

# Novel polyethylene-*b*-polyurethane-*b*-polyethylene triblock copolymers: Facile synthesis and application

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**ABSTRACT:** A series of novel polyethylene-*b*-polyurethane-*b*-polyethylene (EUE) triblock copolymers is successfully prepared through a facile route combining the thiol-ene chemistry, addition polymerization, and coupling reaction. The resulting EUE triblock copolymers are characterized by Nuclear magnetic resonance ( $^1\text{H}$  NMR), Fourier transform-infrared spectra (FT-IR), High temperature gel permeation chromatography (HT-GPC), Differential scanning calorimetry (DSC), Thermogravimetric analysis (TGA), and Transmission electron microscopy (TEM). In addition, the EUE triblock copolymers have been evaluated as compatibilizers in the polymer blends of thermoplastic polyurethane elastomer (TPU) and high-density polyethylene (HDPE). The SEM results show that the compatibility of immiscible blends is enhanced greatly after the addition of EUE triblock copolymers. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42967.

**KEYWORDS:** blends; copolymers; polyolefins; polyurethanes

Received 6 August 2015; accepted 21 September 2015

DOI: 10.1002/app.42967

## INTRODUCTION

From daily necessities (e.g. packaging, films) to building materials (e.g. pipes, fibers) and automotive parts, polyethylene (PE) has become one of the most important thermoplastics. However, due to its low polarity and poor dissolution, polyethylene exhibits poor adhesion and incompatibility with other materials, which impedes its application in broader fields.<sup>1–4</sup> Compatibilizers can be used to effectively improve the interfacial adhesion of immiscible polyethylene blends, thus extending general PE products to high value-added advanced polymer materials.<sup>5–15</sup> Block or graft copolymers containing PE segments are widely considered as high-performance compatibilizers for the blends of polyethylene with other materials. Various types of polyethylene-based block or graft copolymers have been synthesized and proven to be very impactful compatibilizers, such as polyethylene-*b*-poly( $\epsilon$ -caprolactone) (PE-*b*-PCL),<sup>16–18</sup> poly(methyl methacrylate)-*b*-polyethylene-*b*-poly(methyl methacrylate) (PMMA-*b*-PE-*b*-PMMA),<sup>19</sup> polyethylene-*b*-poly(ethylene glycol) (PE-*b*-PEG),<sup>20</sup> polyethylene-*b*-poly(lactic acid) (PE-*b*-PLA),<sup>21</sup> polyethylene-*b*-poly(dimethylsiloxane) (PE-*b*-PDMS),<sup>22</sup> polymethylene-*b*-polystyrene (PM-*b*-PS),<sup>23</sup> polyethylene-*g*-poly(methyl methacrylate) (PE-*g*-PMMA),<sup>24</sup> and polyethylene-*g*-polystyrene (PE-*g*-PS).<sup>25</sup>

Targeting its numerous desirable features, for example hardness, mechanical strength, good abrasion, oil and ozone resistance, low temperature flexibility, and biocompatibility, thermoplastic polyurethane elastomer (TPU) has been rapidly developed since

1961.<sup>26–30</sup> However, TPU is a relatively expensive material. Many attempts have been made to blend TPU with other materials and opened the door to novel materials with unique, improved, and desired properties, such as polyurethane/poly(lactic acid) (TPU/PLA),<sup>31</sup> polyurethane/polypropylene (TPU/PP),<sup>32–34</sup> ethylene vinyl acetate copolymer/thermoplastic polyurethane (EVA/TPU),<sup>35,36</sup> poly(methyl methacrylate)/thermoplastic polyurethane (PMMA/TPU),<sup>37,38</sup> thermoplastic polyurethane/poly(vinylidene fluoride) (TPU/PVdF),<sup>39,40</sup> thermoplastic polyurethane/natural rubber (TPU/NR),<sup>41</sup> polyamide/thermoplastic polyurethane (PA/TPU),<sup>42</sup> thermoplastic polyurethane elastomer/thermoplastic polyolefin elastomer (TPU/TPO),<sup>43</sup> ethylene-vinyl acetate copolymer rubber/thermoplastic polyurethane (EVM/TPU),<sup>44</sup> and thermoplastic polyurethane/polydimethylsiloxane rubber (TPU/PDMS).<sup>45</sup> Among these blend systems, the TPU/PE blends are rarely reported so far because of the poor compatibility and the lack of suitable compatibilizer. Herein, we report for the first time the facile synthesis and characterization of novel polyethylene-*b*-polyurethane-*b*-polyethylene (EUE) triblock copolymers and their application as effective compatibilizers in the polymer blends of immiscible TPU and HDPE.

## EXPERIMENTAL

### Materials

Vinyl end functionalized polyethylenes (PE-ene, nearly 100% of functionality,  $M_{n,NMR} = 940 \sim 1840 \text{ g mol}^{-1}$ , PDI = 2.2  $\sim$  2.4)

were prepared according to our previous results.<sup>22</sup> Toluene (HPLC grade, Tedia) was distilled over sodium/potassium under nitrogen with benzophenone as an indicator prior to use. Chlorobenzene (PhCl, 99.5%) was dried over 4 Å molecular sieves. 2-Mercaptoethanol (95%) was degassed by bubbling of nitrogen gas prior to use. 2,2'-Azobisisobutyronitrile (AIBN, J&K Scientific, 99%) was purified by recrystallization from anhydrous ethanol (two repeats). Dibutyltin dilaurate (DBDTL, 97.5%), hexamethylene diisocyanate (HDI, 99%), and di-*n*-butylamine (99.5%) were provided by J&K Scientific and used as received. Polyethylene glycol (PEG,  $M_n = 580 \text{ g mol}^{-1}$ ) was stored with 4 Å molecular sieves and dried under vacuum at 80°C for 24 h prior to use. High-density polyethylene (HDPE,  $M_w = 8.4 \times 10^4 \text{ g mol}^{-1}$ ,  $T_m = 135^\circ\text{C}$ ) and polyether-based polyurethane thermoplastic elastomer (TPU) were purchased from Jam Petrochemical and Nanjing Xianbang Technical Company, respectively. All other chemicals were obtained commercially and used without further purification unless otherwise stated.

#### Synthesis of hydroxyl-Terminated Polyethylene (PE-OH)

To a stirring clear solution of PE-ene (0.89 g, 1.0 equiv.) in dried chlorobenzene at 105°C, 2-mercaptoethanol (1.01 g, 20 equiv.), and AIBN (0.05 g, 0.5 equiv.) were added. The reaction mixture was stirred at 105°C for 5 h. After that, the final solution was poured into ethanol and the product was collected by filtration, washed with ethanol for several times, and dried *in vacuo* at 60°C to constant weight (0.80 g in 85% yield).

#### Synthesis of polyethylene-*b*-polyurethane-*b*-Polyethylene Triblock Copolymers (EUE)

Firstly, the isocyanate-terminated polyurethane prepolymers (OCN-PU-NCO) were synthesized. A three-necked round bottom flask charged with dried PEG (7.44 g, 1.0 equiv.), equipped with a mechanical stirrer, nitrogen inlet, and dropping funnel, was kept in an oil bath at 35°C. After purging with nitrogen for 15 min, HDI (2.45 g, 1.14 equiv.) and 12 mL of toluene was added with constant stirring at 500 rpm and the mixture was heated up to 80°C slowly. The reaction took place under nitrogen atmosphere for 90 min to form the prepolymer OCN-PU-NCO and the content of NCO groups was titrated by di-*n*-butylamine.

Secondly, the polyethylene-*b*-polyurethane-*b*-polyethylene (EUE) triblock copolymers were prepared by the coupling reaction of OCN-PU-NCO and PE-OH. A Schlenk flask (100 mL) charged with PE-OH (0.76 g, 1.0 equiv. of -OH) was degassed with nitrogen for 20 min and dried toluene (30 mL) was then introduced via a syringe. After heating to 110°C to dissolve the PE-OH completely, OCN-PU-NCO (3.75 g, 0.9 equiv. of -NCO) and DBDTL were injected into the reactor and the mixture was stirred for 2 h. The resulting solution was then cooled to room temperature and the solvent was removed by rotary evaporation. The product was swollen in chloroform overnight. The EUE copolymers were transparent like a piece of gel in chloroform due to their highly extended chains, whereas the residual unreacted PE-OH remained unchanged as small solid particles. Thus based on their tremendous dimensional difference, the resulting swollen polymers were filtered with a Buchner funnel and washed with large amount of methanol to remove the

residual PE-OH and dried under vacuum to constant weight (translucent white solid, 3.50 g in 80% yield).

#### Preparation of TPU/HDPE Blends

The TPU/HDPE blends with various amounts of EUE copolymer were prepared using a miniature high performance hybrid composites molding system (HAAKE MiniLab II, 7 cm<sup>3</sup> capacity). All the components in each blend were premixed manually, introduced into MiniLab subsequently, and melt mixed for 10 min at 100 rpm and 190°C. The blends were then extruded and cooled to room temperature.

#### Characterization

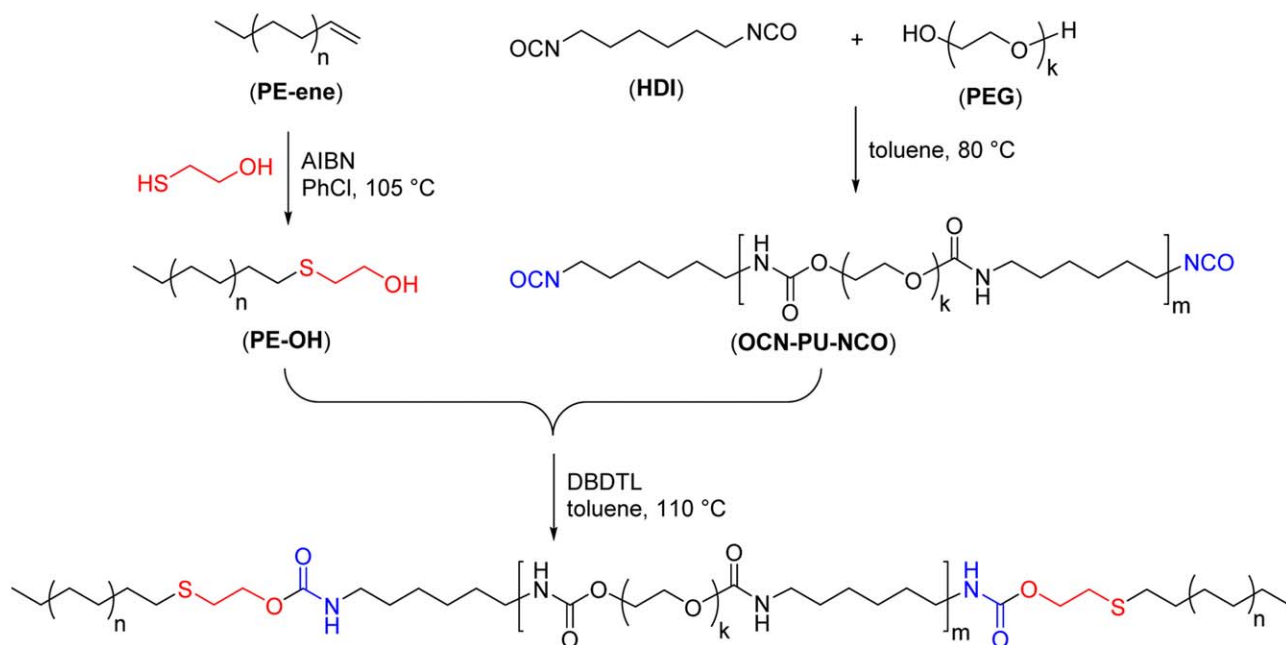
High temperature gel permeation chromatography (HT-GPC) measurements were carried out on a Viscotek 350A HT-GPC system with 1,2,4-trichlorobenzene as the eluent (1.0 mL min<sup>-1</sup> at 150°C). All the <sup>1</sup>H NMR spectra were recorded on a Varian Mercury 300 pulse NMR Spectrometer with deuterated solvent (*o*-dichlorobenzene-*d*<sub>4</sub>) and tetramethylsilane as an internal standard. Fourier transform-infrared spectra (FT-IR) were performed on a Nicolet 5700 spectrometer at room temperature over the range of 4000–400 cm<sup>-1</sup>. Differential scanning calorimetry (DSC) experiments were conducted on a TA Q200 thermal analyzer under N<sub>2</sub> atmosphere. Two heating cycles were recorded at 10°C min<sup>-1</sup>. Thermogravimetric analysis (TGA) of polymers were carried out in a dry nitrogen atmosphere (40 mL min<sup>-1</sup> flow) on a TA Q500 analyzer heating from 30 to 600°C at 10°C min<sup>-1</sup>. Transmission electron microscopy (TEM) was used for the morphological investigation of EUE triblock copolymers with a JEM1230 microscope. Scanning electron microscopy (SEM) images were captured on a Carl Zeiss ULTRA 55 instrument (Germany) at an accelerating voltage of 5 kV. Fractured surfaces of the samples were fractured in liquid nitrogen and coated with a thin gold film using a gold sputter.

## RESULTS AND DISCUSSION

#### Synthesis and Characterization of EUE Triblock Copolymers

The vinyl-terminated linear polyethylenes (PE-ene) with different molecular weights were prepared via ethylene polymerization catalyzed by a bis[N-(3-*tert*-butylsalicylidene) cyclopentylamino]-zirconium (IV) dichloride complex in combination with dried methylaluminoxane (*d*MAO).<sup>22,46</sup> By modifying the literature methods,<sup>47,48</sup> the corresponding hydroxyl-terminated polyethylenes (PE-OH) were achieved through the thiol-ene click reactions of PE-ene with the excess of 2-mercaptoethanol in chlorobenzene at 105°C in the presence of AIBN (Scheme 1).

The <sup>1</sup>H NMR analysis of PE-OH samples (Figure 1) showed the disappearance of characteristic peaks at 2.02 (–CH<sub>2</sub>CH=), 4.95 (CH<sub>2</sub>=CH–), and 5.78 (–CH=CH<sub>2</sub>) ppm, corresponding to the resonances of terminated vinyl group in the starting materials (PE-ene).<sup>22</sup> The new resonances at 2.33 (peak 2'), 2.50 (peak 3'), and 3.52 ppm (peak 4') were assigned to the protons of methylene groups adjacent to the sulfur atom and terminated hydroxyl group in PE-OH, respectively. The chain end functionality of PE-OH samples were calculated using the integrations of the resonances in the <sup>1</sup>H NMR spectrum and found to be almost 100%. Consistent with <sup>1</sup>H NMR analysis, FT-IR spectra also confirmed the complete consumption of the vinyl groups

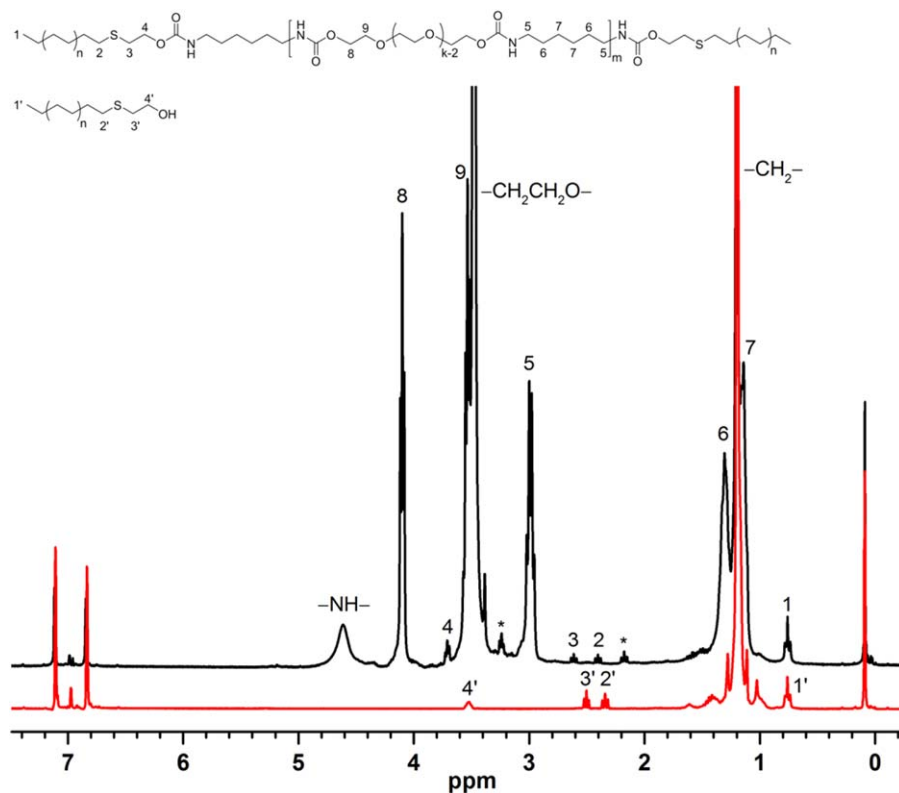


**Scheme 1.** Synthetic route of PE-*b*-PU-*b*-PE triblock copolymers (EUE). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

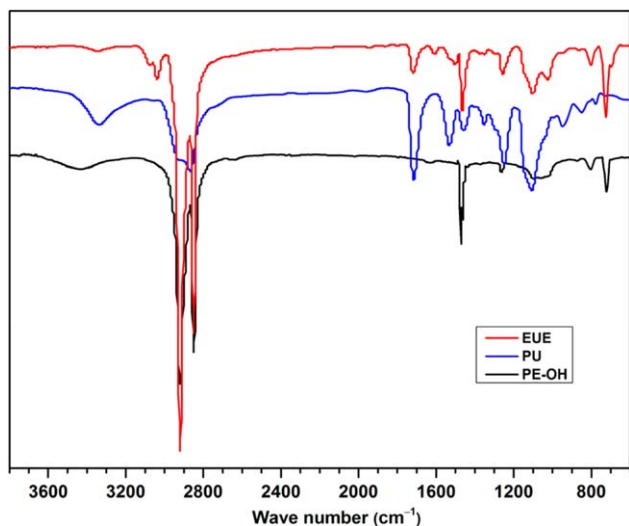
(bands at 1632 and 880 cm<sup>-1</sup>) and the appearance of hydroxyl groups (O–H stretching vibration at 3435 cm<sup>-1</sup>) (Figure 2).

The isocyanate-terminated polyurethane prepolymers (OCN-PU-NCO) were prepared via the addition polymerization of

PEG and HDI. The molecular weight of OCN-PU-NCO prepolymers was controlled by varying the reaction time from 90 to 120 min. The content of NCO groups in the prepolymers for the synthesis of EUE triblock copolymers were determined by



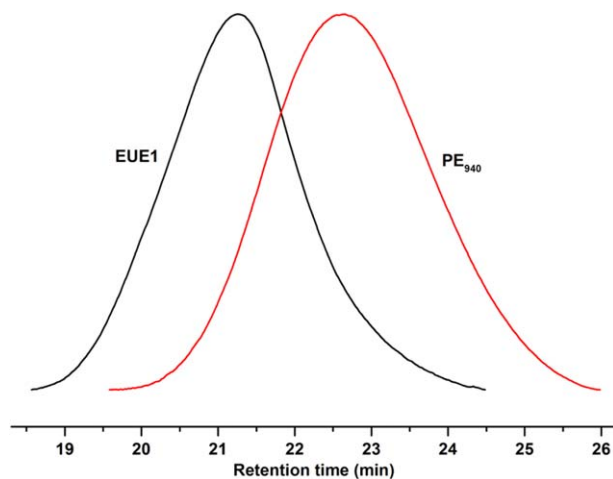
**Figure 1.** <sup>1</sup>H NMR spectra of PE-OH (bottom) and EUE triblock copolymer (top) in C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub>. \*: Not assigned. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 2.** FT-IR spectra of PE-OH (black), PU prepolymer (blue), and EUE triblock copolymer (red). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the titration according to the standard method. In order to characterize the structure of prepolymers, a sample withdrawn from the reaction medium was terminated with methanol and the solvent was removed *in vacuo*. In the FT-IR spectra of the sample (Figure 2), the characteristic absorption bands of carbamate bonds appear at 3336 (N–H stretching vibration), 1717 (C=O stretching vibration), 1531 (N–H bending vibration), 1249 (C–N stretching vibration), and 1106  $\text{cm}^{-1}$  (asymmetric C–O–C stretching vibration).

The polyethylene-*b*-polyurethane-*b*-polyethylene (EUE) triblock copolymers were obtained by the coupling reaction between OCN-PU-NCO prepolymer and hydroxyl-terminated polyethylene (PE-OH) (Scheme 1). The reaction was carried out by reacting OCN-PU-NCO prepolymer with an excess of PE-OH (NCO/OH molar ratio 1 : 1.1) using DBDTL as the catalyst at 110°C for 2 h in toluene. The crude copolymers were purified by swelling, filtration, and washing for several times to remove the residual PE-OH. The chemical structure of the final triblock copolymers was analyzed by  $^1\text{H}$  NMR and FT-IR. In the



**Figure 3.** HT-GPC traces of EUE triblock copolymer (EUE1 in Table I) and corresponding PE precursor (PE<sub>940</sub> in Table I). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$^1\text{H}$  NMR spectra (Figure 1), the peaks of methylene groups from PU segment appear at  $\delta$  4.10 (–NHC(O)OCH<sub>2</sub>–, peak 8), 3.53 (–C(O)OCH<sub>2</sub>CH<sub>2</sub>O–, peak 9), 3.48 (–OCH<sub>2</sub>CH<sub>2</sub>O– from PEG), and 3.00 (–O(O)CNHCH<sub>2</sub>–, peak 5), 1.31 (–CH<sub>2</sub>– from HDI, peak 6), and 1.14 (–CH<sub>2</sub>– from HDI, peak 7) ppm, while the triplet peaks of methylene groups from PE-OH segment were shifted to slightly lower field due to deshielding effect ( $\delta$  = 2.40, 2.61, and 3.71 ppm (peaks 2, 3, and 4 in Figure 1) corresponding to –CH<sub>2</sub>SCH<sub>2</sub>– and –CH<sub>2</sub>OC(O)– protons, respectively). The FT-IR spectra (Figure 2) displayed the characteristic bands of both polyethylene and polyurethane segments with the disappearance of the hydroxyl band at 3435  $\text{cm}^{-1}$ , which proved the success of the coupling reaction.

In comparison with the high-temperature GPC traces of a typical EUE triblock copolymer and the corresponding PE precursor (Figure 3), a distinct shift to higher molecular weight was observed. The apparent absence of residual PE-OH indicated the successful formation of the targeted EUE triblock copolymers.

The results obtained from DSC analysis of these EUE triblock copolymers are shown in Table I and Figure 4. The EUE triblock

**Table I.** Molecular Characteristics of EUE Triblock Copolymers and PE Precursors

Samples	$M_n^a$ (g mol <sup>-1</sup> )	PDI <sup>b</sup>	$W_{PE}^c$	$T_g^d$ (°C)	$T_m^d$ (°C)	$\Delta H^d$ (J g <sup>-1</sup> )	$X_c^e$ (%)	PE precursors <sup>f</sup>		
								$M_n$ (g mol <sup>-1</sup> )	$T_m$ (°C)	$X_c$ (%)
EUE1	950-7450-950	2.0	0.203	-46.4	121.4	3.4	6	940	126	70
EUE2	1120-5660-1120	2.1	0.283	-47.1	120.5	5.3	7	1080	127	77
EUE3	1520-5570-1520	2.3	0.353	-45.9	123.0	11.7	11	1460	128	77
EUE4	1890-5800-1890	2.4	0.395	-47.8	122.3	14.3	12	1840	128	81

<sup>a</sup> Calculated from  $^1\text{H}$  NMR spectra of EUE triblock copolymers.

<sup>b</sup> Determined by GPC based on poly(styrene) standard calibration.

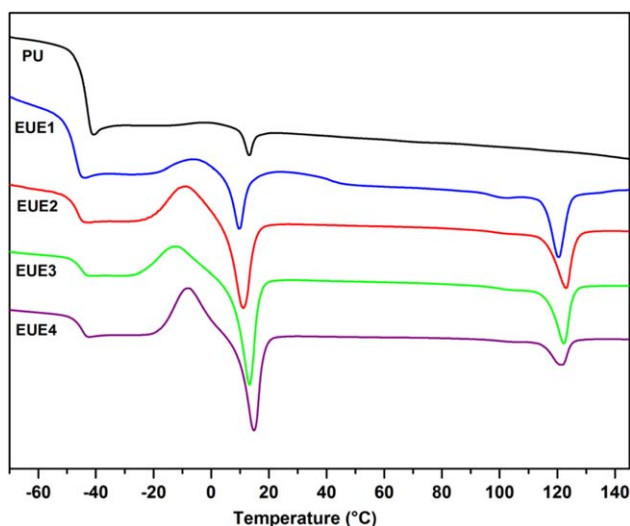
<sup>c</sup> PE weight fraction calculated from  $^1\text{H}$  NMR spectra.

<sup>d</sup> Determined by DSC (second heating cycle) at 10°C min<sup>-1</sup>.

<sup>e</sup>  $X_c$  is the degree of crystallinity, determined based on PE content.

<sup>f</sup> Previous results.<sup>22</sup>

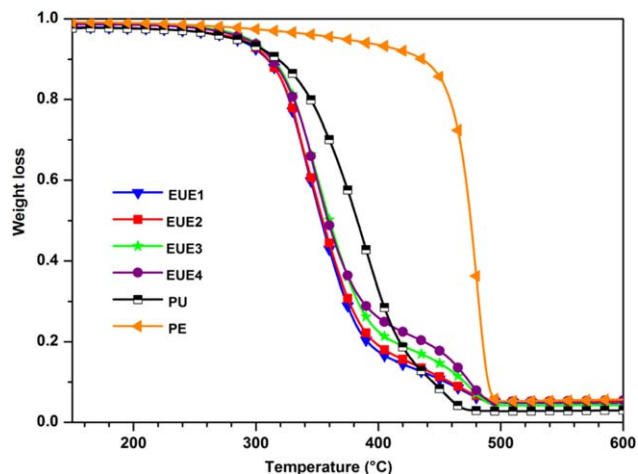




**Figure 4.** DSC curves of EUE triblock copolymers and PU prepolymer (corresponding to EUE4 in Table I). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

copolymers exhibited a glass transition temperature around  $-46^{\circ}\text{C}$ , a melting endothermic peak around  $15^{\circ}\text{C}$  corresponding to the polyurethane phase and the other melting peak at *ca.*  $122^{\circ}\text{C}$  as expected for the semicrystalline polyethylene phase. However, it should be noted that the  $T_g$  value of the polyurethane phase was slightly higher than that of the PU prepolymer ( $-48^{\circ}\text{C}$ ) because of the constraints influenced by the polyethylene crystalline blocks. In addition, the crystallinity of PE segments in the EUE triblock copolymers calculated based on the enthalpy and PE weight fraction was found to be much lower than the corresponding PE precursor (Table I), indicating that the large amorphous PU phase could perturb the crystallinity of PE segments.

The thermal stability of EUE triblock polymers as well as PE precursor and PU prepolymer were evaluated by TGA in a  $\text{N}_2$  environment and presented in Figure 5. For each EUE triblock copolymers, the degradation takes place with four stages. The first-stage degradation around  $170\text{--}260^{\circ}\text{C}$  is due to the presence



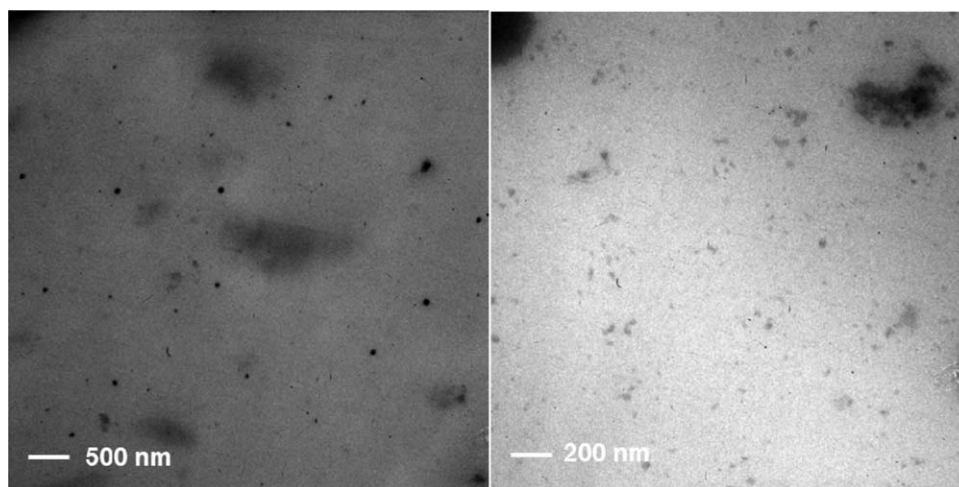
**Figure 5.** TGA curves of EUE triblock copolymers, PE precursor ( $\text{PE}_{1460}$ ), and PU prepolymer (corresponding to EUE4 in Table I) between 150 and  $600^{\circ}\text{C}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

of adsorbed moisture and solvents. The degradation at  $260\text{--}390^{\circ}\text{C}$  and  $390\text{--}430^{\circ}\text{C}$  corresponded to the decomposition of PU segments. The last stage showed an inflection at  $430^{\circ}\text{C}$ , which is consistent with PE precursor. It could be obviously observed from these curves that the thermal stability of EUE triblock copolymers increased along with the increase of PE weight fraction.

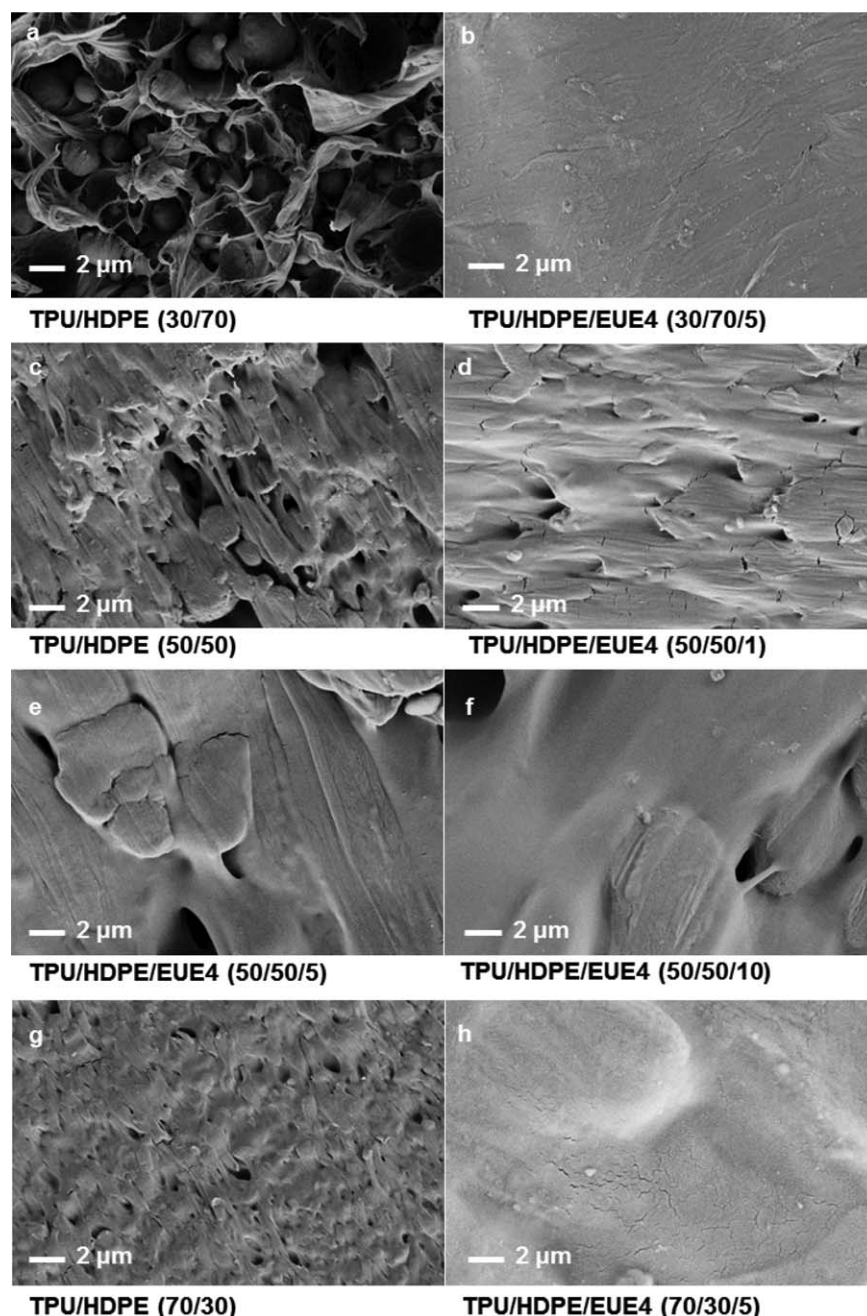
The typical TEM micrographs of EUE triblock polymers showed that the PU phase acted as the dispersion medium, in which the PE segments huddled together, thus forming an apparent micro-phase separation (Figure 6).

#### Compatibilization for TPU/HDPE Blends

To estimate the efficiency of EUE triblock copolymers as compatibilizers, EUE4 as a representative sample was applied in the TPU/HDPE blends and the surface morphology of polymer blends was investigated (Figure 7). The SEM micrographs of TPU/HDPE binary blends with different weight ratios (TPU/HDPE = 30/70, 50/50, and 70/30) showed the gross phase



**Figure 6.** TEM images of EUE triblock copolymers (EUE1 in Table I).



**Figure 7.** SEM images of TPU/HDPE blends with/without EUE triblock copolymer as a compatibilizer.

separation and the distinct boundary observed between TPU and HDPE indicated the strong incompatibility and poor interfacial adhesion [Figure 7(a,c,g)]. After the addition of EUE4 (5 wt %) into the TPU/HDPE blends [Figure 7(b,e,h)], the ternary polymer blends exhibited a much flatter surface morphology, suggesting that the EUE triblock copolymer obviously enhanced the compatibility of the immiscible TPU/HDPE blends. Furthermore, the effect of the amount of EUE4 on the microstructure of the ternary blends was also studied. As seen in Figure 7(d-f), the interface boundary between TPU and HDPE became smaller and unclearer as the amount of EUE4 increased. In a word, the EUE triblock copolymers were

effective compatibilizers in the TPU/HDPE blends and worthy of the further exploration.

## CONCLUSIONS

A series of novel polyethylene-*b*-polyurethane-*b*-polyethylene (EUE) triblock copolymers was synthesized via the combination of radical initiated thiol-ene reaction and addition polymerization, followed by the facile coupling reaction. The chain lengths of both PE and PU segments could be well controlled. The analysis of chemical structure by  $^1\text{H}$  NMR, FT-IR, and HT-GPC, as well as the thermal properties and micro-phase morphology by DSC,

TGA, and TEM, confirmed the successful synthesis of the EUE triblock copolymers. To the best of our knowledge, this is the first time to successfully synthesize the polyethylene-*b*-polyurethane-*b*-polyethylene triblock copolymers. Additionally, the SEM images proved that the EUE triblock copolymers could be used as effective compatibilizers for the TPU/HDPE blends.

## ACKNOWLEDGMENTS

The work was supported by the National Basic Research Program of China (No. 2011CB606004).

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