamma}$ ~ 10-30 s^{-1}. The complex viscosity h^* of the amino-functional reactive ($\bar{M}_n$ = 102 kg mol^{-1}) and non-reactive MA/AN copolymer ($\bar{M}_n$ = 61 kg mol^{-1}) was 300-600 Pa·s while that of the PE-MAn was 1100 Pa·s). Applying the Cox-Merz rule ($\eta(\dot{\gamma}) = |\eta^*(\omega)| \quad (\dot{\gamma} = \omega)$) [24] for these blends gives h_r ~ 0.2-0.6 and dispersed phase particle sizes ~ 1 μm. The MA/AN copolymers in the present study had lower molecular weights ($\bar{M}_n$= 27.7 kg mol^{-1} for the reactive one and $\bar{M}_n$= 15.4 kg mol^{-1} for the non-reactive MA/AN copolymer), which would suggest lower viscosity and hence lower h_r and poorer dispersion. However, we still observed stable, sub-micron dispersions of the reactive MA/AN copolymers in a PE-g-MA matrix, suggesting that the reaction was sufficiently effective. Certainly, with a viscosity ratio closer to unity, better dispersion would be achieved, and the MA/An terpolymer domain size could have been further lowered [23-25]. However, dispersed phase particle sizes ~ 1 μm are sufficiently effective in most polymer blends against stress propagation during mechanical deformation [26].

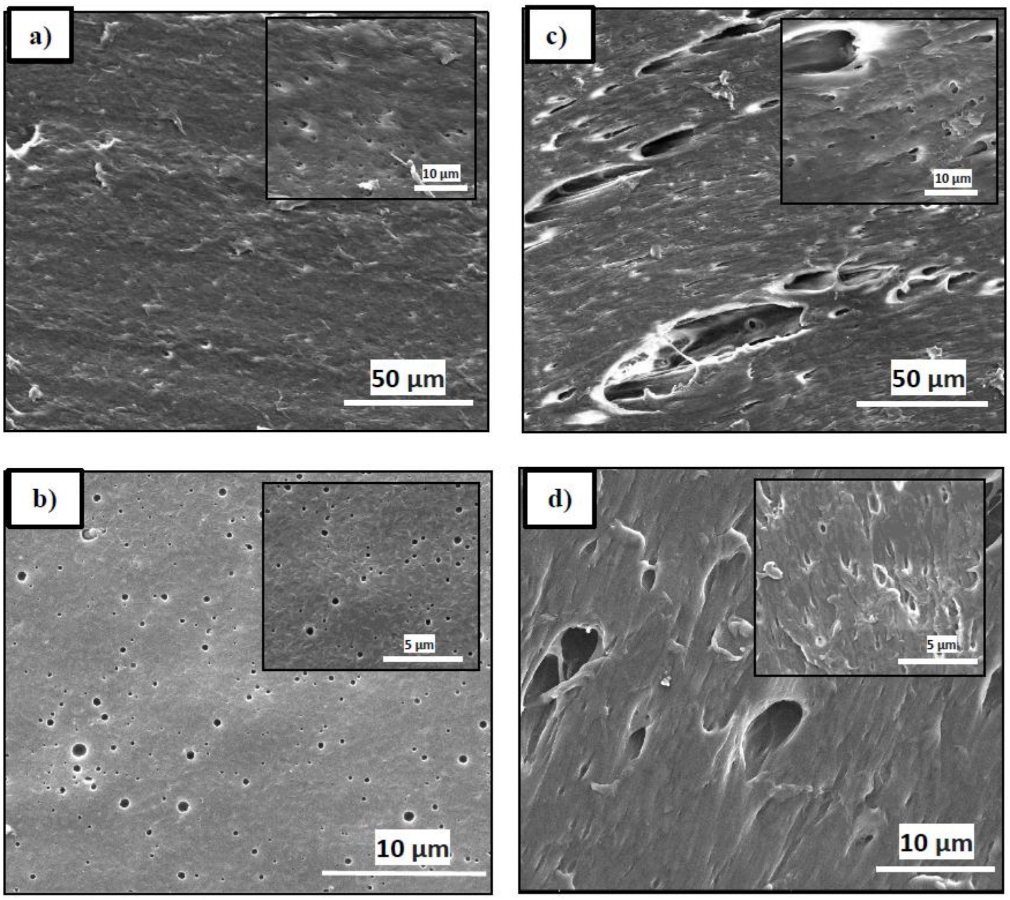

FIG. 5 SEM IMAGES OF a) PE-MAn/MA-AN-IDBA (80/20) non-annealed, b) PE-MAn/MA-AN-IDBA (80/20), ANNEALED AT 130 °C FOR 18 H, c) PE-MAn/MA-AN-AMS (80/20) NON-ANNEALED, d) PE-MAn/MA-AN-AMS (80/20), ANNEALED AT 130 °C FOR 18 H

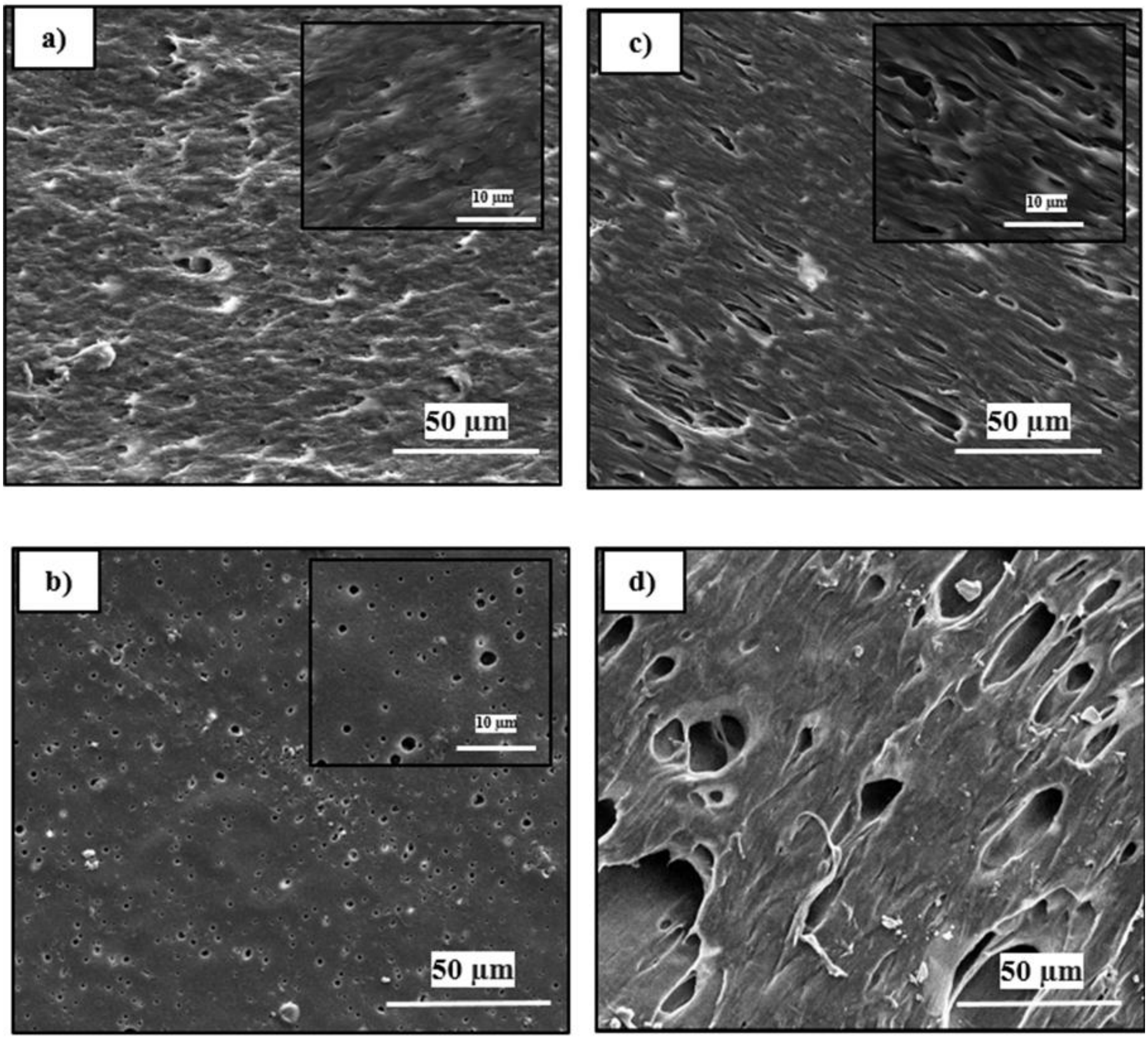

FIG. 6 a) PE-MAn/MA-AN-IDBA (60/40) NON-ANNEALED BLEND, b) PE-MAn/MA-AN-IDBA (60/40) BLEND, ANNEALED AT 130 °C FOR 18 H, c) PE-MAn/MA-AN-AMS (60/40) BLEND NON-ANNEALED, d) PE-MAn/MA-AN-AMS (60/40) BLEND, ANNEALED AT 130 °C FOR 18 H.

Conclusions

In this paper, primary amine containing MA-AN-IDBA terpolymers were successfully synthesized using conventional free – radical polymerization with AIBN initiator. A multi-gram scalable process was shown to produce the IDBA monomer. These functional MA-AN-IDBA terpolymers were melt blended with PE-MAn.

The blend morphology of the dispersed MA-AN-IDBA phase was finer with smaller $\langle D\rangle_{VS}$ compared with the non-functional MA-AN-AMS blends with PE-MAn. Viscosity ratios suggested that mixing was equivalent for reactive versus non-reactive blends. This showed that the amine-functional polymers were enabling compatibilization of the blend by prevention of dynamic coalescence and subsequent static coalescence. This study provides an alternative set of acrylonitrile-based barrier materials beyond typical polyesters and polyamides for value-added poly(ethylene) that can be achieved by reactive blending.

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