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Non-Migratory Internal Plasticization of Poly(Vinyl Chloride) via Pendant Triazoles Bearing Alkyl or Polyether Esters

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ABSTRACT: Branched and linear non-migratory internal plasticizers attached to PVC by a pendant triazole linkage were synthesized and investigated. Copper-free azide-alkyne thermal cycloaddition was employed to covalently bind triazole-based phthalate mimics to PVC. To systematically investigate the effect of plasticizer structure on glass transition temperature, several architectural motifs were explored. Free volume theory was considered when designing many of these internal plasticizers: hexyl-tethers were utilized to generate additional space between the triazole-phthalate mimic and the polymer backbone. Miscibility of these triazole-plasticizers in PVC is important: variation of the ester moieties on the triazole possessing alkyl and/or poly(ethylene oxide) chains produced a wide range of glass transition temperatures (T_g): from anti-plasticizing 96 °C, to highly efficient plasticized materials exhibiting T_g values as low as -42 °C.

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most utilized thermoplastics, with worldwide demand reaching 41.5 million tons in 2016.¹ However, PVC by itself is brittle and not readily processable. This material reached the success of its worldwide demand because of phthalates, a cost-effective additive (emollient) that imparts flexibility and resistivity towards weathering, temperature extremes and electrical conductivity. The use of phthalates as plastic emollients is widespread, representing 78% of global plasticizer demand in 2012, with applications ranging from industrial to consumer products such as coatings for electrical materials, building supplies, car interiors, flooring, sealants, cosmetics and personal care products.²

The pervasive utilization of low molecular weight blended phthalates as emollients inevitably leads to leaching and contamination of the environment. Human exposure is widespread and unavoidable. Routes of exposure come in many forms: ingestion, inhalation, dermal absorption, and intravenous

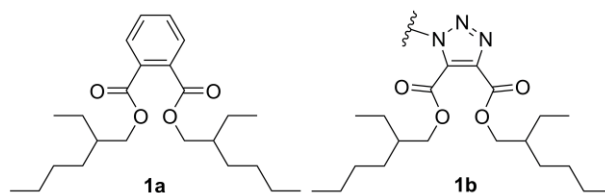


FIGURE 1 Di-(2-ethylhexyl) phthalate (DEHP) **1a** and Di-(2-ethylhexyl) Triazole Phthalate Mimic **1b**.

leaching.³ Ingestion has been shown to be the primary source of phthalate exposure in the general population through dietary intake of contaminated food.³ Medical devices³⁻⁸ also introduce phthalate, most notably di-(2-ethylhexyl) phthalate, DEHP **1a** into hospital patients via containers holding blood, nutritional formulas, and respiratory gases. Phthalates and their metabolites have displayed negative effects on various organs,⁹⁻¹⁵ and act as potent endocrine disrupting chemicals that cause deleterious pre- and postnatal developmental effects, notably in males.¹⁶⁻¹⁹ Bans of DEHP by the European Union²⁰⁻²³ and the United States²⁴ in children's articles has spurred the development of less toxic PVC plasticizer alternatives.^{4,25-31} A strategy known as

tethering involves covalently bonding a plasticizer to PVC. This prevents leaching and migration, leading to internally plasticized materials.

Recent efforts have explored internal plasticizers via thioether tethering: Michel³² described 2-ethylhexyl esters of thiosalicylate and thioglycolate as plasticizing agents via nucleophilic substitution of the chlorine atoms in PVC. Reinecke³³ utilized 2-ethylhexyl-mercapto-phthalates as internal plasticizers for PVC. Subsequently, aliphatic non-phthalate analogues containing ester/amide, carbonate/carbamate, and sulfonyl-ester/amide groups to functionalize the thiophenols with alkyl chains were developed.³⁴ Recently, a one-pot approach using thiolated trichlorotriazines (TCTA) gave self-plasticized PVC.³⁴⁻³⁶ These strategies are summarized graphically in the Supporting Information, Figure S1a.

Natural product-derived inexpensive internal plasticizers have also been developed.³⁷⁻³⁹ Zhou³⁷ functionalized PVC with aminated tung oil, exploiting the nucleophilic nature of an amine generated by trans-amidation to displace the chlorides on PVC. This approach was also applied to waste cooking oil³⁸ and cardanol (Supporting Information, Figure S1b).³⁹

The copper-mediated azide-alkyne cycloaddition (CuAAC) has become a popular strategy to covalently attach plasticizing moieties.⁴⁰⁻⁴⁴ All of these polymers suffer from residual copper contamination in the plasticized PVC.⁴⁰⁻⁴⁴ Both Yang⁴⁰ and Zhou⁴³ utilized CuAAC to functionalize PVC-azide with cardanol⁴⁰ and commercially available triethyl citrate.⁴³ Kwak⁴² also used this method to graft a hexyl ester-terminated hyperbranched polyglycerol plasticizer onto PVC-azide. Tasdelen and Demirci⁴¹ grafted poly(ϵ -caprolactone) in a similar fashion (Supporting Information, Figure S1c).

In a departure from the commonplace copper-catalyzed cyclizations, Braslau and Earla^{44,45} employed mild copper-free thermal azide-alkyne cycloadditions to attach acetylenedicarboxylate esters bearing alkyl groups, with the intended purpose of creating triazole-based phthalate analogues along the backbone to furnish internally plasticized PVC (Supporting Information, Figure S1c).

In this current study, non-migratory plasticizers attached to pendant triazole linkages were investigated. Copper-free thermal azide-alkyne cycloadditions were employed to functionalize PVC with an array of triazole-based phthalate mimics **1b**. Design rules for internal plasticizers on PVC have not yet been firmly established: this study aims to systematically investigate the effect of plasticizer structure on glass transition temperature. Factors such as branching, plasticizing group composition, and miscibility were explored. The concept of free volume theory⁴⁶ led to introduction of a flexible hexyl tether to generate increased volume between the internal plasticizer and the polymer backbone. Three architectural types of triazole-plasticizers were developed (Figure 2): “Type 0” **1a-b** has no tether, “Type 1” **1c** contains a single tether, and “Type 2” **1d** possesses two tethers. The “D” or “M” designation after Type 0 derivatives represents *di*-substituted **1a** or *mono*-substituted **1b** ester triazoles. The solubility of the triazole anchored plasticizers is important for both alkyl and poly(ethylene oxide) (PEO) derivatives. A range of glass transition temperatures (T_g) were obtained, from an anti-plasticizing 96 °C, to highly efficient internally plasticized PVC with a T_g of -42 °C.

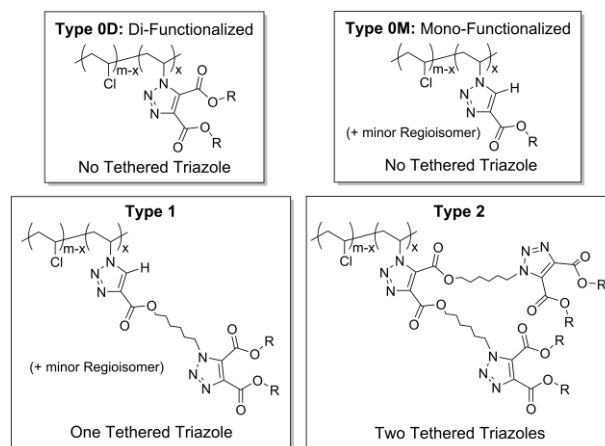


FIGURE 2 “Type” Designation of Triazole-Plasticizers.

EXPERIMENTAL

Materials

PVC (M_w : 43000 g/mol, PDI: 1.95) was supplied by Sigma-Aldrich and purified by dissolution of 20.00 grams of PVC in 240 mL of THF at 50 °C. This solution was allowed to cool to room temperature and precipitated in 800 mL of methanol. The mother liquor was filtered and the dissolution-precipitation process was repeated two more times.

Tetrahydrofuran was supplied by Fisher Scientific and was dried over sodium and benzophenone, under argon when anhydrous conditions were required. Silica gel (Grade 60, 230-400 mesh, 40-63 μm particle size) was supplied by Sorbent Technologies and was utilized for column chromatography. Hexanes (4.2% methylpentanes), ethyl acetate, dichloromethane (stabilized HPLC grade, submicron filtered), methanol, ethanol (absolute, 200 proof, molecular biology grade), acetonitrile (Optima™, LC/MS grade), tetrahydrofuran (HPLC grade, submicron filtered, uninhibited), toluene (HPLC grade), acetone (HPLC grade), dimethylformamide (sequencing grade), pentanes (HPLC grade, submicron filtered), diethyl ether (BHT stabilized), sodium chloride (crystalline), sodium bromide (granular), sodium bicarbonate (granular powder), potassium hydroxide (pellets), magnesium sulfate (anhydrous, powder), sodium sulfate (anhydrous, granular), concentrated hydrochloric acid (36.9%), concentrated sulfuric acid, bromine, zinc powder (99.2%), *n*-butanol (HPLC grade), and Celite™ 545 filtering aid (non-acid washed) were supplied by Fisher Scientific and used as delivered without additional purification. Dimethylsulfoxide ($\geq 99.9\%$), carbon tetrachloride (anhydrous, $\geq 99.5\%$), 3-pentanone ($\geq 99\%$), phosphorous pentachloride ($\geq 98.0\%$, purum p.a.), pyridine (anhydrous, 99.8%), iodine ($\geq 99.99\%$ trace metals basis), tri(ethylene glycol) monomethyl ether (95%), poly(ethylene glycol) monomethyl ether 350, and poly(ethylene glycol) monomethyl ether 550 were supplied by Sigma-Aldrich and used as delivered without additional purification. 6-Chlorohexanol ($>96\%$), poly(ethylene glycol) monomethyl ether 1000, poly(ethylene glycol) monomethyl ether 2000, acetylenedicarboxylate monopotassium salt ($>95\%$), tetrabutylammonium hydrogensulfate ($>98\%$), vinyl chloroacetate ($>99\%$, MEHQ stabilizer), and 3-pentanone ($>98.0\%$) were supplied by Tokyo Chemical Industries (TCI) and used as delivered without additional purification. Sodium azide (99%, extra pure), acetylenedicarboxylic acid (98%), propiolic acid (98%), *p*-toluenesulfonic acid monohydrate (99%, extra pure), pyridine (99%), and potassium bromide were supplied by Acros Organics and used as delivered without additional purification. Dimethyl acetylenedicarboxylate (98%), 2-ethyl-1-hexanol (99%), propiolic acid ($>98\%$) and *n*-hexane (95% HPLC distilled in glass) were supplied by Alfa Aesar and used as delivered without additional

purification. Dioctyl phthalate (CAS: 117-81-7), and sodium bisulfite (granular, F.C.C.) were supplied by Spectrum and used as delivered without additional purification. Chloroform-*d* (D, 99.8%) and benzene-*d*₆ (D, 99.5%) were supplied by Cambridge Isotope Laboratories and used as delivered without additional purification.

Measurements

Nuclear Magnetic Resonance (NMR) spectra were recorded with a Bruker Avance III HD 4 channel 500 MHz Oxford Magnet NMR Spectrometer with Automation, Varian Unity Plus 500 MHz Oxford Magnet NMR Spectrometer, or Bruker Avance III HD 800 MHz NMR Spectrometer. ¹H-NMR spectra taken in deuterated chloroform (CDCl₃) used the CHCl₃ signal (δ 7.26 ppm) as an internal standard, and the CDCl₃ triplet (δ 77.27 ppm) for ¹³C-NMR. ¹H-NMR spectra taken in benzene-*d*₆ utilized the C₆H₆ (δ 7.15 ppm) as an internal standard, and the C₆D₆ triplet (δ 127.68 ppm) for ¹³C-NMR. Fourier Transform Infrared Spectroscopy (FTIR) was recorded with a Perkin-Elmer Spectrum One Spectrometer, with sodium chloride (NaCl) plates. Liquids were measured neat. Polymers were measured as dried thin films. Solid molecules were combined, ground and pressed into potassium bromide (KBr) plates using a Carver press. High Resolution Mass Spectroscopy (HRMS) was recorded with a Thermo Scientific LTQ-Orbitrap Velos Pro MS. HRMS was taken with samples dissolved in acetonitrile (CH₃CN). Elemental analysis was performed by MHW Laboratories. Modulated Differential Scanning Calorimetry (MDSC) was performed on each polymer using a TA Instruments DSC Q2000 with a heat-cool-heat protocol. The general scanning ranges of MDSC analyses ranged from -90 °C to 200 °C, with a heating rate of 10 °C per minute. Derivative thermogravimetry (DTG) and thermal gravimetric analyses (TGA) were performed with a TA Instruments TGA Q500. TGA was performed within a scanning range of 30 °C to 500 °C, with a heating rate of 10 °C per minute in air or nitrogen.

Plasticizer Migration Study

The degree of plasticizer migration was determined by a process derived from an ASTM International standard test method (ASTM-D5227). Samples were extracted as square films (approximately 15 x 15 mm²), dried by high vacuum overnight and weighed.

A Berzelius beaker (150 mL) with a stir bar (25 mm x 8 mm diameter) was utilized as the extraction apparatus. 50 mL of *n*-hexane was pre-heated at 50 °C for 15 minutes prior to placing the polymer in the beaker. A stir rate of 100 revolutions per minute was used for all extractions. Each sample was extracted for 2 hours at 50 °C. After the extraction, the solvent was decanted. The polymer was placed in a 20 mL scintillation vial and dried under high vacuum at room temperature overnight. The mass of each sample post-extraction was determined.

Warning on Organic Azides

Organic azides can be dangerous in nature: low molecular weight organic azides have a propensity to violently decompose. A formula to determine if an organic azide is safe to handle has been created:⁴⁷ $(N_{\text{Carbon}} + N_{\text{Oxygen}}) / N_{\text{Azide Nitrogen}} \geq 3$, where N = number of atoms. While 6-azidohexanol and PVC-azide did not show signs of violent decomposition, it should be noted that extreme caution should be taken at all times when synthesizing or handling organic azides.

Syntheses of Triazole Plasticized PVC

Representative experimentals have been selected for each triazole (TRZ) plasticizer Type due to the large total amount of molecules and polymers synthesized for the study. Experimentals for all samples are given in the Supporting Information.

PVC-Azide Synthesis

Preparation of 15% PVC-Azide^{44,45,48} Purified poly(vinyl chloride) (2.000 g, 21.68 mmol) was added to a 100 mL round bottom flask and dissolved in 20 mL of dimethylformamide at 62 °C. Sodium azide (2.000 g, 30.76 mmol) was subsequently added and stirred for 2 h. The reaction was immediately filtered through a large Buchner funnel with a WhatmanTM grade 1 qualitative filter paper into a vacuum flask. The reaction solution was slowly precipitated into 200 mL of MeOH then filtered through a Buchner funnel and WhatmanTM grade 1 qualitative filter paper into a vacuum flask. The polymer was dried for 15 min under house vacuum, then dissolved in 20 mL of THF. The dissolved polymer was slowly precipitated into 100 mL of MeOH then filtered through a Buchner funnel and WhatmanTM grade 1 qualitative filter paper into a vacuum flask. This process was repeated once more with MeOH. The dissolved PVC was dissolved into 10 mL of THF and slowly precipitated in 100 mL of a 3:1 mixture of

MeOH:H₂O, filtered and dried for 15 min under house vacuum then dissolved in 20 mL of THF. The final precipitation was performed in MeOH. The isolated polymer was dried under house vacuum for 5 days *via* Buchner funnel to give 1.206 g of the title compound as a flocculent white solid. ¹H NMR (500 MHz, CDCl₃, δ, ppm): 4.68 – 4.26 (br m, *Cl-C-H*), 4.20 (br s, *N-C-H*), 4.09 (br s, *N-C-H*), 2.51 – 2.02 (br m, *Cl-C-CH₂-C-Cl*), 1.98 – 1.77 (br m, *Cl-C-CH₂-C-N₃* and *N₃-C-CH₂-C-N₃*). ¹³C NMR (125 MHz, CDCl₃, δ, ppm): 57.0 – 56.9 (CH syndio), 56.1 – 55.7 (CH hetero), 55.1 – 54.9 (CH iso), 47.3 – 44.8 (family of CH₂ peaks), 44.0 – 42.8 (N-C-CH₂). IR (NaCl, neat, cm⁻¹): 2975 (m, alkane CH), 2911 (m, alkane CH), 2114 (s, N₃), 1435 (m, methylene stretch CH₂), 615 (w, C-Cl). DSC (*T_g*): 78 °C.

Alkyl Type 0D Syntheses

Preparation of 1,4-bis(2-ethylhexyl) but-2-ynedioate (2c)^{44,45} But-2-ynedioic acid (3.422 g, 30.00 mmol) was added to a 100 mL round bottom flask. 2-Ethylhexan-1-ol (8.595 g, 66.00 mmol) was then added along with 4-methylbenzenesulfonic acid (0.342 g, 1.800 mmol) and 42 mL of dry toluene. Using a Dean-Stark apparatus, the reaction was heated and stirred at reflux for 1 h. The organic layer was concentrated *in vacuo* to give a crude brown oil. Purification *via* flash chromatography using 95:5 hexanes:ethyl acetate afforded 9.211 g (27.21 mmol, 73.69% yield) of a colorless oil, as a mixture of diastereomers. *R_f*: 0.80 (SiO₂, hexanes:ethyl acetate, 95:5). ¹H NMR (500 MHz, CDCl₃, δ, ppm): 4.19 – 4.13 (m, 4H), 1.66 – 1.61 (m, 2H), 1.42 – 1.36 (m, 4H), 1.35 – 1.25 (m, 12H), 0.91 (t, 12H). ¹³C NMR (125 MHz, CDCl₃, δ, ppm): 152.0 (C=O), 74.7 (4°), 69.2 (O-CH₂), 38.6 (CH), 30.1 (CH₂), 28.8 (CH₂), 23.5 (CH₂), 22.9 (CH₂), 14.0 (CH₃), 10.8 (CH₃). IR (NaCl, neat, cm⁻¹): 2962 (s, alkane CH), 2932 (s, alkane CH), 2875 (s, alkane CH), 2862 (s, alkane CH), 1725 (s, ester C=O), 1464 (s, methylene bending CH₂), 1255 (s, ester stretch C-O). HRMS (*m/z*): calcd for C₂₀H₃₅O₄ 339.2529; found, 339.2525 [M+H]⁺.

Preparation of 15% PVC-TRZ-DiEH (3c) Poly(vinyl chloride) 15% azide (1.000 g, 16.00 mmol) was added to a 100 mL round bottom flask and dissolved in 20 mL of 3-pentanone at 90 °C. 1,4-Bis(2ethylhexyl) but-2-ynedioate (2.437 g, 7.200 mmol) was added to the PVC solution and stirred for 24 h. The reaction was precipitated in 80 mL of MeOH, three times each. The isolated polymer was dried under house vacuum for 2 days to yield 0.930 g of a flocculent white solid.

^1H NMR (500 MHz, CDCl_3 , δ , ppm): 5.65 – 5.40 (br m, *C-CH-triazole*), 4.67 – 4.40 (br m, *Cl-C-H*), 4.39 – 4.10 (br m, *Cl-C-H* and *O-CH₂-C*), 2.92 – 2.81 (br t, *Cl-C-CH₂-C-triazole* and *triazole-C-CH₂-C-triazole*), 2.81 – 2.67 (br m, *Cl-C-CH₂-C-triazole* and *triazole-C-CH₂-C-triazole*), 2.50 – 1.85 (br m, *Cl-C-CH₂-C-Cl*), 1.80 – 1.60 (br m, *O-C-CH-C*), 1.52 – 1.36 (br m, *O-C-C-CH₂*), 1.35 – 1.26 (br s, *O-C-C-C-CH₂-CH₂*), 0.97 – 0.85 (m, *CH₃*). ^{13}C NMR (125 MHz, CDCl_3 , δ , ppm): 160.1 (C=O), 158.7 (C=O), 139.5 (4°), 132.6 (4°), 70.0 (O-CH₂), 69.9 (O-CH₂), 68.5 (O-CH₂), 57.0 – 56.9 (CH syndio), 56.4 (CH-triazole syndio), 56.1 – 55.9 (CH hetero), 55.2 – 54.9 (CH iso), 47.3 – 44.8 (family of CH₂ PVC peaks), 38.7 (CH), 38.6 (CH), 30.2 (CH₂), 30.1 (CH₂), 28.9 (CH₂), 28.8 (CH₂), 23.6 (CH₂), 23.5 (CH₂), 23.0 (CH₂), 14.1 (CH₃), 10.9 (CH₃). IR (NaCl, thin film, cm^{-1}): 2961 (s, alkane CH), 2932 (s, alkane CH), 2874 (s, alkane CH), 2862 (s, alkane CH), 1721 (s, ester C=O), 1555 (w, triazole C=C), 1463 (m, methylene stretch CH₂), 1255 (s, ester stretch C-O), 616 (w, C-Cl). DSC (T_g): 57 $^\circ\text{C}$.

PEO Type 0D Syntheses

Preparation of 1,4-bis({2-[2-(2-methoxyethoxy)ethoxy]ethyl})but-2-ynedioate (2d)
But-2-ynedioic acid (1.000 g, 8.767 mmol) was added to a 50 mL round bottom flask. Triethylene glycol monomethyl ether (3.167 g, 19.29 mmol) was then added along with 4-methylbenzenesulfonic acid (0.167 g, 0.876 mmol) and 13 mL of dry toluene. Using a Dean-Stark apparatus, the reaction was heated and stirred at reflux for 5 h. The reaction was transferred to a 150 mL separatory funnel and diluted with 40 mL of toluene and washed with 20 mL of saturated NaHCO_3 three times each. The aqueous layer was extracted with 60 mL of ethyl acetate, three times each. The combined organic layers were dried with MgSO_4 , filtered, and concentrated *in vacuo*. Purification *via* flash chromatography using 95:5 CH_2Cl_2 :MeOH afforded 2.673 g (6.576 mmol, 75.02% yield) of the title compound as a colorless oil. R_f : 0.53 (SiO_2 , CH_2Cl_2 :MeOH, 95:5). ^1H NMR (500 MHz, CDCl_3 , δ , ppm): 4.39 – 4.31 (m, 4H), 3.74 – 3.70 (m, 4H), 3.65 – 3.60 (m, 12H), 3.56 – 3.49 (m, 4H), 3.37 – 3.33 (m, 6H). ^{13}C NMR (125 MHz, CDCl_3 , δ , ppm): 151.6 (C=O), 74.7 (alkyne 4°), 71.9 (CH₂), 70.7 (CH₂), 70.6 (CH₂), 68.4 (CH₂), 65.8 (CH₂), 58.9 (CH₃). IR (NaCl, neat, cm^{-1}): 2879 (s, alkane CH), 1725 (s, ester C=O), 1259 (s, ester stretch C-O), 1110 (s, ether stretch C-O). HRMS

(m/z): calcd for $\text{C}_{18}\text{H}_{30}\text{O}_{10}$ 407.1912; found, 407.1895 [$\text{M}+\text{H}$] $^+$.

Preparation of 15% PVC-TRZ-DiPEO_{16d}Me (3d)

Poly(vinyl chloride) 15% azide (1.000 g, 16.00 mmol) was added to a 100 mL round bottom flask and dissolved in 20 mL of 3-pentanone at 90 $^\circ\text{C}$. 1,4-Bis({2-[2-(2-methoxyethoxy)ethoxy]ethyl})but-2-ynedioate (2.424 g, 6.000 mmol) was added to the PVC solution and stirred for 72 h. The reaction was concentrated to approximately half its volume *in vacuo*, then precipitated in 80 mL of MeOH, three times each. The isolated polymer was dried under house vacuum for 1 day, then in a vacuum oven at 40 $^\circ\text{C}$ for 3 days to yield 1.330 g of a white solid. ^1H NMR (500 MHz, CDCl_3 , δ , ppm): 5.66 – 5.44 (br m, *C-CH-triazole*), 4.63 – 4.54 (br s, *Cl-C-H*), 4.54 – 4.39 (br s, *Cl-C-H* and *triazole-O-CH₂*), 4.36 – 4.24 (br m, *Cl-C-H*), 3.87 – 3.79 (br m, *triazole-O-C-CH₂-O*), 3.76 – 3.68 (br m, *triazole-O-C-C-O-CH₂-CH₂-O-CH₂-C*), 3.58 – 3.53 (br m, *C-CH₂-O-CH₃*), 3.40 – 3.36 (br s, *O-CH₃*), 2.92 – 2.81 (br m, *Cl-C-CH₂-C-triazole* and *triazole-C-CH₂-C-triazole*), 2.80 – 2.66 (br m, *Cl-C-CH₂-C-triazole* and *triazole-C-CH₂-C-triazole*), 2.50 – 1.95 (br m, *Cl-C-CH₂-C-Cl*). ^{13}C NMR (125 MHz, CDCl_3 , δ , ppm): 159.7 (C=O), 158.3 (C=O), 138.6 (4°), 131.7 (4°), 71.9 (CH₂), 70.67 (CH₂), 70.62 (CH₂), 70.57 (CH₂), 68.7 (CH₂), 68.4 (CH₂), 66.2 (CH₂), 64.9 (CH₂), 59.0 (CH₃), 57.0 – 56.9 (CH syndio), 56.1 – 55.9 (CH hetero), 55.2 – 54.9 (CH iso), 47.3 – 44.8 (family of CH₂ peaks). IR (NaCl, thin film, cm^{-1}): 2879 (s, alkane CH), 1734 (s, ester C=O), 1549 (s, triazole C=C), 1452 (s, methylene stretch CH₂), 1259 (s, ester stretch C-O), 1200 (s, ester stretch C-O), 1107 (s, ether stretch C-O), 611 (w, C-Cl). DSC (T_g): 42 $^\circ\text{C}$.

Alkyl Type 1 Syntheses

Preparation of 6-azidohexan-1-ol (4)⁴⁹
6-chlorohexan-1-ol (1.500 g, 10.98 mmol) was added to a 100 mL round bottom flask with 20 mL of dimethyl sulfoxide. NaN_3 (1.071 g, 16.47 mmol) was carefully added to the reaction flask and stirred for 24 h at 50 $^\circ\text{C}$. After 24 h, 40 mL of water was poured into the round bottom flask. The reaction was extracted five times using 30 mL each of ethyl acetate. The organic layers were washed with brine four times using 20 mL each, then dried with Na_2SO_4 . The volatiles were evaporated *in vacuo* affording 1.572 g (10.98 mmol, quantitative yield) of the title compound as a colorless oil. R_f : 0.46 (SiO_2 , hexanes:ethyl acetate,

3:2). ^1H NMR (500 MHz, CDCl_3 , δ , ppm): 3.60 (t, J = 6.6 Hz, 2H), 3.24 (t, J = 6.9 Hz, 2H), 1.61 – 1.52 (m, 4H), 1.41 – 1.31 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3 , δ , ppm): 62.7 ($\text{CH}_2\text{-OH}$), 51.4 ($\text{CH}_2\text{-N}_3$), 32.5 (CH_2), 28.8 (CH_2), 26.5 (CH_2), 25.3 (CH_2). IR (NaCl, neat, cm^{-1}): 3351 (s, OH), 2937 (s, alkane CH), 2862 (s, alkane CH), 2097 (s, N_3), 1457 (m, methylene bending CH_2), 1056 (s, 1° alcohol stretch C-O). HRMS (m/z): calcd for $\text{C}_6\text{H}_{13}\text{N}_3\text{O}$ 144.1131; found, 144.9812 [$\text{M}+\text{H}$] $^+$.

Preparation of 4,5-bis(2-ethylhexyl) 1-(6-hydroxyhexyl)-1H-1,2,3-triazole-4,5-dicarboxylate (5c)

6-Azidohexan-1-ol (1.570 g, 10.98 mmol) was added to a 100 mL round bottom flask with 35 mL of CHCl_3 . 1,4-Bis(2-ethylhexyl) but-2-ynedioate (4.830 g, 14.27 mmol) was added to the reaction flask and stirred at 50 °C for 24 h. The volatiles were evaporated *in vacuo* affording a colorless crude oil. Purification *via* flash chromatography using 7:3 hexanes:ethyl acetate afforded 5.264 g (10.93 mmol, 99.53% yield) of a colorless oil, as a mixture of diastereomers. R_f : 0.29 (SiO_2 , hexanes:ethyl acetate, 7:3). ^1H NMR (500 MHz, CDCl_3 , δ , ppm): 4.58 (t, J = 7.3 Hz, 2H), 4.33 – 4.22 (m, 4H), 3.63 (t, J = 6.5 Hz, 2H), 1.91 (p, J = 7.5 Hz, 2H), 1.77 – 1.64 (m, 2H), 1.55 (p, J = 6.6 Hz, 2H), 1.44 – 1.26 (m, 21H), 0.97 – 0.80 (m, 12H). ^{13}C NMR (125 MHz, CDCl_3 , δ , ppm): 160.5 (C=O), 158.8 (C=O), 140.4 (4°), 129.7 (4°), 69.1 (CH_2), 68.3 (CH_2), 62.5 (CH_2), 50.4 (CH_2), 38.7 (CH), 38.7 (CH), 32.4 (CH_2), 30.2 (CH_2), 28.9 (CH_2), 26.1 (CH_2), 25.1 (CH_2), 23.6 (CH_2), 23.5 (CH_2), 22.9 (CH_2), 14.0 (CH_3), 10.9 (CH_3). IR (NaCl, neat, cm^{-1}): 3436 (s, OH), 2959 (s, alkane CH), 2932 (s, alkane CH), 2861 (s, alkane CH), 1733 (s, ester C=O), 1555 (m, triazole C=C), 1466 (s, methylene bending CH_2), 1279 (m, ester stretch C-O), 1060 (1° alcohol stretch C-O). HRMS (m/z): calcd for $\text{C}_{26}\text{H}_{47}\text{N}_3\text{O}_5$ 482.3588; found, 482.3588 [$\text{M}+\text{H}$] $^+$.

Preparation of 4,5-bis(2-ethylhexyl)-1-[6-(prop-2-ynoyloxy)hexyl]-1H-1,2,3-triazole-4,5-dicarboxylate (6c)

Propiolic acid (0.500 g, 7.138 mmol) was added to a 25 mL round bottom flask with 7 mL of toluene. 4,5-Bis(2-ethylhexyl) 1-(6-hydroxyhexyl)-1H-1,2,3-triazole-4,5-dicarboxylate (4.126 g, 8.565 mmol) and 4-methylbenzenesulfonic acid (0.082 g, 0.428 mmol) was added to the reaction flask and stirred at reflux for 2 h. The volatiles were evaporated *in vacuo*, affording a light brown crude oil. Purification *via* flash chromatography using 4:1 hexanes:ethyl acetate afforded 2.7286 g (5.1126 mmol, 71.64% yield) of a

colorless oil, as a mixture of diastereomers. R_f : 0.56 (SiO_2 , hexanes:ethyl acetate, 4:1). ^1H NMR (500 MHz, CDCl_3 , δ , ppm): 4.59 (t, J = 7.3 Hz, 2H), 4.35 – 4.23 (m, 4H), 4.19 (t, J = 6.6 Hz, 2H), 2.90 (s, 1H), 1.93 (p, J = 7.3 Hz, 2H), 1.71 (m, 4H), 1.50 – 1.27 (m, 20H), 0.96 – 0.87 (m, 12H). ^{13}C NMR (125 MHz, CDCl_3 , δ , ppm): 160.5 (C=O), 158.8 (C=O), 152.7 (C=O), 140.5 (4°), 129.6 (4°), 74.7 (alkyne 4°), 74.6 (alkyne CH), 69.2 (CH_2), 68.4 (CH_2), 66.0 (CH_2), 50.3 (CH_2), 38.73 (CH), 38.70 (CH), 30.20 (CH_2), 30.15 (CH_2), 30.1 (CH_2), 28.9 (CH_2), 28.9 (CH_2), 28.1 (CH_2), 26.0 (CH_2), 25.3 (CH_2), 23.6 (CH_2), 23.5 (CH_2), 22.94 (CH_2), 22.93 (CH_2), 14.0 (CH_3), 10.88 (CH_3), 10.87 (CH_3). IR (NaCl, neat, cm^{-1}): 3255 (s, alkyne CH), 2960 (s, alkane CH), 2931 (s, alkane CH), 2862 (s, alkane CH), 2117 (s, alkyne CC), 1717 (s, ester C=O), 1555 (m, triazole C=C), 1465 (s, methylene bending CH_2), 1268 (s, ester stretch C-O), 1220 (s, ester stretch C-O). HRMS (m/z): calcd for $\text{C}_{29}\text{H}_{47}\text{N}_3\text{O}_6$ 534.3538; found, 534.3521 [$\text{M}+\text{H}$] $^+$.

Preparation of 15% PVC-TRZ-Hexyl-TRZ-DiEH (7c)

Poly(vinyl chloride) 15% azide (1.000 g, 16.00 mmol) was added to a 100 mL round bottom flask and dissolved in 20 mL of 3-pentanone at 90 °C. 4,5-Bis(2-ethylhexyl)-1-[6-(prop-2-ynoyloxy)hexyl]-1H-1,2,3-triazole-4,5-dicarboxylate (3.843 g, 7.200 mmol) was added to the PVC solution and stirred for 24 h. The reaction was precipitated in 80 mL of MeOH, three times each. The isolated polymer was dried under house vacuum for 1 day, then in a vacuum oven at 40 °C for 2 days to yield 1.110 g of an off-white solid. ^1H NMR (500 MHz, CDCl_3 , δ , ppm): 8.25 – 8.20 (br m, PVC-triazole-H), 8.19 – 8.07 (br m, PVC-triazole-H), 5.26 – 5.10 (br m, C-CH-triazole), 4.65 – 4.52 (br m, Cl-C-H and PVC-linker-C-CH₂-triazole), 4.45 (br s, Cl-C-H), 4.40 – 4.22 (br m, Cl-C-H and PVC-triazole-O-CH₂-linker and PVC-linker-triazole-O-CH₂), 2.87 – 2.79 (br m, Cl-C-CH₂-C-triazole and triazole-C-CH₂-C-triazole), 2.78 – 2.69 (br s, Cl-C-CH₂-C-triazole and triazole-C-CH₂-C-triazole), 2.68 – 2.51 (br m, Cl-C-CH₂-C-triazole and triazole-C-CH₂-C-triazole), 2.50 – 1.99 (br m, Cl-C-CH₂-C-Cl), 1.98 – 1.86 (br s, PVC-linker-CH₂-C-triazole), 1.85 – 1.77 (br s, PVC-triazole-O-C-CH₂-linker), 1.76 – 1.65 (br m, PVC-linker-triazole-O-C-CH-C), 1.55 – 1.25 (br m, linker CH₂'s and linker-triazole-O-C-C-CH₂-CH₂-CH₂-C), 0.97 – 0.86 (br m, CH₃). ^{13}C NMR (125 MHz, CDCl_3 , δ , ppm): 160.6 (C=O), 158.8 (C=O), 140.4 (4°), 129.6 (4°), 69.2 (O- CH_2), 68.4 (O- CH_2), 65.2 (O- CH_2), 57.1 – 56.9 (CH syndio), 56.1 – 55.9 (CH hetero), 55.0 – 54.9 (CH iso), 50.4 (CH_2), 47.3 – 44.8 (family of CH_2 PVC peaks), 38.72 (CH), 38.69 (CH), 30.19 (CH_2),

30.16 (CH₂), 30.1 (CH₂), 28.88 (CH₂), 28.86 (CH₂), 28.4 (CH₂), 26.0 (CH₂), 25.4 (CH₂), 23.6 (CH₂), 23.5 (CH₂), 22.96 (CH₂), 22.94 (CH₂), 14.1 (CH₃), 10.9 (CH₃). IR (NaCl, thin film, cm⁻¹): 3139 (w, triazole CH), 2960 (s, alkane CH), 2932 (s, alkane CH), 2861 (s, alkane CH), 1733 (s, ester C=O), 1552 (m, triazole C=C), 1465 (m, methylene stretch CH₂), 1436 (m, methyl stretch CH), 1202 (s, ester stretch C-O), 616 (w, C-Cl). DSC (*T_g*): 41 °C.

PEO Type 1 Syntheses

Preparation of 4,5-bis({2-[2-(2-methoxyethoxy)ethoxy]ethyl}) 1-(6-hydroxyhexyl)-1H-1,2,3-triazole-4,5-dicarboxylate (5d) 6-Azidohexan-1-ol (1.000 g, 6.983 mmol) was added to a 100 mL round bottom flask with 30 mL of CHCl₃. 1,4-Bis({2-[2-(2-methoxyethoxy)ethoxy]ethyl})but-2-ynedioate (3.406 g, 8.381 mmol) was added to the reaction flask and stirred at 50 °C for 24 h. The volatiles were evaporated *in vacuo* affording a colorless crude oil. Purification *via* flash chromatography using 95:5 CH₂Cl₂:MeOH afforded 2.853 g (5.191 mmol, 74.34% yield) of the title compound as a colorless oil. *R_f*: 0.48 (SiO₂, CH₂Cl₂:MeOH, 95:5). ¹H NMR (500 MHz, CDCl₃, δ, ppm): 4.60 (t, *J* = 7.2 Hz, 2H), 4.55 (t, *J* = 4.5, 2H), 4.51 (t, *J* = 4.9 Hz, 2H), 3.82 (overlapping t, *J* = 4.8 Hz, 4H), 3.72 – 3.60 (m, 14H), 3.56 – 3.53 (m, 4H), 3.37 – 3.36 (m, 6H), 1.93 (p, *J* = 7.2 Hz, 2H), 1.69 (s, 1H), 1.56 (p, *J* = 6.7 Hz, 2H), 1.47 – 1.30 (m, 4H). ¹³C NMR (125 MHz, CDCl₃, δ, ppm): 160.1 (C=O), 158.5 (C=O), 140.0 (4°), 130.1 (4°), 71.9 (CH₂), 70.7 (CH₂), 70.6 (CH₂), 70.6 (CH₂), 70.6 (CH₂), 70.5 (CH₂), 68.8 (CH₂), 68.5 (CH₂), 65.6 (CH₂), 64.8 (CH₂), 62.5 (CH₂), 59.0 (CH₃), 50.5 (CH₂), 32.4 (CH₂), 30.1 (CH₂), 26.0 (CH₂), 25.1 (CH₂). IR (NaCl, neat, cm⁻¹): 3472 (s, OH), 2930 (s, alkane CH), 2874 (s, alkane CH), 1733 (s, ester C=O), 1552 (m, triazole C=C), 1468 (s, methylene bending CH₂), 1281 (s, ester stretch C-O), 1247 (s, ether stretch C-O), 1111 (s, ether stretch C-O), 1067 (s, 1° alcohol stretch C-O). HRMS (*m/z*): calcd for C₂₄H₄₃N₃O₁₁ 550.2970; found, 550.2948 [M+H]⁺.

Preparation of 4,5-bis({2-[2-(2-methoxyethoxy)ethoxy]ethyl})-1-[6-(prop-2-ynoyloxy)hexyl]-1H-1,2,3-triazole-4,5-dicarboxylate (6d) Propiolic acid (1.000 g, 14.276 mmol) was added to a 50 mL round bottom flask with 14 mL of toluene. 4,5-Bis({2-[2-(2-methoxyethoxy)ethoxy]ethyl})-1-(6-hydroxyhexyl)-1H-1,2,3-triazole-4,5-dicarboxylate (9.415 g, 17.131 mmol) and 4-methylbenzenesulfonic

acid (0.272 g, 1.428 mmol) was added to the reaction flask and stirred at reflux for 3 h. The volatiles were evaporated *in vacuo*, affording a light brown crude oil. Purification *via* flash chromatography using 95:5 CH₂Cl₂:MeOH afforded 6.612 g (10.990 mmol, 76.98% yield) of the title compound as a colorless oil. *R_f*: 0.50 (SiO₂, CH₂Cl₂:MeOH, 95:5). ¹H NMR (500 MHz, CDCl₃, δ, ppm): 4.59 (t, *J* = 7.2 Hz, 2H), 4.54 (t, *J* = 4.8, 2H), 4.50 (t, *J* = 4.9 Hz, 2H), 4.18 (t, *J* = 6.5 Hz, 2H), 3.82 (overlapping t, *J* = 4.9 Hz, 4H), 3.72 – 3.60 (m, 12H), 3.57 – 3.49 (m, 4H), 3.37 (s, 3H), 3.36 (s, 3H), 2.93 (s, 1H), 1.93 (p, *J* = 7.2 Hz, 2H), 1.68 (p, *J* = 6.5 Hz, 2H), 1.45 – 1.34 (m, 4H). ¹³C NMR (125 MHz, CDCl₃, δ, ppm): 160.1 (C=O), 158.4 (C=O), 152.7 (C=O), 140.0 (4°), 129.6 (4°), 74.7 (alkyne 4°), 74.6 (alkyne CH), 71.9 (CH₂), 70.7 (CH₂), 70.60 (CH₂), 70.56 (CH₂), 68.8 (CH₂), 68.5 (CH₂), 66.0 (CH₂), 65.6 (CH₂), 64.8 (CH₂), 59.0 (CH₃), 50.4 (CH₂), 30.0 (CH₂), 28.1 (CH₂), 25.9 (CH₂), 25.2 (CH₂). IR (NaCl, neat, cm⁻¹): 3220 (m, alkyne CH), 2874 (s, alkane CH), 2114 (s, alkyne CC), 1732 (s, ester C=O), 1715 (s, ester C=O), 1552 (triazole C=C), 1469 (methylene bending CH₂), 1271 (m, ester stretch C-O), 1235 (s, ester stretch C-O), 1108 (s, ether stretch C-O). HRMS (*m/z*): calcd for C₂₇H₄₃N₃O₁₂ 602.2920; found, 602.2917 [M+H]⁺.

Preparation of 15% PVC-TRZ-Hexyl-TRZ-DiPEO₁₆₄Me (7d) Poly(vinyl chloride) 15% azide (1.000 g, 16.00 mmol) was added to a 100 mL round bottom flask and dissolved in 30 mL of 3-pentanone at 90 °C. 4,5-Bis({2-[2-(2-methoxyethoxy)ethoxy]ethyl})-1-[6-(prop-2-ynoyloxy)hexyl]-1H-1,2,3-triazole-4,5-dicarboxylate (3.610 g, 6.000 mmol) was added to the PVC solution and stirred for 24 h. The reaction was concentrated to approximately half its volume *in vacuo*, then precipitated in 80 mL of MeOH, three times each. The isolated polymer was dried under house vacuum for 1 day, then in a vacuum oven at 40 °C for 2 days to yield in a vacuum oven at 40 °C for 3 days to yield 1.920 g of a white solid. ¹H NMR (500 MHz, CDCl₃, δ, ppm): 8.35 – 8.05 (br m, PVC-triazole-H), 5.32 – 5.12 (br m, C-CH-triazole), 4.70 – 4.59 (br m, Cl-C-H and PVC-linker-C-CH₂-triazole), 4.58 – 4.54 (br s, Cl-C-H and triazole-O-CH₂-C-O), 4.54 – 4.50 (br m, Cl-C-H and triazole-O-CH₂-C-O), 4.49 – 4.42 (br s, Cl-C-H), 4.41 – 4.26 (br m, Cl-C-H and PVC-triazole-O-CH₂-linker), 3.90 – 3.81 (br m, triazole-O-C-CH₂-O), 3.73 – 3.62 (br m, triazole-O-C-C-O-CH₂-CH₂-O-CH₂-C), 3.58 – 3.53 (br m, C-CH₂-O-CH₃), 3.39 (br s, O-CH₃), 3.38 (br s, O-CH₃), 2.87 – 2.79 (br s, Cl-C-CH₂-C-

triazole and triazole-*C-CH₂-C-triazole*), 2.78 – 2.61 (br m, *Cl-C-CH₂-C-triazole* and *triazole-C-CH₂-C-triazole*), 2.51 – 2.00 (br m, *Cl-C-CH₂-C-Cl*), 1.86 – 1.72 (br m, *PVC-linker-CH₂-C-triazole*), 1.72 – 1.62 (br s, *PVC-triazole-O-C-CH₂-linker*), 1.56 – 1.33 (br m, *linker CH₂'s*). ¹³C NMR (125 MHz, CDCl₃, δ, ppm): 160.2 (C=O), 158.4 (C=O), 71.9 (CH₂), 70.67 (CH₂), 70.61 (CH₂), 70.57 (CH₂), 68.8 (CH₂), 68.5 (CH₂), 65.7 (CH₂), 64.8 (CH₂), 59.0 (CH₃), 57.0 – 56.9 (CH syndio), 50.5 (CH₂), 47.3 – 44.8 (family of CH₂ peaks), 30.0 (CH₂), 28.4 (CH₂), 26.0 (CH₂), 25.4 (CH₂). IR (NaCl, thin film, cm⁻¹): 3137 (w, triazole CH), 2936 (s, alkane CH), 2874 (s, alkane CH), 1733 (s, ester C=O), 1551 (m, triazole C=C), 1466 (s, methylene stretch CH₂), 1438 (s, methyl stretch CH), 1247 (s, ester stretch C-O), 1203 (s, ester stretch C-O), 1121 (s, ether stretch C-O), 615 (w, C-Cl). DSC (*T_g*): 18 °C.

Alkyl Type 2 Syntheses

Preparation of Dibromofumaric Acid (8)⁵⁰ Acetylenedicarboxylic acid monopotassium salt (5.522 g, 36.30 mmol) was added to a 500 mL round bottom flask and dissolved into ~20 mL of 2M aqueous KOH solution while stirring. NaBr (102.89 g, 26.149 mmol) was dissolved in 80 mL of H₂O *via* sonication. Br₂ (6.381 g, 39.93 mmol) was quickly added to the NaBr aqueous solution. The resulting orange NaBr/Br₂ solution was subsequently added to the acetylenedicarboxylate solution. Stirring was ceased for the remainder of the reaction to prevent Br₂ degradation. The reaction flask was covered in aluminum foil, and an additional 50 mL of H₂O was added to bring the total volume to 150 mL, and was left for 24 h at room temperature. After 24 h, a transparent colorless solution was observed. To the reaction flask, 3 mL of saturated aqueous NaHSO₃ solution was added to quench the excess Br₂ while stirring. The reaction was saturated with NaCl and acidified with 12 mL of concentrated HCl and extracted with 50 mL of ethyl acetate each four times. The organic layers were dried with Na₂SO₄. The volatiles were evaporated *in vacuo* to afford a white solid. After recrystallization in chloroform, 8.000 g (29.21 mmol, 80.47% yield) of the title compound was recovered as colorless needles. mp 239 – 240 °C. ¹³C NMR (125 MHz, d₆-Acetone, δ, ppm): 162.8 (C=O), 111.7 (C-Br). IR (KBr pellet, cm⁻¹): 3013 (s, OH stretch), 1699 (s, carboxylic acid C=O), 1405 (m, alcohol bending OH), 686 (m, C-Br).

Preparation of 4,5-bis(2-ethylhexyl) 1-(6-((2E)-4-((6-[4,5-bis((2-ethylhexyl)oxy)carbonyl)]-1H-1,2,3-triazol-1-yl)hexyl)oxy)-2,3-dibromo-4-oxobut-2-enoyl]oxy)hexyl)-1H-1,2,3-triazole-4,5-dicarboxylate (10c) Dibromofumaric acid (1.520 g, 5.550 mmol) and PCl₅ (2.427 g, 11.655 mmol) was added to a 25 mL round bottom flask with 5 mL of pentane. The reaction was refluxed for 2 h while stirring. Reaction completeness was determined by observing the dissolution of solids into a clear yellow solution. After the dissolution of solids was noted, the reaction was immediately diluted with 5 mL of pentane. The diluted reaction was added slowly to a 150 mL beaker of crescent-cube ice, and was allowed to stand for 10 min with occasional swirling. The quenched reaction solution was transferred to a 150 mL separatory funnel. The organic layer was collected and dried with Na₂SO₄. The volatiles were evaporated *in vacuo*, affording a clear yellow oil (1.656 g, 5.329 mmol, 96.02% yield) of (2E)-dibromobut-2-enedioyl dichloride. The acid chloride was immediately diluted with 30 mL of CCl₄ under N₂ in a 250 mL pear flask. Next, 4,5-bis(2-ethylhexyl) 1-(6-hydroxyhexyl)-1H-1,2,3-triazole-4,5-dicarboxylate (5.392 g, 11.193 mmol) and pyridine (0.885 g, 11.193 mmol) were added to a 250 mL round bottom flask with 60 mL of CCl₄ and cooled to 0 °C under N₂ with stirring. The acid chloride solution was slowly added *via* syringe over 10 min, noting an orange-brown color and the formation of pyridine salts in solution. After the addition of the acid chloride, the reaction was allowed to stir at 0 °C for 30 min, then at room temperature for an additional 2 h. The reaction was poured into a 500 mL separatory funnel and washed with 20 mL of 5% aqueous HCl, two times each. The organic layer was collected, dried with MgSO₄ and filtered. The volatiles were then evaporated *in vacuo*, affording a dark red oil. Purification *via* flash chromatography using 7:3 hexanes:ethyl acetate was performed, affording 5.146 g (4.284 mmol, 80.38% yield) of a colorless oil, as a mixture of diastereomers. *R_f*: 0.64 (SiO₂, hexanes:ethyl acetate, 7:3). ¹H NMR (500 MHz, CDCl₃, δ, ppm): 4.55 (t, *J* = 7.3 Hz, 4H), 4.30 – 4.19 (m, 12H), 1.89 (p, *J* = 7.4 Hz, 4H), 1.73 – 1.62 (m, 8H), 1.47 – 1.21 (m, 40H), 0.93 – 0.79 (m, 24H). ¹³C NMR (125 MHz, CDCl₃, δ, ppm): 162.2 (C=O), 160.6 (C=O), 158.8 (C=O), 140.5 (4°), 129.6 (4°), 112.7 (C-Br), 69.1 (CH₂), 68.4 (CH₂), 66.9 (CH₂), 50.3 (CH₂), 38.7 (CH), 30.2 (CH₂), 30.2 (CH₂), 30.1 (CH₂), 28.9 (CH₂), 28.1 (CH₂), 25.9 (CH₂), 25.2 (CH₂), 23.6 (CH₂), 23.5 (CH₂), 22.9 (CH₂), 14.0 (CH₃),

10.9 (CH₃). IR (NaCl, neat, cm⁻¹): 2959 (s, alkane CH), 2932 (s, alkane CH), 2872 (s, alkane CH), 2861 (s, alkane CH), 1736 (s, ester C=O), 1554 (m, triazole C=C), 1466 (s, methylene bending CH₂), 1267 (s, ester stretch C-O), 1235 (s, ester stretch C-O), 758 (m, alkene bending C=C). HRMS (*m/z*): calcd for C₅₆H₉₂Br₂N₆O₁₂ 1199.5213; found, 1199.5212 [M+H]⁺. (Br isotopes): 1201.5193, 1203.5179, 1204.5198 [M+H]⁺.

Preparation of 4,5-bis(2-ethylhexyl) 1-(6-{{4-{{6-{{4,5-bis(((2-ethylhexyl)oxy)carbonyl}}-1H-1,2,3-triazol-1-yl]hexyl)oxy}-4-oxobut-2-ynoyl]oxy}hexyl)-1H-1,2,3-triazole-4,5-dicarboxylate (11c) To a 250 mL round bottom flask, 4,5-bis(2-ethylhexyl) 1-(6-{{(2E)-4-{{6-{{4,5-bis(((2-ethylhexyl)oxy)carbonyl}}-1H-1,2,3-triazol-1-yl]hexyl)oxy}-2,3-dibromo-4-oxobut-2-enoyl]oxy}hexyl)-1H-1,2,3-triazole-4,5-dicarboxylate (7.207 g, 6.000 mmol) was added to 60 mL of anhydrous THF. Subsequently, Zn metal (2.353 g, 36.00 mmol) and I₂ (0.183 g, 0.721 mmol) were added and stirred at reflux for 5 h under N₂. The reaction was cooled and filtered through Celite™. The reaction was concentrated *in vacuo* and diluted with 80 mL of ethyl acetate. The solution was poured into a 500 mL separatory funnel and washed with 20 mL of 10% aqueous NaHSO₃, two times each. The organic layer was collected and dried with MgSO₄. The volatiles were then evaporated *in vacuo*, and immediately purified *via* flash chromatography using 7:3 hexanes:ethyl acetate, affording 5.322 g (5.111 mmol, 85.18% yield) of a colorless oil, as a mixture of diastereomers. R_f: 0.63 (SiO₂, hexanes:ethyl acetate, 7:3). ¹H NMR (500 MHz, CDCl₃, δ, ppm): 4.56 (t, *J* = 7.2 Hz, 4H), 4.31 – 4.22 (m, 8H), 4.19 (t, *J* = 6.6 Hz, 4H), 1.90 (p, *J* = 7.2 Hz, 4H), 1.74 – 1.63 (m, 8H), 1.48 – 1.28 (m, 40H), 0.91 – 0.87 (m, 24H). ¹³C NMR (125 MHz, CDCl₃, δ, ppm): 160.6 (C=O), 158.8 (C=O), 151.8 (C=O), 140.5 (4°), 129.6 (4°), 74.7 (alkyne 4°), 69.2 (CH₂), 68.4 (CH₂), 66.7 (CH₂), 50.3 (CH₂), 38.7 (CH), 30.2 (CH₂), 30.2 (CH₂), 30.0 (CH₂), 28.9 (CH₂), 28.1 (CH₂), 25.9 (CH₂), 25.2 (CH₂), 23.6 (CH₂), 23.6 (CH₂), 23.0 (CH₂), 14.1 (CH₃), 10.9 (CH₃). IR (NaCl, neat, cm⁻¹): 2959 (s, alkane CH), 2932 (s, alkane CH), 2872 (s, alkane CH), 2862 (s, alkane CH), 1727 (s, ester C=O), 1554 (m, triazole C=C), 1466 (s, methylene bending CH₂), 1256 (s, ester stretch C-O), 1215 (s, ester stretch C-O). HRMS (*m/z*): calcd for C₅₆H₉₂N₆O₁₂ 1041.6846; found 1041.6843, [M+H]⁺.

Preparation of 15% PVC-TRZ-DiHexyl-TRZ-DiEH (12c) Poly(vinyl chloride) 15% azide (1.000 g, 16.00 mmol) was added to a 100 mL round bottom flask and dissolved in 20 mL of 3-pentanone at 90 °C. 4,5-Bis(2-ethylhexyl) 1-(6-{{4-{{6-{{4,5-bis(((2-ethylhexyl)oxy)carbonyl}}-1H-1,2,3-triazol-1-yl]hexyl)oxy}-4-oxobut-2-ynoyl]oxy}hexyl)-1H-1,2,3-triazole-4,5-dicarboxylate (7.498 g, 7.200 mmol) was added to the PVC solution and stirred for 28 h. The reaction was concentrated to approximately half its volume *in vacuo*, then precipitated in 80 mL of MeOH, four times each. The polymer was dried under house vacuum for 1 day, then in a vacuum oven at 40 °C for 3 days to yield 2.397 g of a flexible pale yellow solid. ¹H NMR (500 MHz, CDCl₃, δ, ppm): 5.63 – 5.34 (br m, C-CH-triazole), 4.67 – 4.52 (br m, Cl-C-H and PVC-linker-C-CH₂-triazole), 4.51 – 4.38 (br m, Cl-C-H and PVC-triazole-O-CH₂-linker and PVC-linker-triazole-O-CH₂-C), 4.38 – 4.15 (br m, Cl-C-H), 2.92 – 2.80 (br s, Cl-C-CH₂-C-triazole and triazole-C-CH₂-C-triazole), 2.80 – 2.66 (br s, Cl-C-CH₂-C-triazole and triazole-C-CH₂-C-triazole), 2.50 – 1.98 (br m, Cl-C-CH₂-C-Cl), 1.98 – 1.87 (br s, PVC-linker-CH₂-C-triazole), 1.84 – 1.64 (br m, PVC-triazole-O-C-CH₂-linker and PVC-linker-triazole-O-C-CH-C), 1.54 – 1.24 (br m, linker CH₂'s and linker-triazole-O-C-C-CH₂-CH₂-CH₂-C), 0.98 – 0.83 (br m, CH₃). ¹³C NMR (125 MHz, CDCl₃, δ, ppm): 160.6 (C=O), 158.8 (C=O), 140.5 (4°), 129.6 (4°), 69.1 (O-CH₂), 68.3 (O-CH₂), 66.4 (O-CH₂), 65.7 (O-CH₂), 57.0 – 56.9 (CH syndio), 56.1 – 55.9 (CH hetero), 50.4 (CH₂), 47.3 – 45.2 (family of CH₂ PVC peaks), 38.72 (CH), 38.68 (CH), 30.2 (CH₂), 30.14 (CH₂), 30.1 (CH₂), 28.87 (CH₂), 28.85 (CH₂), 28.4 (CH₂), 28.1 (CH₂), 26.1 (CH₂), 26.0 (CH₂), 25.3 (CH₂), 25.2 (CH₂), 25.16 (CH₂), 23.6 (CH₂), 23.5 (CH₂), 22.95 (CH₂), 22.93 (CH₂), 14.0 (CH₃), 10.90 (CH₃), 10.88 (CH₃). IR (NaCl, thin film, cm⁻¹): 2960 (s, alkane CH), 2932 (s, alkane CH), 2861 (s, alkane CH), 1729 (s, ester C=O), 1553 (s, triazole C=C), 1465 (s, methylene stretch CH₂), 1437 (m, methyl stretch CH), 1260 (s, ester stretch C-O), 1204 (s, ester stretch C-O), 616 (w, C-Cl). DSC (*T_g*): -6 °C.

PEO Type 2 Syntheses

Preparation of 4,5-bis(2-[2-(2-methoxyethoxy)ethoxy]ethyl) 1-(6-{{(2E)-4-{{6-[[bis(2,5,8,11-tetraoxadodecanoyl)-1H-1,2,3-triazol-1-yl]hexyl]oxy}-2,3-dibromo-4-oxobut-2-enoyl]oxy}hexyl)-1H-1,2,3-triazole-4,5-dicarboxylate (10d) Dibromofumaric acid (1.500 g, 5.477 mmol)

and PCl_5 (2.394 g, 11.501 mmol) was added to a 25 mL round bottom flask with 5 mL of pentane. The reaction was refluxed for 2 h while stirring. Reaction completeness was determined by observing the dissolution of solids into a clear yellow solution. After the dissolution of solids was noted, the reaction was immediately diluted with 5 mL of pentane. The diluted reaction was added slowly to a 150 mL beaker of crescent-cube ice, and was allowed to stand for 10 min with occasional swirling. The quenched reaction solution was transferred to a 150 mL separatory funnel. The organic layer was collected and dried with Na_2SO_4 . The volatiles were evaporated *in vacuo* affording a clear yellow oil (1.701 g, 5.477 mmol, quantitative yield) of (2E)-dibromobut-2-enedioyl dichloride. The acid chloride was immediately diluted with 30 mL of CCl_4 under N_2 in a 250 mL pear flask. Next, 4,5-bis({2-[2-(2-methoxyethoxy)ethoxy]ethyl})-1-(6-hydroxyhexyl)-1H-1,2,3-triazole-4,5-dicarboxylate (6.321 g, 11.501 mmol) and pyridine (0.910 g, 11.501 mmol) were added to a 250 mL round bottom flask with 60 mL of CCl_4 and cooled to 0 °C under N_2 with stirring. The acid chloride solution was slowly added *via* syringe over 10 min, noting a light-yellow color and the formation of pyridine salts in solution. After the addition of the acid chloride, the reaction was allowed to stir at 0 °C for 2 hours, then at room temperature for an additional 22 hours. The reaction was poured into a 500 mL separatory funnel and washed with 20 mL 5% aqueous HCl two times each. The organic layer was collected, dried with MgSO_4 and filtered. The volatiles were then evaporated *in vacuo*. Purification *via* flash chromatography using 95:5 CH_2Cl_2 :MeOH was performed, affording 5.262 g (3.935 mmol, 71.85% yield) of the title compound as a colorless oil. R_f : 0.47 (SiO_2 , CH_2Cl_2 :MeOH, 95:5). ^1H NMR (500 MHz, Benzene- d_6 , δ , ppm): 4.36 (t, J = 4.9 Hz, 4H), 4.30 (t, 4H), 4.11 (t, J = 7.3 Hz, 4H), 3.91 (t, J = 6.5 Hz, 4H), 3.50 – 3.45 (m, 8H), 3.45 – 3.39 (m, 24H), 3.36 – 3.30 (m, 8H), 3.13 (s, 6H), 3.12 (s, 6H), 1.49 (p, J = 7.4 Hz, 4H), 1.22 (p, J = 6.6 Hz, 4H), 1.00 – 0.84 (m, 8H). ^{13}C NMR (125 MHz, Benzene- d_6 , δ , ppm): 162.0 (C=O), 160.6 (C=O), 158.5 (C=O), 141.0 (4°), 129.5 (4°), 112.9 (C-Br), 72.0 (CH_2), 71.98 (CH_2), 70.63 (CH_2), 70.59 (CH_2), 70.51 (CH_2), 70.50 (CH_2), 70.47 (CH_2), 68.7 (CH_2), 68.3 (CH_2), 66.7 (CH_2), 65.3 (CH_2), 64.7 (CH_2), 58.3 (CH_3), 49.7 (CH_2), 29.6 (CH_2), 27.8 (CH_2), 25.5 (CH_2), 24.9 (CH_2). IR (NaCl, neat, cm^{-1}): 2874 (s, alkane CH), 1733 (s, ester C=O), 1552 (m, triazole C=C), 1468 (methylene bending CH_2), 1270 (s, ester

stretch C-O), 1242 (s, ester stretch C-O), 1111 (s, ether stretch C-O), 755 (m, alkene bending C=C). HRMS (m/z): calcd for $\text{C}_{52}\text{H}_{84}\text{Br}_2\text{N}_6\text{O}_{24}$ 1335.3976; found, 1335.3981 [$\text{M}+\text{H}$] $^+$.

Preparation of 4,5-bis({2-[2-(2-methoxyethoxy)ethoxy]ethyl})-1-(6-{{[4-{{6-[[bis(2,5,8,11-tetraoxadodecanoyl)-1H-1,2,3-triazol-1-yl]hexyl]oxy}-4-oxobut-2-ynoyl]oxy}hexyl)-1H-1,2,3-triazole-4,5-dicarboxylate (11d) To a 250 mL round bottom flask, 4,5-bis({2-[2-(2-methoxyethoxy)ethoxy]ethyl})-1-(6-{{[2E]-4-{{6-[[bis(2,5,8,11-tetraoxadodecanoyl)-1H-1,2,3-triazol-1-yl]hexyl]oxy}-2,3-dibromo-4-oxobut-2-enoyl]oxy}hexyl)-1H-1,2,3-triazole-4,5-dicarboxylate (5.221 g, 3.905 mmol) was added to 40 mL of anhydrous THF. Subsequently, Zn metal (1.532 g, 23.432 mmol) and I_2 (0.047 g, 0.185 mmol) were added and stirred at reflux for 5 h under N_2 . The reaction was cooled and filtered through CeliteTM. The reaction was concentrated *in vacuo* and diluted with 80 mL of ethyl acetate. The solution was poured into a 500 mL separatory funnel and washed with 10 mL of 10% aqueous NaHSO_3 , two times each. The organic layer was collected and dried with MgSO_4 . The volatiles were then evaporated *in vacuo*, and immediately purified *via* flash chromatography using 95:5 CH_2Cl_2 :MeOH, affording 3.852 g (3.272 mmol, 83.79% yield) of the title compound as a pale yellow oil. R_f : 0.47 (SiO_2 , CH_2Cl_2 :MeOH, 95:5). ^1H NMR (500 MHz, Benzene- d_6 , δ , ppm): 4.36 (t, J = 4.9 Hz, 4H), 4.31 (t, J = 4.8 Hz, 4H), 4.09 (t, J = 7.3 Hz, 4H), 3.76 (t, J = 6.6 Hz, 4H), 3.47 (t, J = 4.9 Hz, 8H), 3.45 – 3.39 (m, 24H), 3.35 – 3.30 (m, 8H), 3.13 (s, 6H), 3.12 (s, 6H), 1.45 (p, J = 7.2 Hz, 4H), 1.10 (p, J = 6.7 Hz, 4H), 0.87 – 0.80 (m, 8H). ^{13}C NMR (125 MHz, Benzene- d_6 , δ , ppm): 160.6 (C=O), 158.5 (C=O), 151.6 (C=O), 140.9 (4°), 129.5 (4°), 74.9 (alkyne 4°), 72.0 (CH_2), 70.6 (CH_2), 70.6 (CH_2), 70.49 (CH_2), 70.48 (CH_2), 70.46 (CH_2), 68.7 (CH_2), 68.3 (CH_2), 66.3 (CH_2), 65.3 (CH_2), 64.7 (CH_2), 58.3 (CH_3), 49.7 (CH_2), 29.6 (CH_2), 27.7 (CH_2), 25.5 (CH_2), 24.7 (CH_2). IR (NaCl, neat, cm^{-1}): 2874 (s, alkane CH), 1727 (s, ester C=O), 1552 (m, triazole C=C), 1469 (s, methylene bending CH_2), 1259 (s, ester stretch C-O), 1110 (s, ether stretch C-O). HRMS (m/z): calcd for $\text{C}_{52}\text{H}_{84}\text{N}_6\text{O}_{24}$ 1177.5610; found, 1177.5616 [$\text{M}+\text{H}$] $^+$.

Preparation of 15% PVC-TRZ-DiHexyl-TRZ-DiPEO_{16d}Me (12d) Poly(vinyl chloride) 15% azide (1.000 g, 16.00 mmol) was added to a 100 mL round

bottom flask and dissolved in 30 mL of 3-pentanone at 90 °C. 4,5-Bis({2-[2-(2-methoxyethoxy)ethoxy]ethyl}) 1-(6-{{4-{{6-[bis(2,5,8,11-tetraoxadodecanoyl)-1H-1,2,3-triazol-1-yl]hexyl}oxy)-4-oxobut-2-ynoyl]oxy}hexyl)-1H-1,2,3-triazole-4,5-dicarboxylate (7.064 g, 6.000 mmol) was added to the PVC solution and stirred for 24 h. The reaction was concentrated to approximately one-third its volume *in vacuo*. To a 250 mL beaker, 100 mL of MeOH was added, then placed in a dry ice-acetone bath for 2 min. The polymer was precipitated by dropwise addition of the reaction solution in 2 mL increments into the cooled MeOH. After the addition of reaction solution, the mother liquor was decanted and replaced with 100 mL of fresh MeOH. The beaker was cooled to -78 °C for 2 min, upon which another 2 mL of reaction solution was added dropwise. This process was repeated until the entire polymer was precipitated. When all of the reaction solution was precipitated, the last volume of mother liquor was decanted. Subsequently, the neat polymer was cooled to -78 °C and washed with 50 mL of MeOH four times each. The isolated polymer was dried under house vacuum for 1 day, then in a vacuum oven at 40 °C for 3 days to yield 3.382 g of a flexible pale yellow solid. ¹H NMR (500 MHz, CDCl₃, δ, ppm): 5.65 – 5.35 (br m, C-CH₂-triazole), 4.67 – 4.58 (br s, Cl-C-H and PVC-linker-C-CH₂-triazole), 4.58 – 4.54 (br s, Cl-C-H and triazole-O-CH₂-C-O), 4.54 – 4.48 (br m, Cl-C-H and triazole-O-CH₂-C-O), 4.39 – 4.24 (br m, Cl-C-H and PVC-triazole-O-CH₂-linker), 3.88 – 3.78 (br m, triazole-O-C-CH₂-O), 3.75 – 3.60 (br m, triazole-O-C-C-O-CH₂-CH₂-O-CH₂-C), 3.59 – 3.48 (br m, C-CH₂-O-CH₃), 3.43 – 3.31 (br s, O-CH₃), 2.90 – 2.80 (br s, Cl-C-CH₂-C-triazole and triazole-C-CH₂-C-triazole), 2.80 – 2.53 (br m, Cl-C-CH₂-C-triazole and triazole-C-CH₂-C-triazole), 2.50 – 1.90 (br m, Cl-C-CH₂-C-Cl), 1.89 – 1.60 (br m, PVC-linker-CH₂-C-triazole and PVC-triazole-O-C-CH₂-linker), 1.57 – 1.30 (br m, linker CH₂'s). ¹³C NMR (200 MHz, CDCl₃, δ, ppm): 160.1 (C=O), 158.4 (C=O), 140.0 (4°), 129.9 (4°), 129.5 (4°), 71.9 (CH₂), 70.67 (CH₂), 70.60 (CH₂), 70.56 (CH₂), 68.8 (CH₂), 68.5 (CH₂), 66.2 (CH₂), 65.6 (CH₂), 64.8 (CH₂), 59.0 (CH₃), 56.9 (CH syndio), 55.9 (CH hetero), 55.0 – 54.9 (CH iso), 50.5 (CH₂), 47.3 – 44.8 (family of CH₂ peaks), 30.0 (CH₂), 29.7 (CH₂), 28.4 (CH₂), 28.1 (CH₂), 26.04 (CH₂), 25.96 (CH₂), 25.3 (CH₂), 25.2 (CH₂). IR (NaCl, thin film, cm⁻¹): 2928 (s, alkane CH), 2874 (s, alkane CH), 1733 (s, ester C=O), 1552 (m, triazole C=C), 1464 (s, methylene stretch CH₂), 1279 (s, ester stretch C-

O), 1202 (s, ester stretch C-O), 1111 (s, ether stretch C-O), 615 (w, C-Cl). DSC (*T_g*): -17 °C.

Type 0M Syntheses

Preparation of methoxy poly(ethylene glycol) 2000 prop-2-ynoate (13b) Propiolic acid (2.100 g, 30.00 mmol) was added to a 250 mL round bottom flask with 40 mL of toluene. Methoxy poly(ethylene glycol) 2000 (20.000 g, 10.00 mmol) and 0.2 mL H₂SO₄ was added to the reaction flask and stirred at reflux for 2 h. The reaction was concentrated *in vacuo*, and diluted with 100 mL ethyl acetate. The solution was transferred to a 500 mL separatory funnel and washed with 10 mL of saturated NaHCO₃ three times each. The aqueous layer was extracted with 100 mL ethyl acetate two times each. The organic layers were combined and dried with MgSO₄, filtered, and concentrated *in vacuo*, affording 11.514 g (5.611 mmol, 56.11% gravimetric yield) of the title compound as a white waxy solid of varying chain lengths. *R_f*: 0.45 (SiO₂, CH₂Cl₂:MeOH, 93:7). ¹H NMR (500 MHz, CDCl₃, δ, ppm): 4.41 – 4.33 (m, 2H), 3.84 – 3.78 (m, 1H), 3.77 – 3.73 (m, 2H), 3.73 – 3.61 (m, 176H), 3.59 – 3.54 (m, 2H), 3.54 – 3.47 (m, 1H), 3.42 – 3.35 (m, 2H), 2.99 (s, 1H). ¹³C NMR (125 MHz, CDCl₃, δ, ppm): 153.4 (C=O), 75.4 (alkyne 4°), 74.7 (alkyne CH), 71.8 (CH₂), 70.6 (CH₂), 70.5 (CH₂), 68.5 (CH₂), 65.1 (CH₂), 60.3 (CH₂), 58.9 (CH₃). IR (NaCl, neat, cm⁻¹): 3216 (w, alkyne CH), 2876 (s, alkane CH), 2112 (m, alkyne CC), 1715 (m, ester C=O), 1244 (m, ester stretch C-O), 1111 (s, ether stretch C-O). HRMS (*m/z*): calcd for (n=40) C₈₄H₁₆₄O₄₂ 1868.0589; found, 1868.0557 [M+H]⁺.

Preparation of 15% PVC-TRZ-PEO₂₀₀₀Me (14b)

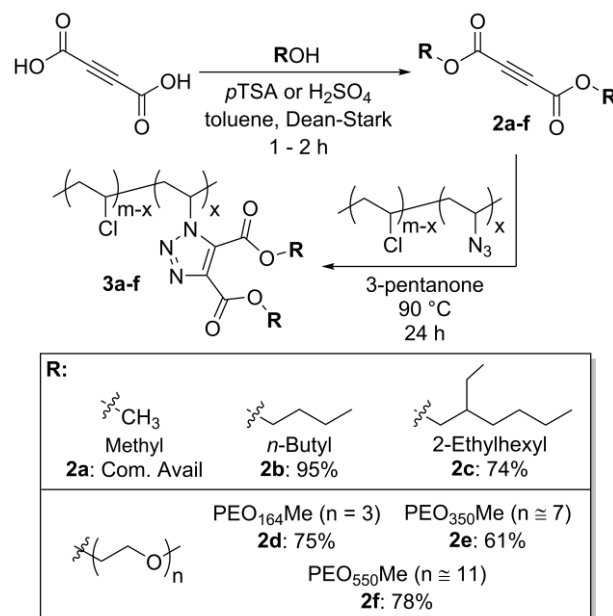
Poly(vinyl chloride) 15% azide (1.000 g, 16.00 mmol) was added to a 100 mL round bottom flask and dissolved in 25 mL of 3-pentanone at 90 °C. Methoxy poly(ethylene glycol) 2000-prop-2-ynoate (7.387 g, 3.600 mmol) was added to the PVC solution and stirred for 72 h. The reaction was concentrated to approximately half its volume *in vacuo*. To a 250 mL beaker, 100 mL of MeOH was added, then placed in a dry ice-acetone bath for 2 min. The polymer was precipitated by dropwise addition of the reaction solution in 2 mL increments into the cooled MeOH. After the addition of reaction solution, the mother liquor was decanted and replaced with 100 mL of fresh MeOH. The beaker was cooled to -78 °C for 2 min, upon which another 2 mL of reaction solution was added dropwise. This process was repeated until

the entire polymer was precipitated. When all of the reaction solution was precipitated, the last volume of mother liquor was decanted. Subsequently, the neat polymer was cooled to $-78\text{ }^{\circ}\text{C}$ and washed with 50 mL of MeOH four times each. The isolated polymer was dried under house vacuum for 1 day, then in a vacuum oven at $40\text{ }^{\circ}\text{C}$ for 3 days to yield 2.926 g of a flexible transparent yellow solid. ^1H NMR (500 MHz, CDCl_3 , δ , ppm): 8.40 – 8.15 (br m, *PVC-triazole-H*), 5.35 – 5.05 (br m, *C-CH-triazole*), 4.65 – 4.55 (br s, *Cl-C-H*), 4.55 – 4.36 (br m, *Cl-C-H* and *triazole-O-CH₂*), 4.36 – 4.15 (br m, *Cl-C-H*), 3.95 – 3.40 (br s, *triazole-O-C-CH₂-O* and *triazole-O-C-C-O-CH₂-CH₂-O-* and *C-CH₂-O-CH₃*), 3.38 (br s, *O-CH₃*), 3.36 (br s, *O-CH₃*), 2.50 – 1.75 (br m, *Cl-C-CH₂-C-Cl*). ^{13}C NMR (125 MHz, CDCl_3 , δ , ppm): 161.0 (C=O), 72.5 (CH_2), 71.9 (CH_2), 70.6 (CH_2), 68.9 (CH_2), 63.0 (CH_2), 61.7 (CH_2), 59.0 (CH_3), 57.0 (CH syndio), 55.9 (CH hetero), 54.9 (CH iso), 47.3 – 44.8 (family of CH_2 peaks). IR (NaCl, thin film, cm^{-1}): 3120 (w, triazole CH), 2871 (s, alkane CH), 1726 (m, ester C=O), 1544 (w, triazole C=C), 1455 (m, methylene stretch CH_2), 1251 (s, ester stretch C-O), 1111 (s, ether stretch C-O), 615 (w, C-Cl). DSC (T_g): $-42\text{ }^{\circ}\text{C}$.

RESULTS AND DISCUSSION

Thermal azide-alkyne cycloaddition efficacy is determined by the energy gap between the highest occupied molecular orbital (HOMO) of the alkyl azide and the lowest unoccupied molecular orbital (LUMO) of the alkyne.⁵¹ Enhanced reactivity is achieved by lowering the LUMO of the alkyne via adjacent electron-withdrawing groups.⁵¹⁻⁵³ Selection of electron-deficient alkynes with functionalizable electron-poor esters enabled cycloadditions to occur with PVC-azide under thermal, copper-free conditions.

Alkyne diesters were synthesized via Fischer esterification⁴⁵ followed by thermal dipolar cycloaddition to directly functionalize PVC with a triazole-based phthalate mimic (Scheme 1). Acetylenedicarboxylic acid was treated with either alkyl alcohols (*n*-butanol or 2-ethylhexyl alcohol) or monomethyl ethers of polyethylene oxide (PEO) with $n = 3$, $n \cong 7$, and $n \cong 11$ polyether repeat units. Acid catalyst (*p*-toluenesulfonic acid, for alkyl derivatives or sulfuric acid, for polyether derivatives) was utilized in combination with toluene in a Dean-Stark apparatus. After 1 to 2 hours under reflux, di(*n*-butyl)



SCHEME 1 Synthesis of Type OD Triazole-Phthalate Mimics Attached to PVC.

2b, di(2-ethylhexyl) **2c**, and three di(methoxy polyethylene oxide) acetylenedicarboxylates **2d-f** were obtained in satisfactory yields. PVC-azide (azide displacement of chloride at either 5 or 15 mol %) was thermally cyclized with the alkyne diesters. 3-Pentanone was the optimized solvent for these thermal dipolar cycloadditions due to its relatively high boiling point, yet has the ability to be evaporated *in vacuo* during workup. Reactions were carried out at $90\text{ }^{\circ}\text{C}$ for 24 hours, with 2.5 to 3.0 equivalents of electron-deficient alkyne to each molar equivalent of azide. Cycloadditions were monitored via FTIR, noting the disappearance of the azide stretch at $\sim 2110\text{ cm}^{-1}$ and the appearance of the triazole sp^2 carbon-carbon stretch at $\sim 1550\text{ cm}^{-1}$. After purification, the ester carbonyl stretch at $\sim 1730\text{ cm}^{-1}$ was also indicative of the successful formation of "Type OD" triazole-phthalate mimics on PVC **3a-f**.

Thermal measurements were obtained for each internally plasticized polymer. Glass transition temperatures (T_g) were measured using differential scanning calorimetry (DSC) with heat-cool-heat cycling to erase sample thermal history. Unmodified PVC exhibits a T_g of $81\text{ }^{\circ}\text{C}$, while PVC-azide at 5 and 15 mol % gave T_g values of $83\text{ }^{\circ}\text{C}$ and $78\text{ }^{\circ}\text{C}$. Glass transition temperatures of selected internally plasticized PVC samples are given in Figure 3a. T_g versus plasticizer weight percent of these triazole plasticized polymers is illustrated in Figure 3b.

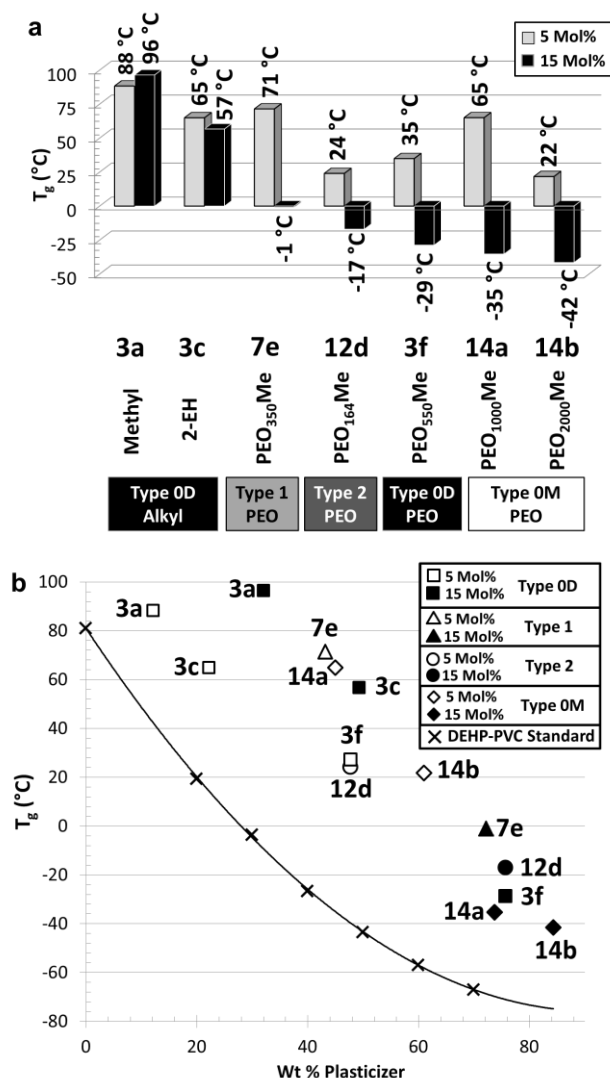


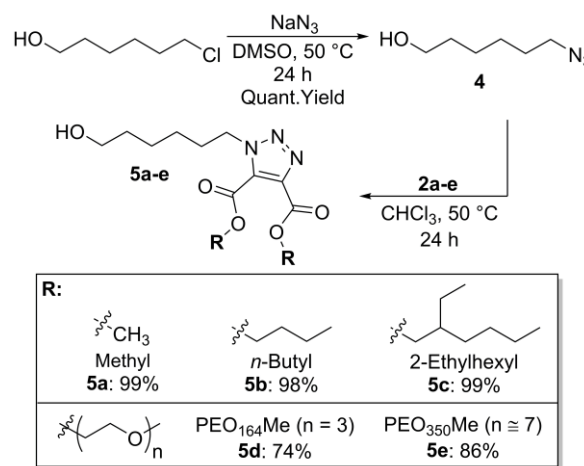
FIGURE 3 (a) Glass Transition Temperatures of Selected Triazole-Phthalate Mimics. (b) Glass Transition Temperatures vs. Wt % Plasticizer.

Glass transition temperatures of all Type 0D alkyl functionalized PVC samples are given in the Supporting Information, Figure S2a. T_g versus plasticizer weight percent of these covalently-bound triazole plasticized polymers is depicted in Figure S2b. Most alkyl functionalized Type 0D derivatives **3b-c** displayed moderate T_g depressions. However, **3a** (PVC-TRZ-DiMe) containing only methyl ester triazoles demonstrate substantial *anti*-plasticization at 5 and 15 mol % internal plasticizer (T_g 5 mol % = 88 °C, T_g 15 mol % = 96 °C, Figure 3). This is likely due to the rigid aromatic nature of the triazole anchor: π - π stacking of these triazole rings in the three-dimensional matrix of PVC can impart crystallinity and stiffness to the modified polymer. DSC data

gathered from PVC samples containing Type 0D alkyl emollients implies that plasticization occurs, albeit inefficiently, due to the inability of the triazole to move within the polymeric matrix, stemming from anchoring the short alkyl triazole motif directly to PVC.

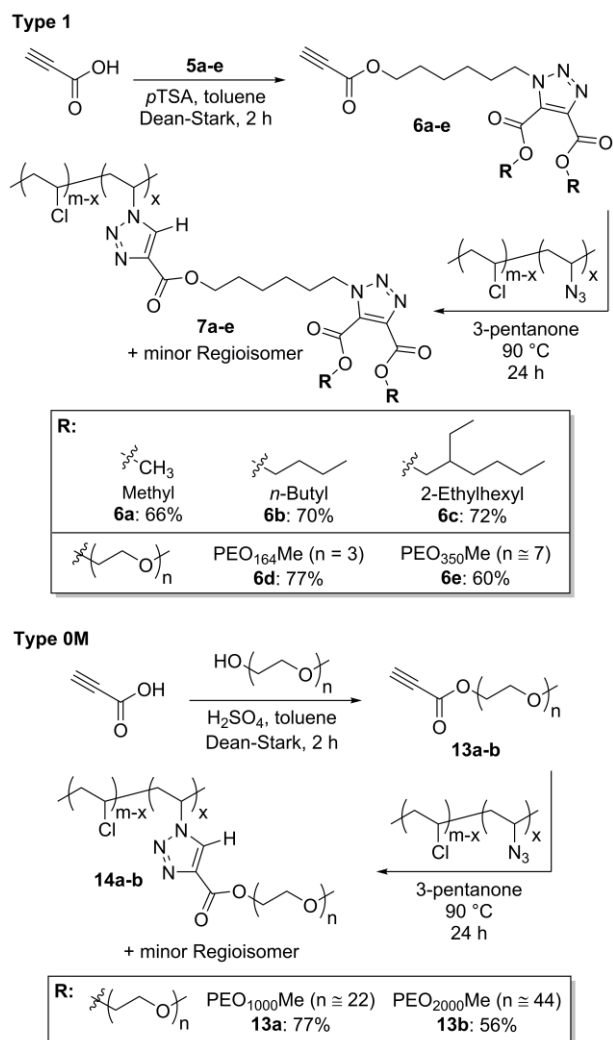
To compensate for anti-plasticization engendered by the direct attachment of the rigid triazole, space was introduced to enhance the flexibility of the plasticizer. It was envisioned that a tether between the triazole attachment to PVC (primary triazole) and a triazole-phthalate mimic (secondary triazole) would boost plasticizing efficiency by distancing the emollient from the PVC main chain. This extension would maintain a covalent attachment to PVC, while generating additional space and mobility between the secondary triazole and the polymer. The facile thermal azide-alkyne cycloaddition remained the method of attachment to PVC for Type 1 and Type 2 triazole-plasticizers.

Selection of the tether was guided by synthetic accessibility and structural simplicity (Scheme 2): the inexpensive hexyl tether was chosen. Synthesis of the hexyl tether began with 6-chlorohexan-1-ol via an S_N2 reaction using sodium azide in DMSO at 50 °C for 24 hours. This led to 6-azidohexan-1-ol⁴⁹ **4** in quantitative yield, with no need for chromatographic purification. The azide **4** was combined with acetylenedicarboxylates **2a-e** in chloroform at 50 °C for 24 hours to give alcohols **5a-e** tethered to pendant triazole-phthalate mimics. High yields (74% to 99%) were achieved after column chromatography.



SCHEME 2 Synthesis of Alcohol Tether with Pendant Triazole-Phthalate Mimics.

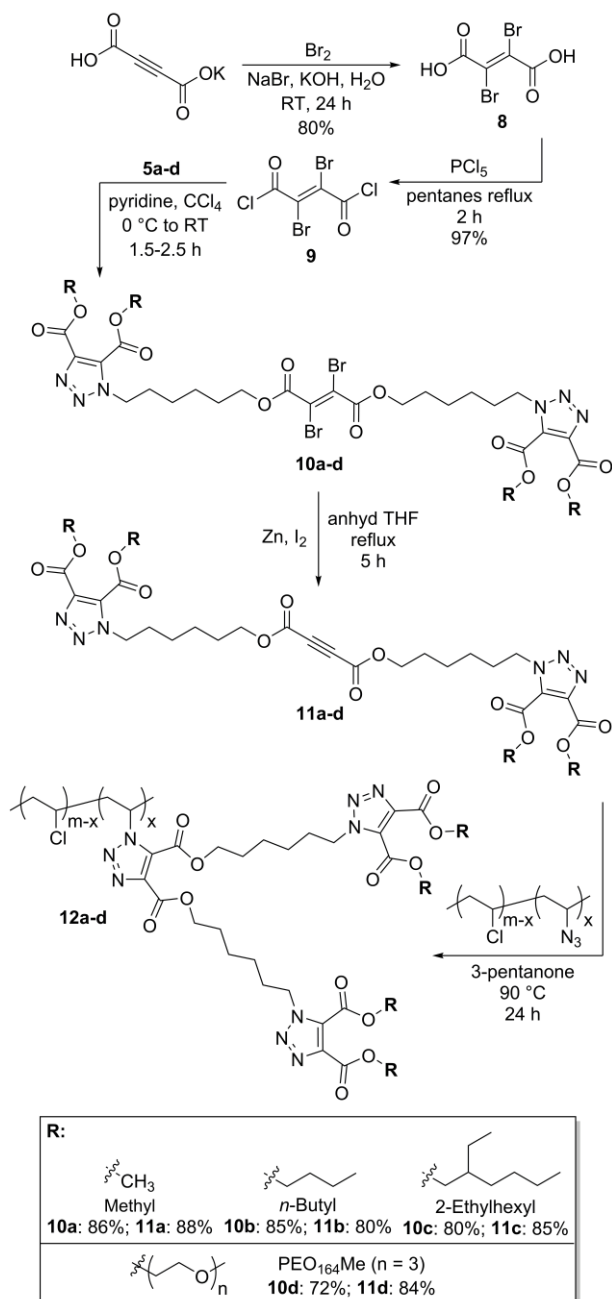
Fischer esterifications were performed to obtain Type 1 electron-deficient alkynes (Scheme 3). Propionic acid was combined with alcohols **5a-e**, catalytic *p*TSA or H₂SO₄, and toluene reflux in a Dean-Stark apparatus. The reactions were complete after 2 to 3 hours to form **6a-e**, with yields ranging from 60% to 77% after purification. PVC-azide was treated with propiolate esters **6a-e** in 3-pentanone at 90 °C. To monitor the process by FTIR, aliquots of the reaction mixture were taken at 12 hour intervals, and then precipitated three times in methanol to remove the unreacted propiolate ester. Cycloadditions with PVC-azide were complete after 24 hours, affording Type 1 internally plasticized PVC **7a-e**.



SCHEME 3 Synthesis of Type 1 and Type OM Triazole-Phthalate Mimics Attached to PVC.

Alkyl functionalized Type 1 PVC **7a-c** demonstrated moderate glass transition temperature depressions (Supporting Information, Figure S3a). T_g versus plasticizer weight percent of Type 1 PVC is given in Figure S3b. When PEO₁₆₄Me **7d** and PEO₃₅₀Me **7e** were incorporated in the secondary triazole, both samples give T_g values similar to their Type 1 alkyl relatives at 5 mol %. Miscibility of the internal plasticizer in PVC plays a crucial role in effectively imparting flexibility to the polymer.^{54,55} Introduction of the hexyl tether with 5 mol % PEO functionalized triazole esters in **7d-e** does result in decreased T_g values (**7d** T_g = 57 °C, **7e** T_g = 71 °C) compared to unmodified PVC (Figure S3a). At 15 mol %, substantially lower T_g values of Type 1 PEO triazole-plasticizers were observed: **7d** (T_g = 18 °C) and **7e** (T_g = -1 °C, Figure 3).

It was envisaged that one could further increase the weight percentage of covalently-bound plasticizer by synthesizing an alkyne functionalized with two hexyl tethered triazoles. This would further depress glass transition temperatures by introducing increased molecular weight and an additional branch point compared to Type 1 plasticizers. Synthesis of Type 2 electron-deficient acetylenedicarboxylates **11a-d** was not a trivial task: Fischer esterifications, triazine,⁵⁶ and carbodiimide⁵⁷⁻⁵⁹ couplings were unsuccessful, largely due to competing intramolecular Michael additions to the activated acetylenedicarboxylate intermediates.^{58,59} Modification of a synthetic strategy^{60,61} involving the protection of the electron-poor alkyne and subsequent acid chloride formation proved successful in furnishing Type 2 alkynes (Scheme 4). Acetylenedicarboxylate monopotassium salt was protected by bromination. The acid chloride was obtained by treating dibromofumaric acid **8** with PCl₅. After workup on ice, dibromofumaroyl chloride **9** and alcohols **5a-d** were combined to afford the dibromofumarate esters **10a-d** in 72% to 86% yield. Deprotection of **10a-d** was accomplished by Zn/I₂, producing Type 2 acetylenedicarboxylates **11a-d** (80% to 88%). According to FTIR, cycloadditions between PVC-azide and **11a-d** required 24 to 36 hours at 90 °C, furnishing Type 2 internally plasticized PVC **12a-d**.



SCHEME 4 Synthesis of Type 2 Triazole-Phthalate Mimics Attached to PVC.

This strategy was effective at enhancing glass transition temperature depressions relative to alkyl-based Type OD and Type 1 internally plasticized PVC (Supporting Information, Figure S4a and S4b). Type 2 alkyl triazole-plasticizers **12a-c** give lower glass transition temperatures compared to their Type 1 **7a-c** and Type OD **3a-c** analogues. At 15 mol %, **12c** (PVC-TRZ-DiHexyl-TRZ-DiEH) displays the only sub-zero T_g ($T_g = -6\text{ }^\circ\text{C}$) of any alkyl-based triazole internal

plasticizer. PEO functionalized **12d** (PVC-TRZ-DiHexyl-TRZ-DiPEO₁₆₄Me) displays diminished T_g values relative to the alkyl-based Type 2 derivatives (T_g 15 mol % = $-17\text{ }^\circ\text{C}$). As seen in Figure 3, this also holds true against Type 1 **7e** containing PEO triazole esters at both mole percentages.

These encouraging results prompted an investigation into Type OD PEO-functionalized triazoles as internal plasticizers (Supporting Information, Figure S5a and S5b). PEO chains significantly enhance T_g depressions with increasing length: **3d** containing triethylene oxide monomethyl ether (PEO₁₆₄Me) displays only a slight reduction in T_g compared to **3c** (PVC-TRZ-DiEH, Figure S2a). Incorporation of longer PEO chains with average molecular weights of 350 g/mol in **3e** and 550 g/mol in **3f** exhibit striking glass transition temperature depressions; most notably **3f** ($T_g = -29\text{ }^\circ\text{C}$) at 15 mol % (Figure 3).

In a quest to minimize the number of synthetic steps to obtain internally plasticized PVC, while further decreasing T_g values, propiolates of large PEO monomethyl ethers were synthesized (Scheme 3). Fischer esterification of propiolic acid and PEO (average molecular weight of 1000 or 2000 g/mol) gave PEO propiolates **13a-b** with yields of 56% and 77%. Cycloadditions to PVC-azide were carried out with **13a-b**, affording Type OM internally plasticized PVC **14a-b**, as mixtures of major and minor regioisomers.

Glass transition temperatures of Type OM PEO plasticized PVC are depicted in Figure 3a, while T_g versus plasticizer weight percent are given in Figure 3b. Detailed thermal data of Type OM plasticized samples are illustrated in the Supporting Information, Figure S6. Polymers **14a-b** exhibit impressively low T_g values at 15 mol %: **14a** ($T_g = -35\text{ }^\circ\text{C}$) and **14b** ($T_g = -42\text{ }^\circ\text{C}$).

Plasticization Efficiency

Plasticizing efficiencies of these new triazole internal plasticizers were determined relative to the traditional DEHP-PVC system utilized industrially. Plasticizer efficiency values⁵⁴ ($E\Delta T_g$) were modified for this investigation using the equation:

$$E\Delta T_g = (\Delta T_g \text{ TRZ} / \Delta T_g \text{ DEHP}) \times 100 \quad (1)$$

$E\Delta T_g$ corresponds to the difference in glass transition temperature between unmodified PVC and triazole-plasticized PVC (ΔT_g TRZ), divided by the T_g difference between unperturbed PVC and an analogous weight percentage of DEHP plasticizer in traditional PVC blends (ΔT_g DEHP). Typical values for $E\Delta T_g$ range from 0 to 100, however negative values indicate anti-plasticization, while values above 100 belong to internal plasticizers more efficient than DEHP. $E\Delta T_g$ values grouped by mole percent and Type are illustrated in Figure 4 (Exact $E\Delta T_g$ and T_g values of all internally plasticized PVC samples are given in the Supporting Information Table S1, Table S2).

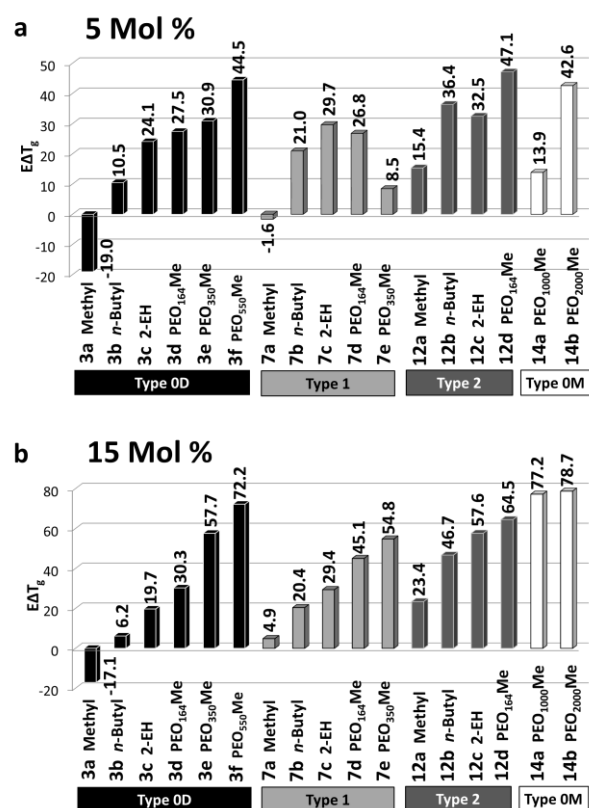


FIGURE 4 (a) Efficiency Values ($E\Delta T_g$) of 5 Mol % Triazole Internal Plasticizers. (b) Efficiency Values ($E\Delta T_g$) of 15 Mol % Triazole Internal Plasticizers.

For Type 0D methyl esters **3a**, negative efficiency values are observed at both percentages of substitution, corresponding to anti-plasticization. Long or branched chains are necessary to obtain lower glass transition temperatures. This is apparent in Type 0D **3c** containing 2-ethylhexyl triazole esters and the *n*-butyl congener **3b**. Type 0D triazoles **3d-f** possessing PEO chains exhibit significant improvements. Longer PEO chains enhance

plasticization efficacy, which is further amplified with higher mole percentages of covalently-bound emollient.

Type 1 internal plasticizers containing a single hexyl tether with alkyl triazole esters generally demonstrated enhanced plasticization capabilities over the Type 0D relatives (Figure 4). This is likely due to the space created between PVC and the secondary triazole, maximizing the mobility of the plasticizer in the polymeric matrix. Derivative **7c** incorporating the hexyl tether and 2-ethylhexyl triazole esters exhibited the highest efficiency values compared to the Type 1 *n*-butyl **7b** and methyl **7a** relatives. In addition, **7c** displays an improvement in plasticization efficiency over its Type 0D predecessor **3c**, notably at 15 mol %. The anti-plasticization effect of the rigid primary triazole directly on PVC is compensated by the addition of the flexible hexyl tether. Efficiencies of Type 1 PEO triazole-plasticizers **7d-e** at 15 mol % exceed that of 2-ethylhexyl (2-EH) **7c**.

Type 2 triazole-plasticizers exhibit superior $E\Delta T_g$ values compared to the Type 1 system (Figure 4). Extended branching and longer alkyl chains in both the primary and secondary triazoles are imperative for improved plasticizing efficiency when utilizing alkyl esters. For PEO esters, architectural branching does not always confer lower T_g values. For example, 15 mol % Type 2 **12d** (PVC-TRZ-DiHexyl-TRZ-DiPEO₁₆₄Me) contains the same weight percentage of plasticizer as Type 0D PEO **3f** (PVC-TRZ-DiPEO₅₅₀Me), yet gives a T_g of -17°C , compared to **3f** with a T_g of -29°C . Type 0M PEO samples **14a-b** exhibit the two best $E\Delta T_g$ values (Figure 4b). At 15 mol % of covalently-bound plasticizer, factors such as branching and secondary triazole spacing become less important than the use of long PEO chains.

The highest overall $E\Delta T_g$ values at 5 mol % plasticizer belong to Type 2 PEO **12d**, Type 0D PEO **3f**, and Type 0M PEO **14b** (Figure 4a). A significant increase in plasticizer efficiency is noted amongst these top three polymers compared to the next most efficient samples: Type 2 alkyl **12b-c**. These alkyl emollients possess the same three triazole branch points as **12d**, with the only critical difference being the composition of the secondary triazole ester chains. This illustrates the necessity of multiple branch points and the incorporation of long PEO segments for maximal internal plasticizer efficacy, particularly at low mole percentages.

Due to the reduced amount of anchoring points at 5 mol %, aspects such as branching, spacing, and miscibility have an augmented effect on $E\Delta T_g$ compared to the 15 mol % analogues. A large disparity in T_g values for Type OM **14a** and **14b** at 5 mol % plasticizer was observed: $T_g = 65^\circ\text{C}$ versus $T_g = 22^\circ\text{C}$, with concomitant plasticizer efficiency values of $E\Delta T_g = 13.9$ and $E\Delta T_g = 42.6$. In contrast, at 15 mol %, **14a** and **14b** give nearly identical $E\Delta T_g$ values.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) were measured to quantitatively determine degradation properties (details in Supporting Information, Tables S3 – S7). DTG of unmodified PVC reveals two peaks, indicative of a multistage decomposition process with an initial decrease in mass at the first derivative peak ($T_{d,PVC1}$) of 289°C , and a second loss ($T_{d,PVC2}$) at 442°C when measured in air. $T_{d,PVC1}$ signifies the dehydrochlorination of PVC with concomitant loss of hydrochloric acid, formation of various cyclic aromatic compounds, and vinyl chloride.⁶² $T_{d,PVC2}$ is indicative of the loss of higher molecular weight hydrocarbon fragments due to chain scission of the carbonaceous backbone.

DTG events of internally plasticized samples occurring at approximately 430°C are indicative of triazole hydrolysis to alcohol and carboxylic acid. Interestingly, methyl triazoles cause a notable decrease in $T_{d,PVC1}$, particularly at 15 mol %. This may stem from the relative ease of methyl ester hydrolysis, compared to congeners with larger alkyl esters, which exhibit progressively elevated $T_{d,PVC1}$ temperatures as the size of the carbon chain increases (Supporting Information, Table S4-S6). Broad DTG peaks originating from the hexyl tether in Type 1 and 2 plasticized PVC occur between 325°C and 350°C (Supporting Information, Table S5-S7).

All polymers containing PEO esters exhibit decreased $T_{d,PVC1}$ temperatures compared to unmodified PVC. However, many of these samples containing higher weight percentages of PEO-based emollient produce a second DTG peak adjacent to $T_{d,PVC1}$, ranging from 270°C to 309°C . This may be due to a secondary dehydrochlorination event ($T_{d,PVC1.5}$, Supporting Information, Table S7). For many 15 mol % PEO

functionalized polymers, two unique DTG peaks stemming from PEO appear between 350°C to 366°C and 383°C to 398°C . Generally, emollients possessing a PEO peak ($T_{d,PEO}$) at approximately 360°C contain relatively short PEO chains compared to Type OM derivatives, which exhibit degradation events around 390°C ($T_{d,PEO2}$).

Degree of Plasticizer Migration

The degree of plasticizer migration in *n*-hexane was determined by a process derived from ASTM-D5227. The remaining polymer mass was measured post-extraction in triplicate. The top three polymers with the highest plasticizing efficiency values ($E\Delta T_g$) were chosen. A traditional DEHP-PVC blend (containing 60 weight percent DEHP) was used as a standard. Plasticizer migration data is depicted in Figure 5 (See Supporting Information, Table S8 and Figure S2 for detailed data). The traditional DEHP-PVC blend exhibits complete plasticizer migration ($99.96 \pm 0.07\%$). In contrast, PVC internally plasticized by triazole emollients display no appreciable plasticizer migration.

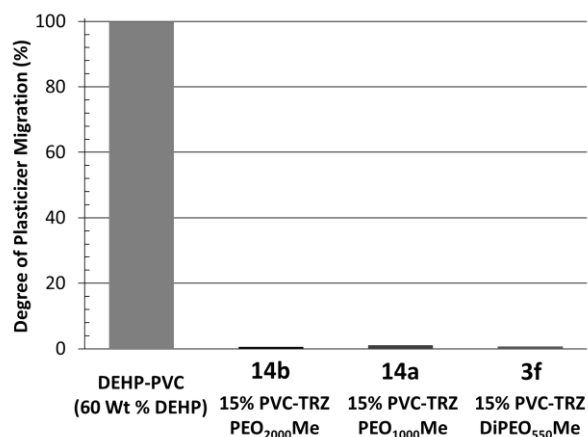


FIGURE 5 Degree of Plasticizer Migration of DEHP-PVC Blend and PVC Internally Plasticized by Triazole-Phthalate Mimics.

CONCLUSIONS

Type OD methyl triazole esters directly appended to PVC illustrates the inherent anti-plasticization effect of the pendant triazole ring. Plasticization improves with increasing molecular weight and branching of the alkyl ester chains. Introduction of a flexible hexyl tether to a secondary triazole group (Type 1) acts as additional molecular weight and branching, lowering T_g values. Attachment of two hexyl tethered secondary triazoles (Type 2) follows this trend by

enforcing another branch point and increasing molecular weight. Utilization of PEO esters in all architectural Types significantly enhances T_g depressions, with longer PEO chains exhibiting remarkable results. It will be interesting to evaluate if unmodified PVC can be blended with these PEO functionalized polymers to fine-tune the desired plasticity of the material. Single PEO ester triazoles (Type OM) easily prepared from propiolic esters using low-cost, commercially available materials combine excellent plasticization with straightforward synthesis, making these non-migratory internal plasticizers potentially attractive for industrial applications.

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GRAPHICAL ABSTRACT

Chad M. Higa,¹ Andy T. Tek,² Rudy J. Wojtecki,² Rebecca Braslau¹**Non-Migratory Internal Plasticization of Poly(Vinyl Chloride) via Pendant Triazoles Bearing Alkyl or Polyether Esters**

This study aims to systematically investigate the effect of non-migratory plasticizers attached to pendant triazole linkages plasticizer on poly(vinyl chloride) (PVC) glass transition temperature. Factors such as branching, plasticizing group composition, and miscibility are investigated. Copper-free thermal azide-alkyne cycloadditions are employed to functionalize PVC with an array of triazole-based phthalate mimics.

