Segmented Block Copolyesters Using Click Chemistry

Stephen M. June, Philippe Bissel, Timothy E. Long

Department of Chemistry, Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, Virginia 24061-0344 Correspondence to: T. E. Long (E-mail: telong@vt.edu)

Received 15 March 2012; accepted 16 April 2012; published online DOI: 10.1002/pola.26168

ABSTRACT: Copper(I) catalyzed azide-alkyne 1,3-Huisgen cycloaddition reaction afforded the synthesis of triazole-containing polyesters and segmented block copolyesters at moderate temperatures. Triazole-containing homopolyesters exhibited significantly increased (~40 °C) glass transition temperatures (T_g) relative to high temperature, melt synthesis of polyesters with analogous structures. Quantitative synthesis of azido-terminated poly(propylene glycol) (PPG) allowed for the preparation of segmented polyesters, which exhibited increased solubility and mechanical ductility relative to triazole-containing homopolyesters. Differential scanning calorimetry demonstrated a soft segment (SS) T_g near -60 °C for the segmented polyesters, consistent with microphase separation. Tensile testing revealed Young's moduli ranging from 7 to 133 MPa as a function of hard segment (HS) content, and stress at break values approached 10 MPa for

INTRODUCTION Polyesters, which Wallace Carothers pioneered in the 1930s,¹ enable a wide range of technologies, including fibers, beverage containers, liquid crystalline structural materials, and coatings. The primary synthetic strategy for polyesters involves the melt polycondensation of a glycol and either a dicarboxylic acid or a dimethyl ester. These polymerizations, which are typically performed in the melt, require extremely high temperatures (>250 °C) and metal catalysts to obtain high conversion and molecular weight. In addition, most common polyesters exhibit glass transition temperatures (T_g 's) below 110 °C.² Utilization of a lower temperature polyaddition methodology may offer advantages over traditional melt polyesterification. Segmented block copolymers also offer many advantages over classical thermoplastic high performance random copolymers. Addition of an alternating flexible soft segment (SS) often offers increased solubility compared to the homopolymer of a hard segment (HS). In addition, segmented block copolymers typically exhibit microphase separation, often leading to elastomeric properties. Classical examples of segmented block copolymers include segmented polyurethanes, poly(siloxane imides), and poly(urethane ureas). Our research group has recently reported the many attributes of segmented block copolymers.³⁻⁵ In addition, our group maintains a significant

50 wt % HS segmented click polyesters. Dynamic mechanical analysis demonstrated an increased rubbery plateau modulus with increased HS content, and the T_g 's of both the SS and HS did not vary with composition, confirming microphase separation. Atomic force microscopy also indicated microphase separated and semicrystalline morphologies for the segmented click polyesters. This is the first report detailing the preparation of segmented copolyesters using click chemistry for the formation of ductile membranes with excellent thermomechanical response. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: atomic force microscopy (AFM); block copolymers; click chemistry; click polyesters; CuAAC; polyesters; segmented block copolymers; step-growth polymerization; triazole

interest in polyester design,^{6,7} and the synthesis of high performance segmented block copolymers using step-growth polymerization.⁸⁻¹⁰

Copper(I) catalyzed azide-alkyne 1,3-Huisgen cycloaddition (CuAAC) offers many advantages in the synthesis of polymeric materials. Sharpless and coworkers first described CuAAC as click chemistry in the early 2000s.¹¹ This reaction proceeds at relatively low reaction temperatures and in a wide variety of solvents, and in particular, click reactions exhibit remarkable tolerance to the presence of other functional groups. In addition, the reaction proceeds quantitatively in the absence of reaction byproducts.¹²⁻¹⁴ For these reasons, click chemistry has featured prominently in many polymer publications in recent years as a convenient route toward monomer synthesis,¹⁵ polymer coupling,^{16–22} post-polymerization pendant functionalization,^{17,23–25} and the synthesis of star and graft copolymers.^{20,26} Relatively few examples exist where azido-alkyne coupling provides the principal polymerization step. For example, due to quantitative reactions, azido-alkyne coupling regularly finds utility in the synthesis of dendrimers.^{14,26-32} Voit and coworkers first reported step-growth polyaddition using click chemistry in the synthesis of hyperbranched polytriazoles, although the

Additional Supporting Information may be found in the online version of this article.

© 2012 Wiley Periodicals, Inc.



WWW.MATERIALSVIEWS.COM

1

final product exhibited insignificant solubility.³³ In 2008, Shi and coworkers described the first soluble, hyperbranched triazole-containing polymer.^{34,35}

The literature presents fewer examples of click chemistry as the principal polymerization step toward linear polymers; however, some key examples do exist.^{26,36,37} In 2005, Matyjaszewski and coworkers described the step-growth polymerization of telechelic azide- and alkvne-functionalized macromonomers for the preparation of linear triazole-containing polymers.³⁷ Only two reports describe the synthesis of "click polyesters", or polyesters where click chemistry acts as the principal polymerization step. Takasu and coworkers reported the synthesis of thermally stable linear polyesters using click chemistry in 2009,³⁸ and again in 2010.³⁹ However, Takasu also reported limited solubility without thermomechanical properties, and most polymer structures were linear and aliphatic. The synthesis of aromatic or alicyclic click polyesters and determination of their mechanical properties remains unprecedented.

In this article, we present the synthesis of polyesters and segmented copolyesters using click chemistry. Comparison of analogous polyesters, which did not contain triazole units in the backbone, with triazole-containing polyesters revealed a dramatic increase in glass transition temperature (T_{σ}) upon triazole incorporation; however, the click homopolyesters polyesters exhibited poor mechanical ductility and solubility. Utilization of azido-terminated poly(propylene glycol) telechelic macromonomers allowed for the synthesis of segmented click polyesters. The segmented click polyesters exhibited solubility in a variety of solvents and formed mechanically robust films, in sharp contrast to previous literature. Thermal and mechanical testing confirmed microphase separation in ductile films, and atomic force microscopy (AFM) further revealed microphase separated and semicrystalline morphologies.

EXPERIMENTAL

Methods and Materials

Terephthaloyl chloride, dimethyl isophthalate, titanium(IV) tetraisopropoxide, 2-bromoethanol, sodium azide, 1,4-butanediol, tetrabutylammonium bromide (TBAB), and diethylene glycol (DEG) were purchased from Aldrich, isophthaloyl chloride, 6-bromohexanoyl chloride, propiolic acid, and cyclohexane dimethanol (70:30 trans:cis) from Alfa Aesar, and ptoluenesulfonic acid (pTsA) from Fluka and used without further purification. Eastman Chemical, Inc generously donated cyclohexane dimethanol (99% trans) and Bayer MaterialScience kindly provided poly(propylene glycol) (PPG) 4200, 2200 (Aclaim), and 1000 (Arcol). Chloroform, N, N-dimethylformamide, N-methylpyrrolidone, dimethylsulfoxide, and tetrahydrofuran were purchased from Fisher Scientific and used as received. Dichloromethane and triethylamine were purchased from Fisher Scientific and distilled from calcium hydride. ¹H and ¹³C NMR spectra were recorded on a 400-MHz Varian Inova spectrometer. Chemical shifts are reported in ppm downfield from the internal standard tetramethylsilane. $^{13}\mathsf{C}$ NMR spectra are included in the supplemental information.

Thermogravimetric analysis (TGA) was conducted on a TA Instruments Hi-Res TGA 2950 at a temperature ramp rate of 10 °C /min under a N_2 atmosphere. T_g 's were reported from the second heat of a heat/cool/heat cycle (0-150 $^\circ\text{C})$ at a heating rate of 10 °C/min and a cooling rate of 50 °C/min on a TA Instrument differential scanning calorimetry (DSC) Q1000 under N₂. Compression molding provided films for mechanical testing and all samples were melt pressed at 200 $^\circ\text{C}$ for approximately 2 min at \sim 15,000 psi. All samples were annealed at 150 °C for a minimum of 18 h prior to use. Dynamic mechanical analysis (DMA) was performed on a TA Instruments DMA Q800 under an N2 atmosphere in tension mode with strains of 15 um, frequencies of 1 Hz, and a ramp rate of 3 °C/min. Tensile testing was performed using rectangular films on an Instron 5500R tensile frame with a crosshead speed of 50 mm/min. AFM was performed in tapping mode on a Veeco Multimode AFM using a low force constant (5 N/m) tip.

Synthesis of Bis(2-bromoethyl)terephthalate (BrTP) (1)

The dropwise addition of 2-bromoethanol (14 mL, 200 mmol) in CH₂Cl₂ (50 mL) to a solution of terephthaloyl chloride (10 g, 49 mmol), and N(Et)₃ (28 mL, 200 mmol) in CH₂Cl₂ (100 mL) at 0 °C followed by subsequent stirring at 23 °C for 20 h afforded BrTP. Washing with 5% aqueous solution of K₂CO₃ (3 × 50 mL), water (2 × 50 mL) and drying over MgSO₄ yielded **1** as a yellow solid. The crude product was recrystallized from ethyl acetate to give pure **1** (13.05 g, 70%) as white crystals; ¹H NMR (CDCl₃, 500 MHz) δ 3.26 (t, 4H), 4.26 (t, 4H), 7.45 (s, 4H).



Synthesis of Bis(2-azidoethyl)terephthalate (BATP) (2)

A mixture of **1** (10 g, 34 mmol), NaN₃ (17.6 g, 270 mmol), and TBAB (0.55 g, 1.7 mmol) in DMF (50 mL) was heated at 80 °C for 48 h. After cooling, a saturated aqueous solution of LiBr (50 mL) was added and the mixture was extracted with ethyl acetate (3 \times 50 mL). The combined organic phases were washed with water (3 \times 50 mL), brine (50 mL), dried over MgSO₄ and the solvent removed under rotary evaporation. The crude was recrystallized from ethyl acetate to give **2** (mp 81–83 °C) (7.62 g, 59%) as white crystals; ¹H NMR (CDCl₃, 500 MHz) δ 3.62 (t, 4H), 4.52 (t, 4H), 8.14 (s, 4H).



Synthesis of Bis(2-bromoethyl)isophthalate (BrIP) (3)

A mixture of isophthaloyl chloride (27.3 g, 0.13 mol), N(Et)₃ (75 mL, 0.54 mol) in CH₂Cl₂ (400 mL), and 2-bromoethanol (38 mL, 0.54 mol) in CH₂Cl₂ (50 mL) was added dropwise at 0 °C. The mixture was stirred at room temperature for 20 h. The mixture was washed with 5% aqueous solution of K₂CO₃ (3 × 150 mL), water (2 × 150 mL) and dried over

MgSO₄. The crude was purified by silica chromatography (CHCl₃/hexanes 7:3) to give **3** (35.3 g, 72%) as white crystals; ¹H NMR (CDCl₃, 500 MHz) δ 3.23 (t, 4H), 4.23 (t, 4H), 7.59 (t, 1H), 8.28 (d, 2H), 8.75 (m, 1H).



Synthesis of Bis(2-azidoethyl)isophthalate (BAIP) (4)

A mixture of **3** (19.5 g, 52 mmol), NaN₃ (26.8 g, 410 mmol), and TBAB (0.84 g, 2.6 mmol) in DMF (100 mL), was heated at 80 °C for 48 h. After cooling, a saturated aqueous solution of LiBr (100 mL) was added and the mixture was extracted with ethyl acetate (3 \times 100 mL). The combined organic phases were washed with water (3 \times 100 mL), brine (100 mL), dried over MgSO₄ and the solvent removed under rotary evaporation. The crude product was purified by silica chromatography (CHCl₃/hexanes 8:2) to give **4** (13.0 g, 66%) as white crystals; (mp 73–75 °C) ¹H NMR (CDCl₃, 500 MHz) δ 3.63 (t, 4H), 4.53 (t, 4H), 7.59 (t, 1H), 8.28 (d, 2H), 8.75 (m, 1H).



Synthesis of trans-1,4-Cyclohexyl Dimethylene Dipropiolate (T-CHDMDP) (5)

A solution of *trans*-1,4-cyclohexyl dimethanol (5g, 35 mmol), pTsA (14.6 g, 77 mmol), and propiolic acid (8.6 mL, 143 mmol) in benzene (100 mL) was heated under reflu× for 20 h. The mixture was washed with water (3 × 100 mL), brine (100 mL) and dried over MgSO₄. The solvent was removed under rotary evaporation. The crude product was purified using silica chromatography (CHCl₃/hexanes 7:3) to give **5** (5.65 g, 65%) as white crystals; (mp 119–121 °C) ¹HNMR (CDCl₃, 500 MHz) δ 1.04 (m, 4H), 1.68 (m, 2H), 1.85 (m, 4H), 2.89 (s, 2H), 4.03 (d, 4H);

Synthesis of cis/trans-1,4-Cyclohexyl Dimethylene Dipropiolate (70:30-CHDMDP) (6)

A solution of *cis/trans*-1,4-cyclohexyl dimethanol (70:30 trans:cis) (5.5 g, 38 mmol), pTsA (15.9 g, 84 mmol), and propiolic acid (9.3 mL, 155 mmol) in benzene (100 mL) was heated under reflu× for 20 h. The mixture was washed with water (3 × 100 mL) and brine (100 mL) and the product was dried over MgSO₄. The solvent was removed under rotary evaporation and the crude was recrystallized from hexanes/ethyl acetate to give **6** (4.43 g, 47%) as white crystals; (mp 109–113 °C) ¹HNMR (CDCl₃, 500 MHz) δ 1.04 (m, 4H), 1.68 (m, 2H), 1.85 (m, 4H), 2.89 (s, 2H), 4.03 (d, 4H).



Synthesis of 1,4-Butanedipropiolate (7)

To a solution of 1,4-butanediol (4.3 g, 48 mmol) in $CHCl_3$ (100 mL), pTsA (106 mmol) and propiolic acid (192 mmol)



were added at 23 °C. The solution was heated under reflu× for 18 h. After cooling, the solution was washed with an aqueous saturated NaHCO₃ solution (50 mL), water (3 × 50 mL), brine (50 mL) and dried over MgSO₄. The solvent was removed under rotary evaporation and the crude was recrystallized from hexanes/ethyl acetate to give compound **7** as pale yellow crystals. (mp 56–58 °C) (6.02 g, 65%); ¹H NMR (CDCl₃, 500 MHz) δ 1.79 (m, 4H), 2.88 (s, 2H), 4.23 (m, 4H).



Synthesis of DEG Dipropiolate (8)

To a solution of DEG (6.2 g, 58 mmol) in CHCl₃ (100 mL), pTsA (128 mmol) and propiolic acid (232 mmol) were added at 23 °C. The solution was heated under reflu× for 18 h. After cooling, the solution was washed with an aqueous saturated NaHCO₃ solution (50 mL), water (3 × 50 mL), brine (50 mL) and dried over MgSO₄. The solvent was removed under rotary evaporation and the crude was purified by silica chromatography compound **8** as a yellow oil. (7.31 g, 60%); ¹H NMR (CDCl₃, 500 MHz) δ 2.91 (s, 2H), 3.73 (t, 4H), 4.33 (t, 4H).



Synthesis of Poly(propylene glycol) Bis-6-bromohexanoate (9)

To a solution of PPG (¹H NMR $M_n = 1932$, 19.8 g 9.0 mmol) in 100 mL of anhydrous dichloromethane, 2.76 mL (19.8 mmols–2.2 molar excess) of triethylamine was added by syringe and the reaction was cooled to 0 °C. 3.02 mL (19.8 mmols–2.2 molar excess) of 6-bromohexanoyl chloride was added dropwise, and the reaction was allowed to equilibrate at room temperature and stirred overnight. The triethylammonium chloride was filtered from the solution, and the solution was washed with saturated sodium bicarbonate (1 × 100 mL), deionized water (3 × 100 mL), and brine (1 × 100 mL). The solution was dried over MgSO₄, and the solvent was removed under rotary evaporation to yield **9** as a clear oil (14.36 g, 72% yield). **10** was used without further purification. The structure was confirmed using ¹H NMR spectroscopy (spectra included in supplemental information).



Synthesis of Poly(propylene glycol) Bis-6-azidohexanoate (10)

To a solution of **10** (¹H NMR M_n = 2289, 14.36 g, 6.4 mmol) in 100 mL DMF, 2.92 g (44.9 mmol) of sodium azide (seven molar excess) was added. The mixture was allowed to react for 48 h at 65 °C. After cooling, a saturated aqueous solution of NaCl (100 mL) was added and the mixture was extracted

3



SCHEME 1 Synthesis of bis-2-bromoethyl terephthalate and isophthalate and subsequent conversion into the corresponding bisazide for utility in Cu(I) catalyzed 1,3-Huisgen cycloaddition.

with ethyl acetate (3 \times 100 mL). The combined organic phases were washed with water (3 \times 100 mL), brine (1 \times 100 mL), dried over MgSO₄, and the solvent removed under rotary evaporation to yield **10** as a clear oil. The crude product was purified by passing over silica with chloroform as an eluent. The structure was confirmed using ¹H NMR spectroscopy (spectra included in supplemental information).



Polymer Synthesis

In a representative synthesis, an equimolar amount of bisazide and bispropiolate were dissolved in N,N-dimethylformamide (DMF) or dimethyl sulfoxide (DMSO). The reaction solution was sparged for at least 10 min with Ar or N₂ to remove any dissolved oxygen. A catalytic amount (100 ppm) of both CuI and Cu powder were added to the reaction mixture. The solution was heated to 60 °C and stirred overnight under an inert atmosphere. The resulting mixture was precipitated into an aqueous solution of *N*, *N*,*N'*, *N''*-pentamethyldiethylene triamine and vacuum filtration yielded the polymer in powder form. The resulting polymer was dried overnight at reduced pressure and 50 °C to afford the dry product. Segmented click polyesters were synthesized using a similar method.

RESULTS AND DISCUSSION

The synthesis of several bisazide and bispropiolate monomers allowed for the utilization of click chemistry for the synthesis of novel segmented polyesters. The reaction of 2-bromoethanol



SCHEME 2 Conversion of various diols into the corresponding propiolates for subsequent synthesis of polyesters using Cu(I) catalyzed 1,3-Huisgen cycloaddition.

TABLE 1 Comparison of Thermal Transitions of Triazole-Containing Polyesters and Structurally Analogous MeltTransesterification Polyesters

	Triazole- Containing Polyesters		Melt Polyesters	
HO-R-OH	<i>T</i> g (°C)	<i>T</i> _m (°C)	<i>T</i> g (°C)	<i>T</i> _m (°C)
cyclohexane dimethanol 99% trans	121	201	80	214
cyclohexane dimethanol trans:cis	117	182	72	ND
butane diol	95	178	25	142
Diethylene glycol	77	ND	25	ND

ND = not detected in the DSC experiment.

with both terephthaloyl dichloride and isophthaloyl dichloride afforded the corresponding dibromides for utilization in the synthesis of bisazide monomers. Reaction of the dibromides with sodium azide resulted in the formation of the corresponding bisazides. ¹H NMR spectroscopy confirmed the structures of the synthesized bisazides. Scheme 1 details the synthesis of these bisazides. Reaction of an excess of propiolic acid with 1,4-butane diol, DEG, *trans*-1,4-cyclohexane dimethanol (CHDM), or a mixture of *trans*- and *cis*-CHDM (the *trans:cis* ratio was 70:30) in refluxing chloroform or benzene at 80 °C for 18 h with an excess of *p*-toluene sulfonic acid yielded monomers with bispropiolate functionality, as depicted in Scheme 2. ¹H NMR spectroscopy confirmed the structures and purity of the bispropiolates.

The utilization of click chemistry resulted in a diverse series of triazole-containing polyesters. Preliminary syntheses with bisazidoterephthalates yielded polymers that exhibited insignificant solubility in most organic solvents. However, utilization of isophthalate-derived bisazides afforded polymers that demonstrated solubility in DMSO and N-methyl-2-pyrrolidone (NMP) upon heating. The resulting polymers meltpressed into free-standing, albeit brittle films. The polymers exhibited remarkably high glass transition temperatures ($T_{\rm g}$) and demonstrated good thermal stability (Table 1). Scheme 3 illustrates the synthesis of polyesters using 1,3 Huisgen CuAAC click chemistry.

Synthesis of non-click polyester analogs using melt transesterification offered a control to elucidate the effects of the triazole ring on the physical and chemical properties of the polymers and to compare the glass transitions of the click polyesters to structurally similar polyesters. The resulting polyesters exhibited good solubility in chloroform and meltpressed into mechanically robust films. Scheme 4 compares the chemical structures and synthetic conditions for both the click polyesters and melt transesterification polyesters.

DSC allowed for a determination of $T_{\rm g}$'s of the click polyesters as well as the melt polyesters to compare the thermal properties of the triazole-containing polyesters with structurally analogous melt polyesters, and Table 1 illustrates these results. Polyesters synthesized using click chemistry in all cases exhibited at least a 40 °C higher $T_{\rm g}$ than their structural analogues, and in most cases demonstrated a crystalline $T_{\rm m}$, in contrast to the structural analogues, which only exhibited crystalline $T_{\rm m}$'s with a high degree of structural regularity. In addition, some triazole-containing polyesters exhibited $T_{\rm g}$'s near 125 °C. These results suggested that triazole incorporation enhances chain stiffness and crystallinity, likely due to intermolecular association.

Because of the high glass transition temperatures of the synthesized triazole-containing polyesters, they were potentially useful as a HS in segmented polyesters. Preparation of segmented polyesters required the synthesis of an azide-functionalized SS. PPG offered good solubility in many solvents, a low T_{g} and commercial availability with high (f = 2) telechelic functionality at a variety of molecular weights. Each of these properties allowed for PPG to serve as the SS in the synthesis of segmented polyesters. The esterification reaction of 6-bromohexanoyl chloride and PPG ($M_{\rm n}$ - 1932) yielded bromine-terminated PPG segments (PPG-dibromide) in \sim 70% isolated yield, in agreement with our previous report.⁵ Subsequent reaction with an excess of sodium azide yielded the azide-functionalized PPG oligomer (PPG-bisazide) in \sim 60% isolated yield. ¹H NMR spectroscopy confirmed the purity, functionality (f = 2), and molecular weight of this difunctional oligomer. Scheme 5 illustrates the synthesis of PPG-dibromide and subsequent conversion into PPGbisazide.



SCHEME 3 1,3-Huisgen CuAAC as a synthetic route for polyesters containing 1,2,3-triazole units.



SCHEME 4 Synthesis of triazole-containing polyesters and their structurally analogous melt transesterification polyesters for comparison of thermal properties.

The reaction of PPG-bisazide, *cis/trans*-1,4-cyclohexyl dimethylene dipropiolate (70:30-CHDMDP), and bis(2-azidoe-thyl)isophthalate (BAIP) in DMSO with catalytic Cu and CuI afforded segmented polyesters with HS contents of 30, 40, and 50 wt % HS, shown as Scheme 6. Equation 1 illustrates the calculations utilized to determine HS content. The obtained polyesters were tan, elastomeric, and readily dispersible in DMF, DMSO, and NMP. However, DLS demonstrated aggregation of the polymers in all available SEC solvents, so molecular weight data was unattainable. Melt pressing yielded light tan, free-standing films that exhibited flexibility and mechanical ductility. These results were in contrast to the homopolyesters prepared using click chemistry, indicating the utility of synthesizing segmented block copolyesters to enhance film ductility.

In situ FTIR spectroscopy offered a method for evaluation of the reaction rates of the click reaction toward segmented

click polyesters. Figure 1 illustrates FTIR spectra at 2106 cm⁻¹ as a function of time. This wavenumber corresponded to the azide stretching frequency. Initially, the absorbance at 2106 cm⁻¹ decreased linearly with time. After approximately 2 h, the peak reached a plateau, indicating a lowered reaction rate due to a decreasing concentration of azide and alkyne functional groups within the solution. After ~8 h, complete azide consumption occurred, indicating high conversion and reaction completion.

DSC and TGA provided analysis of the thermal transitions of the segmented polyesters, and Table 2 summarizes these results. SS $T_{\rm g}$'s near -60 °C indicated microphase separation, while 1st heat $T_{\rm m}$'s illustrated the semicrystalline nature of these polyesters, suggesting elastomeric properties. In addition, TGA demonstrated that these polyesters exhibited $T_{\rm d(on$ $set)}$ temperatures above 300 °C, confirming excellent thermal stability for melt processing.



SCHEME 5 Synthesis of azide-terminated PPG for preparation of segmented polyesters using Cu(I) catalyzed 1,3-Huisgen cycloaddition.



SCHEME 6 Synthesis of segmented polyesters using Cu(I) catalyzed 1,3-Huisgen cycloaddition.



FIGURE 1 In situ FTIR spectra at 2106 cm⁻¹ demonstrating complete azide consumption at \sim 8 h.

% hard segment =
$$\frac{CHDMBP + BAIP}{CHDMBP + BAIP + PPG - bisazide} \times 100$$
(1)

Tensile testing evaluated the ultimate mechanical properties of these segmented click polyesters; Figure 2 shows representative traces for each HS content. Tensile testing of melt pressed films revealed Young's moduli of 7, 22, and 133 MPa for the 30, 40, and 50 wt % HS segmented polyesters, respectively. As expected, the moduli increased with increasing wt % HS, consistent with microphase separated thermoplastic elastomers. Stress at break also increased as a function of HS content with values ranging from 1.4 to 9.2 MPa. Strain at break did not exhibit a dependence on HS content

TABLE 2 Thermal Characterization of Segmented Click

 Polyesters

Hard Segment Content	<i>T</i> _g (°C)	<i>T</i> _m (°C)	<i>T</i> _{d (onset)} (°C)
30 wt %	-61	114	313
40 wt %	-61	168	329
50 wt %	ND	171	321

ND = not detected in the DSC experiment.



10 9 30 wt % HS 8 -- 40 wt % HS **Fensile Stress (MPa)** 7 50 wt % HS 6 5 4 3 2 1 0 0 5 10 15 20 25 30 35 40 45 Tensile Strain (%)

FIGURE 2 Representative tensile traces for segmented click polyesters with varying hard segment content.

with values in all cases near 35%. These properties are consistent with segment block copolymers. Table 3 illustrates these results.

DMA provided an efficient means to further probe microphase separation, as well as the mechanical properties as a function of temperature. Figure 3 illustrates DMA traces of storage moduli as a function of temperature for each HS content segmented click polyester. Table 4 shows the values of the SS T_g , the HS T_g , and the HS T_m . Only minor variation occurred among the SS T_g and HS T_g values, in good agreement with the SS T_g values shown in Table 2. The slightly increased values for T_g 's reported using DMA relative to those obtained using DSC are consistent with the literature.⁴⁰ This is due to the delayed effects of the onset of segmental motion on mechanical properties. The endotherm relating to the onset of segmental motion (DSC T_g) does not significantly affect the mechanical properties until long range

TABLE 3 Tensile Data for Segmented Click Polyesters with	
Varying Hard Segment Content	

		0	
LIC Contont	Stress at	Strain at	E Modulus
HS Content	Dreak (IVIPa)	Dreak (%)	(IVIPa)
30 wt %	1.4 ± 0.1	32 ± 3	7 ± 1
40 wt %	$\textbf{3.5} \pm \textbf{0.3}$	38 ± 2	22 ± 4
50 wt %	9.2 ± 0.6	35 ± 4	133 ± 7

JOURNAL OF POLYMER SCIENCE PART A: POLYMER CHEMISTRY 2012, 000, 000-000

7



FIGURE 3 Dynamic mechanical analysis of segmented click polyesters with varying hard segment content.

segmental motion is achieved throughout the entire SS. The $T_{\rm m}$ of the HS increased with increasing HS content, also consistent with DSC results, perhaps suggesting a lower level of crystallinity in lower HS content segmented click polyesters. The observed glassy storage modulus did not substantially change with HS content; however, the rubbery plateau modulus exhibited a significant increase at room temperature as a function of increasing HS content. These results show good agreement with the tensile data and are consistent with literature precedence on semicrystalline segmented block copolymers with varying HS content.^{41,42}

AFM provided a method to further confirm the microphase separated nature of the segmented click polyesters. Melt pressing and subsequent annealing at 140 °C provided films suitable for AFM. Figure 4(a) shows a 1×1 um image of the 40% HS polyester. In this image, the lighter features represent the HS, whereas the darker features represent the SS. Figure 4(b) shows a 5x5 um image of the same sample. At this magnification, the microphase separated domains are also visible; however, the brighter, ribbon-like features represent the semicrystalline domains. These results further confirm the microphase separated and semicrystalline nature of these segmented click polyesters. Literature precedence exists for AFM observation of short-range ribbon microstructures in semicrystalline segmented block copolymers, similar to those in Figure 4(a), and transmission electron microscopy commonly depicts long-range ribbon microstructures in semicrystalline segmented block copolymers similar to those in Figure 4(b).⁴²

TABLE 4 Thermal Transitions of Segmented Click Polyesterswith Varying Hard Segment Content Obtained from DynamicMechanical Analysis

Hard Segment Content	Sample	<i>T</i> _{g,1} (°C)	<i>T</i> _{g,2} (°C)	<i>T</i> _m (°C)
30 wt %	30 wt % HS	-52	57	87
40 wt %	40 wt % HS	-48	55	154
50 wt %	50 wt % HS	-52	62	175



FIGURE 4 AFM images of 40 wt % HS segmented click polyester demonstrated microphase separated morphology and crystalline domains.

CONCLUSIONS

This manuscript is the first reported synthesis of segmented copolyesters using copper(I) catalyzed azide-alkyne 1,3-Huisgen cycloaddition. Click chemistry offered an efficient, lowtemperature method toward the synthesis of polyesters and segmented block copolyesters. DSC confirmed a significant increase (\sim 40 °C) in $T_{\rm g}$ of the triazole-containing homopolyesters relative to structurally analogous polyesters synthesized using melt transesterification. Utilization of azido-functionalized PPG telechelic macromonomers for the synthesis of segmented click polyesters with varying HS content resulted in a marked increase in polymer solubility and film ductility. DSC demonstrated microphase separation of the segmented click polyesters, suggesting the potential for elastomeric properties. Tensile testing revealed an increase in Young's moduli from 7 to 133 MPa and stress at break from 1.5 to 9 MPa as HS content increased from 30 to 50 wt %, and DMA displayed microphase separation and an increase in rubbery plateau modulus and crystalline $T_{\rm m}$ with

JOURNAL OF POLYMER SCIENCE Chemistry

increasing HS content. AFM confirmed the existence of microphase separated and semicrystalline morphological domains. These results suggest versatility of click chemistry toward the synthesis of high performance polyesters and segmented block copolyesters.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Qin Lin and Dr. Rama Puligadda for insightful discussions during the conception of this research. This research was supported by Brewer Science, Inc. under contract # N00014-07-C-0797.

REFERENCES AND NOTES

1 Carothers, W. H. Trans. Faraday Soc. 1936, 32, 39-53.

2 Rogers, M. E.; Long, T. E.; Turner, S. R. Synthetic Methods in Step-Growth Polymers; John Wiley & Sons, Inc.: Hoboken, New Jersey, **2003**; pp 1–16.

3 Williams, S. R.; Lepene, B. S.; Thatcher, C. D.; Long, T. E. *Bio-macromolecules* 2009, *10*, 155–161.

4 June, S. M.; Suga, T.; Heath, W. H.; Long, T. E.; Lin, Q.; Puligadda, R. J. *Adhes.* **2010**, *86*, 1012–1028.

5 Tamami, M.; Williams, S. R.; Park, J. K.; Moore, R. B.; Long, T. E. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 4159–4167.

6 Lin, Q.; Unal, S.; Fornof, A. R.; Armentrout, R. S.; Long, T. E. *Polymer* 2006, 47, 4085–4093.

7 Ozturk, G. I.; Pasquale, A. J.; Long, T. E. J. Adhes. 2010, 86, 395–408.

8 Cheng, S.; Zhang, M.; Dixit, N.; Moore, R. B.; Long, T. E. *Macromolecules* 2012, *45*, 805–812.

9 Huyck, R. H.; Trenor, S. R.; Love, B. J.; Long, T. E. *J. Macromol. Sci. Part A: Pure Appl. Chem.* **2008**, *45*, 9–15.

10 Layman, J. M.; Borgerding, E. M.; Williams, S. R.; Heath, W. H.; Long, T. E. *Macromolecules* **2008**, *41*, 4635–4641.

11 Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 2004–2021.

12 Himo, F.; Lovell, T.; Hilgraf, R.; Rostovtsev, V. V.; Noodleman, L.; Sharpless, K. B.; Fokin, V. V. *J. Am. Chem. Soc.* **2004**, *127*, 210–216.

13 Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 2596–2599.

14 Wu, P.; Feldman, A. K.; Nugent, A. K.; Hawker, C. J.; Scheel, A.; Voit, B.; Pyun, J.; Fréchet, J. M. J.; Sharpless, K. B.; Fokin, V. V. *Angew. Chem. Int. Ed. Engl.* **2004**, *43*, 3928–3932.

15 Takizawa, K.; Nulwala, H.; Thibault, R. J.; Lowenhielm, P.; Yoshinaga, K.; Wooley, K. L.; Hawker, C. J. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 2897–2912.

16 Golas, P. L.; Tsarevsky, N. V.; Sumerlin, B. S.; Walker, L. M.; Matyjaszewski, K. *Aus. J. Chem.* **2007**, *60*, 400–404.

17 Golas, P. L.; Matyjaszewski, K. *Chem. Soc. Rev.* 2010, *39*, 1338–1354.

18 Johnson, J. A.; Baskin, J. M.; Bertozzi, C. R.; Koberstein, J. T.; Turro, N. J. *Chem. Commun.* **2008**, 3064–3066.

19 Johnson, J. A.; Finn, M. G.; Koberstein, J. T.; Turro, N. J. *Macromolecules* **2007**, *40*, 3589–3598.

20 Qin, A.; Lam, J. W. Y.; Tang, B. Z. *Chem. Soc. Rev.* **2010**, *39*, 2522–2544.

21 Pressly, E. D.; Amir, R. J.; Hawker, C. J. J. Polym. Sci. Part A: Polym. Chem. **2011**, *49*, 814–819.

22 Zhang, C.; Shen, X.; Sakai, R.; Gottschaldt, M.; Schubert, U. S.; Hirohara, S.; Tanihara, M.; Yano, S.; Obata, M.; Xiao, N.; Satoh, T.; Kakuchi, T. J. *Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 746–753.

23 Bernardin, A.; Cazet, A. I.; Guyon, L.; Delannoy, P.; Vinet, F. O.; Bonnaffé, D.; Texier, I. *Bioconj. Chem.* **2010**, *21*, 583–588.

24 Schumers, J. M.; Gohy, J. F.; Fustin, C. A. Polym. Chem. 2010, 1, 161–163.

25 O'Reilly, R. K.; Joralemon, M. J.; Hawker, C. J.; Wooley, K. L. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 5203–5217.

26 Fournier, D.; Hoogenboom, R.; Schubert, U. S. *Chem. Soc. Rev.* 2007, *36*, 1369–1380.

27 Voit, B. I.; Lederer, A. Chem. Rev. 2009, 109, 5924–5973.

28 Franc, G.; Kakkar, A. K. Chem. Soc. Rev. 2010, 39, 1536–1544.

29 Joralemon, M. J.; O'Reilly, R. K.; Matson, J. B.; Nugent, A. K.; Hawker, C. J.; Wooley, K. L. *Macromolecules* **2005**, *38*, 5436–5443.

30 Polaske, N. W.; McGrath, D. V.; McElhanon, J. R. *Macromolecules* 2009, 43, 1270–1276.

31 Sumerlin, B. S.; Vogt, A. P. *Macromolecules* 2010, 43, 1–13.

32 Vestberg, R.; Malkoch, M.; Kade, M.; Wu, P.; Fokin, V. V.; Sharpless, K. B.; Drockenmuller, E.; Hawker, C. J. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 2835–2846.

33 Scheel, A. J.; Komber, H.; Voit, B. I. *Macromol. Rapid Commun.* **2004**, *25*, 1175–1180.

34 Xie, J.; Hu, L.; Shi, W.; Deng, X.; Cao, Z.; Shen, Q. J. *Polym. Sci. Part B: Polym. Phys.* **2008**, *46*, 1140–1148.

35 Xie, J.; Hu, L.; Shi, W.; Deng, X.; Cao, Z.; Shen, Q. *Polym. Int.* **2008**, *57*, 965–974.

36 Gao, Y.; Chen, L.; Zhang, Z.; Gu, W.; Li, Y. *Biomacromolecules* **2010**, *11*, 3102–3111.

37 Tsarevsky, N. V.; Sumerlin, B. S.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 3558–3561.

38 Nagao, Y.; Takasu, A. *Macromol. Rapid Commun.* **2009**, *30*, 199–203.

39 Nagao, Y.; Takasu, A. J. *Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 4207–4218.

40 Odian, G. Principles of Polymerization, 4th ed.; John Wiley & Sons, Inc.: Hoboken, New Jersey, **2004**.

41 Eisenbach, C. D.; Baumgartner, M. In Polyurethane Elastomers with Monodisperse Segments and their Model Precursors: Synthesis and Properties; Springer Publishing: New York City, New York, **1986**; pp 51–87.

42 Reinoud J, G. Prog. Polym. Sci. 2011, 36, 713-748.

