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Internal Plasticization of Poly(vinyl) Chloride using Glutamic Acid as a Branched Linker to Incorporate Four Plasticizers per Anchor Point

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ABSTRACT

Internal plasticization of PVC using thermal azide-alkyne Huisgen dipolar cycloaddition between azidized PVC and electron-poor acetylenediamides incorporating a branched glutamic acid linker resulted in incorporation of four plasticizing moieties per attachment point on the polymer chain. A systematic study incorporating either alkyl or polyethylene glycol esters provided materials with varying degrees of plasticization, with depressed T_g values ranging from -1 to 62 °C. Three interesting trends were observed. First, T_g values of PVC bearing various internal plasticizers were shown to decrease with increasing chain length of the plasticizing ester. Second, branched internal plasticizers bearing triethylene glycol chains had lower T_g values compared to those with similar length long-chain alkyl groups. Finally, thermogravimetric analysis of these internally plasticized PVC samples revealed that these branched internal plasticizers bearing alkyl chains are more thermally stable than similarity branched plasticizers bearing triethylene glycol units. These internal tetra-plasticizers were synthesized and attached to PVC-azide in three simple synthetic steps.

KEYWORDS: PVC, internal plasticization, triazole, glutamic acid, non-migratory

INTRODUCTION

Polyvinyl chloride (PVC) is the third most widely used plastic; uses range from building materials, toys, clothing and medical devices.[1] Pure PVC is rigid and brittle. Typically, in order to modify the flexibility of PVC, small molecule plasticizers are added. In medical devices, the weight percent of plasticizer can reach up to 50%.[2] The most common external plasticizers are phthalate esters.[1] These small molecules leach out of the PVC matrix into the environment; when ingested, absorbed or inhaled into the human body, phthalates and their metabolites pose a significant risk to human health.[3–8]

Several approaches were explored to solve the problem of phthalate toxicity. The easiest direct adoption is to utilize less toxic alternatives. Currently, a variety of small molecule non-phthalate plasticizers are being marketed, including adipates, azelates, succinates, citrates, trimellitates, cyclohexane derivatives, vegetable oil derivatives, and isosorbide esters.[2,9] However, as these plasticizers are not covalently bound to PVC, they also migrate out, with subsequent degradation of the PVC products over time. Polymeric plasticizers have also been developed, examples are polyadipates[10,11] and poly(ε-caprolactone)-co-(ethylene glycol).[12,13] Polymeric plasticizers show significant improvement towards migration resistance

compared to small molecule plasticizers. The major drawbacks are their lack of homogeneous mixing with the PVC resin, and less effective plasticizing efficiency compared to low molecular weight traditional plasticizers. Surface treatments provide an alternative approach to inhibiting plasticizer migration. For example, crosslinking of the surface chains has been investigated,[14–21] but can compromise the flexibility and mechanical properties of the polymer. Covalent attachment of plasticizers to PVC chains, internal plasticization, is an effective way to avoid migration of plasticizers from the PVC. Reports of internal plasticization using sulfide[22–26] and amine[27,28] attachments to PVC demonstrate impressive reduction of the T_g values. However, sulfide linkers are susceptible to oxidation, leading to both discoloration and degradation over time. The disadvantage of using amine nucleophiles to displace chloride on PVC is that amines are also excellent bases, leading to inevitable competitive elimination, resulting in unsaturation in the polymer chain and consequent low thermal stability.[29] Another method to attach plasticizers to PVC is copper-catalyzed azide-alkyne cycloaddtion.[30–38] However, the use of a copper catalyst leaves a toxic copper residue.[39,40] Previous work in the Braslau laboratory on preparing plasticizers covalently linked to PVC has utilized efficient metal-free Huisgen thermal azide-alkyne dipolar cycloadditions.[36,41,42] Post-polymerization functionalization involving azide displacement of chlorine atoms on PVC via a facile S_N2 reaction occurs with no detectable competitive elimination. Reaction of the pendant azide with electron poor alkynes under mild heat gives substituted triazoles. With the goal of increasing the number of internal plasticizing moieties per azide group, the use of electron poor alkynes bearing branched linkers displaying multiple plasticizing species was explored (FIGURE 1). Herein, glutamic acid was selected as the branched linker, as it is inexpensive, and can be incorporated in only two synthetic steps to form the requisite electron-poor alkyne. The use of L-glutamic acid, as opposed to racemic material,

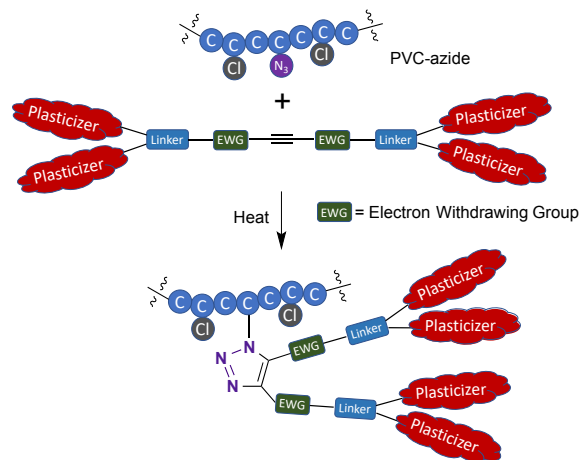was selected solely due to its natural abundance, and thus the low cost of the L-enantiomer.

FIGURE 1 Overview: cycloaddition of disubstituted alkyne bearing branched linkers introduces four plasticizers per azide on PVC

EXPERIMENTAL

Materials

PVC (M_w = 43000, M_n = 22000) was purchased from Sigma-Aldrich. 3-Pentanone (≥99%), tri(ethylene glycol) monomethyl ether (95%), and silica gel (Grade 60, 230–400 mesh particle size, 40–63 μm particle size) were purchased from Sigma-Aldrich. L-Glutamic acid(≥99%) was purchased from Alfa Aesar. n-Butanol (HPLC grade), toluene (HPLC grade), tetrahydrofuran (HPLC grade), acetonitrile (Optima™, LC/MS grade), dimethylformamide (sequencing grade), N-methyl-2-pyrrolidone (NMP) (>99.8%), dichloromethane (stabilized HPLC grade, submicron filtered), methanol, hexanes, ethyl acetate, and tetrahydrofuran (HPLC grade, submicron filtered, uninhibited) were purchased from Fisher Scientific. n-Hexanol (>98%), n-decanol (97%), 2-ethyl-1-hexanol (>99.5%), and tri(ethylene glycol) monobutyl ether (>97%) were supplied by Tokyo Chemical Industries (TCI). p-Tolenesulfonic acid monohydrate(99%, extra pure), sodium azide (99%, extra pure), and acetylenedicarboxylic acid (98%) were purchased from Acros Organics. 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMTMM) (tech)

was purchased from Oakwood Chemical. CDCl$_3$ (D 99.8%) was supplied by Cambridge Isotope Laboratories.

Measurements

Fourier transform infrared spectroscopy (FTIR) was recorded with a Perkin-Elmer Spectrum One Spectrometer. Liquid samples were measured neat. Soild samples (expect for polymers) were measured using the KBr pellet method. Polymers were measured by forming a thin film on a sodium chloride plate. Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker Avance III HD 4 channel 500 MHz Oxford Magnet NMR Spectrometer with Automation or a Varian Unity Plus 500 MHz Oxford Magnet NMR Spectrometer at ambient temperature in CDCl$_3$ as solvent. The signal of residual CHCl$_3$ was used as an internal standard (^{1}H NMR, δ 7.26 ppm; ^{13}C NMR, δ 77.16 ppm). High-resolution mass spectrometry (HRMS) was recorded with a Thermo Scientific LTQ Orbitrap Velos Pro HRMS using acetonitrile (CH$_3$CN) with 0.1 % formic acid as solvent. Elemental analysis was performed by either MHW Laboratories or NuMega Resonance Labs. Glass transition temperatures of polymers were measured using a TA Instruments differential scanning calorimetry (DSC) Q2000 with a heat-cool-heat protocol, and a scaning range of −90 to 200 °C at a heating rate of 10 °C min^{-1}. 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 to 500 °C at a heating rate of 10 °C min^{-1} in air or nitrogen, as specified.

Preparation of 2-aminopentanedioate (1a-f)

These esterifications were carried out following a modified procedure by Ijiro et al.[43]

Preparation of 1,5-dibutyl (2S)-2-aminopentanedioate (1a)

To a 100 mL round-bottom flask was added L-glutamic acid (1.372 g, 9.325 mmol), 1-butanol (2.80 mL, 30.6 mmol), pTSA (2.377 g, 12.50 mmol), and toluene (40 mL). The solution was refluxed with a Dean-Stark apparatus for 4 h. The reaction mixture was then concentrated *in vacuo* and the residue neutralized using sat. NaHCO$_3$ (50 mL). The aqueous solution was extracted with EtOAc (50 mL). The organic layer was washed with sat. NaHCO$_3$ (50 mL), brine (50 mL × 2), and then dried over MgSO$_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography using MeOH/CH$_2$Cl$_2$ (5/95) to give **1a** as a pale yellow liquid (2.041 g, 84.41%). R_f: 0.48 (SiO$_2$, MeOH/CH$_2$Cl$_2$, 5/95). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 4.13 (td, J = 6.7, 1.6 Hz, 2H), 4.08 (t, J = 6.7 Hz, 2H), 3.54 − 3.46 (m, 1H), 2.46 (t, J = 7.5 Hz, 2H), 2.15 − 2.03 (m, 1H), 1.85 (dq, J = 15.1, 7.7 Hz, 1H), 1.78 − 1.56 (m, 6H), 1.44 − 1.32 (m, 4H), 0.94 (t, J = 7.4 Hz, 3H), 0.93 (t, J = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 175.78 (C=O), 173.35 (C=O), 65.06 (O-CH$_2$), 64.54 (O-CH$_2$), 53.97 (NH$_2$-CH), 30.82 (CH$_2$), 30.79 (CH$_2$), 30.78 (CH$_2$), 29.95 (CH$_2$), 19.27 (CH$_2$), 19.25 (CH$_2$), 13.84 (CH$_3$), 13.82 (CH$_3$). IR (NaCl, neat, cm^{-1}): 3387 (w, amine N-H), 3322 (w, amine N-H), 2961 (s, alkane C-H), 2936 (s, alkane C-H), 2875 (m, alkane C-H), 1735 (s, ester C=O), 1607 (w, amine N-H bending), 1183 (s, ester C-O). HRMS (m/z): calcd for C$_{13}$H$_{26}$NO$_4$, 260.1856; found, 260.1836 [M+H]$^+$.

Preparation of 1,5-bihexyl (2S)-2-aminopentanedioate (1b)

To a 100 mL round-bottom flask was added L-glutamic acid (1.472 g, 10.00 mmol), 1-hexanol (2.248 g, 22.00 mmol), pTSA (2.378 g, 12.50 mmol), and toluene (40 mL). The solution was refluxed with a Dean-Stark apparatus for 4 h. The reaction mixture was concentrated *in vacuo* and then the residue was neutralized using sat. NaHCO$_3$ (50 mL). The aqueous solution was extracted with EtOAc (50 mL). The organic layer was washed with sat. NaHCO$_3$ (50 mL), brine (50 mL × 2), and then dried over MgSO$_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography using MeOH/CH$_2$Cl$_2$ (3/97) to give **1b** as a pale yellow liquid (2.077 g, 65.84%). R_f: 0.33 (SiO$_2$, MeOH/CH$_2$Cl$_2$, 3/97). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 4.12 (td, J = 6.8, 1.7 Hz, 2H), 4.07 (t, J = 6.8 Hz, 2H), 3.49 (dd, J = 8.3, 5.2 Hz, 1H), 2.47 (t, J = 7.5 Hz, 2H), 2.09 (dtd, J = 13.1, 7.7, 5.2 Hz, 1H),

1.86 (dq, J = 15.0, 7.6 Hz, 3H), 1.71 − 1.55 (m, 4H), 1.41 − 1.23 (m, 12H), 0.89 (t, J = 6.5 Hz, 6H). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 175.78 (C=O), 173.35 (C=O), 65.36 (O-CH$_2$), 64.84 (O-CH$_2$), 53.97 (NH$_2$-CH), 31.57 (CH$_2$), 31.54 (CH$_2$), 30.83 (CH$_2$), 29.94 (CH$_2$), 28.72 (CH$_2$), 28.70 (CH$_2$), 25.72 (CH$_2$), 25.68 (CH$_2$), 22.67 (CH$_2$), 22.65 (CH$_2$), 14.13 (CH$_3$), 14.12 (CH$_3$).. IR (NaCl, neat, cm^{-1}): 3388 (w, amine N-H), 3324 (w, amine N-H), 2957 (s, alkane C-H), 2932 (s, alkane C-H), 2860 (m, alkane C-H), 1736 (s, ester C=O), 1607 (w, amine N-H bending), 1180 (s, ester C-O). HRMS (*m/z*): calcd for C$_{17}$H$_{34}$NO$_4$, 316.2482; found, 316.2466 [M+H]$^+$.

Preparation of 1,5-bis(2-ethylhexyl) (2S)-2-aminopentanedioate (1c)

To a 100 mL round-bottom flask was added L-glutamic acid (1.471 g, 10.00 mmol), 2-ethyl-1-hexanol (2.866 g, 22.01 mmol), *p*TSA (2.377 g, 12.50 mmol), and toluene (40 mL). The solution was refluxed with a Dean-Stark apparatus for 4 h. The reaction mixture was concentrated *in vacuo* and then the residue was neutralized using sat. NaHCO$_3$ (50 mL). The aqueous solution was extracted with EtOAc (50 mL). The organic layer was washed with sat. NaHCO$_3$ (50 mL), brine (50 mL × 2), and then dried over MgSO$_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography using MeOH/CH$_2$Cl$_2$ (3:97) to give **1c** as a pale yellow liquid (2.899 g, 78.02%). R_f: 0.35 (SiO$_2$, MeOH/CH$_2$Cl$_2$, 3/97). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 4.11 − 4.02 (m, 2H), 4.02 − 3.95 (m, 2H), 3.52 (s, 1H), 2.48 (t, J = 7.5 Hz, 2H), 2.16 − 2.04 (m, 1H), 2.04 − 1.68 (m, 3H), 1.66 − 1.51 (m, 2H), 1.41 − 1.33 (m, 4H), 1.33 − 1.20 (m, 12H), 1.04 − 0.74 (m, 12H). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 175.87 (C=O), 173.43 (C=O), 67.57 (O-CH$_2$), 67.09 (O-CH$_2$), 54.02 (NH$_2$-CH), 38.93 (CH), 38.89 (CH), 30.87 (CH$_2$), 30.54 (CH$_2$), 30.48 (CH$_2$), 29.94 (CH$_2$), 29.07 (CH$_2$), 29.05 (CH$_2$), 23.93 (CH$_2$), 23.90 (CH$_2$), 23.11 (CH$_2$), 23.09 (CH$_2$), 14.18 (CH$_3$ × 2), 11.12 (CH$_3$), 11.09 (CH$_3$).. IR (NaCl, neat, cm^{-1}): 3389 (w, amine N-H), 3324 (w, amine N-H), 2959 (s, alkane C-H), 2931 (s, alkane C-H), 2874 (s, alkane C-H), 2861 (s, alkane C-H), 1736 (s, ester C=O), 1607 (w, amine N-H bending), 1180 (s, ester C-O). HRMS

(*m/z*): calcd for C$_{21}$H$_{42}$NO$_4$: 372.3108; found 372.3094 [M+H]$^+$.

Preparation of 1,5-bis(decyl) (2S)-2-aminopentanedioate (1d)

To a 100 mL round-bottom flask was added L-glutamic acid (1.472 g, 10.01 mmol), 1-n-decanol (4.28 ml, 22.4 mmol), *p*TSA (2.378 g, 12.50 mmol), and toluene (40 mL). The solution was refluxed with a Dean-Stark apparatus for 4 h. The reaction mixture was concentrated *in vacuo* and then the residue was neutralized using sat. NaHCO$_3$ (50 mL). The aqueous solution was extracted with EtOAc (50 mL). The organic layer was washed with sat. NaHCO$_3$ (50 mL), brine (50 mL × 2), and then dried over MgSO$_4$ and concentrated *in vacuo* and then the residue was purified by silica gel column chromatography using MeOH/CH$_2$Cl$_2$ (3/97) to give **1d** as a pale yellow liquid (3.268 g, 76.33%). R_f: 0.43 (SiO$_2$, MeOH/CH$_2$Cl$_2$, 3/97). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 4.11 (t, J = 6.8 Hz, 2H), 4.07 (t, J = 6.8 Hz, 2H), 3.47 (dd, J = 8.3, 5.2 Hz, 1H), 2.46 (t, J = 7.5 Hz, 2H), 2.14 − 2.03 (m, 1H), 1.90 − 1.79 (m, 1H), 1.70 − 1.55 (m, 6H), 1.41 − 1.16 (m, 28H), 0.88 (t, J = 6.8 Hz, 6H). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 175.81 (C=O), 173.35 (C=O), 65.36 (CH$_2$), 64.84 (CH$_2$), 53.98 (NH$_2$-CH), 32.03 (CH$_2$ × 2), 30.83 (CH$_2$), 29.96 (CH$_2$), 29.67 (CH$_2$), 29.65 (CH$_2$), 29.44 (CH$_2$ × 2), 29.40 (CH$_2$), 29.37 (CH$_2$), 28.77 (CH$_2$), 28.75 (CH$_2$), 26.06 (CH$_2$), 26.02 (CH$_2$), 22.82 (CH$_2$ × 2), 14.24 (CH$_3$ × 2). IR (NaCl, neat, cm^{-1}): 3389 (w, amine N-H), 3324.5 (w, amine N-H), 2954.9 (s, alkane C-H), 2925.7 (s, alkane C-H), 2855.4 (s, alkane C-H), 1736.1 (s, ester C=O), 1607.4 (w, amine N-H bending), 1179.5 (s, ester C-O). HRMS (*m/z*): calcd for C$_{25}$H$_{50}$NO$_4$, 428.3734; found, 428.3714 [M+H]$^+$.

Preparation of 1,5-bis({2-[2-(2-methoxyethoxy)ethoxy]ethyl}) (2S)-2-aminopentanedioate (1e)

To a 100 mL round-bottom flask was added L-glutamic acid (1.472 g, 10.01 mmol), triethyleneglycol methyl ether (4.538 g, 27.64 mmol), *p*TSA (2.378 g, 12.50 mmol), and toluene (40 mL). The solution was refluxed with a Dean-Stark apparatus for 4 h. The reaction mixture was concentrated *in vacuo* and then the residue was

neutralized using sat. NaHCO$_3$ (50 mL). The aqueous solution was extracted with DCM (50 mL). The organic layer was washed with sat. NaHCO$_3$ (50 mL), brine (50 mL × 2), and then dried over MgSO$_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography using MeOH/CH$_2$Cl$_2$ (5/95) to give **1e** as a yellow liquid (1.535 g, 34.90%). R_f: 0.30 (SiO$_2$, MeOH/CH$_2$Cl$_2$, 5/95). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 4.28 (t, J = 4.9 Hz, 2H), 4.23 (t, J = 4.9 Hz, 2H), 3.76 − 3.68 (m, 4H), 3.68 − 3.59 (m, 12H), 3.58 − 3.53 (m, 4H), 3.51 (dd, J = 8.4, 5.0 Hz, 1H), 3.38 (s, 6H), 2.51 (t, J = 7.5 Hz, 2H), 2.10 (dtd, J = 13.1, 7.4, 5.1 Hz, 1H), 1.93 − 1.81 (m, 1H), 1.68 (s, 2H). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 175.66 (C=O), 173.21 (C=O), 72.08 (CH$_2$ × 2), 70.76 (CH$_2$ × 2), 70.74 (CH$_2$), 70.72 (CH$_2$ × 2), 69.24 (CH$_2$), 69.14 (CH$_2$), 64.15 (CH$_2$), 64.13 (CH$_2$), 63.75 (CH$_2$), 59.18 (CH$_3$ × 2), 53.90 (NH$_2$-CH), 30.68 (CH$_2$), 29.70 (CH$_2$). IR (NaCl, neat, cm^{-1}): 3382 (w, amine N-H), 3315 (w, amine N-H), 2877 (s, alkane C-H), 1733 (s, ester C=O), 1607 (w, amine N-H bending), 1183 (s, ester C-O), 1112 (s, ether C-O). HRMS (*m/z*): calcd for C$_{19}$H$_{38}$NO$_{10}$, 440.2490; found, 440.2479 [M+H]$^+$.

Preparation of 1,5-Bis({2-[2-(2-butoxyethoxy)ethoxy]ethyl}) (2S)-2-aminopentanedioate (1f)

To a 100 mL round-bottom flask was added L-glutamic acid (1.471 g, 9.998 mmol), triethyleneglycol butyl ether (4.553 g, 22.07 mmol), *p*TSA (2.378 g, 12.50 mmol), and toluene (40 mL). The solution was refluxed with a Dean-Stark apparatus for 4 h. The reaction mixture was concentrated *in vacuo* and then the residue was neutralized using sat. NaHCO$_3$ (50 mL). The aqueous solution was extracted with DCM (50 mL). The organic layer was washed with sat. NaHCO$_3$ (50 mL), brine (50 mL × 2), and then dried over MgSO$_4$ and concentrated *in vacuo*. The residue was purified by silica gel column chromatography using MeOH/CH$_2$Cl$_2$ (4/96) to give **1f** as a pale yellow liquid (2.721g, 51.97%). R_f: 0.47 (SiO$_2$, MeOH/CH$_2$Cl$_2$, 4/96). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 4.27 (t, J = 4.9 Hz, 2H), 4.23 (t, J = 4.9 Hz, 2H), 3.74 − 3.67 (m, 4H), 3.67 − 3.61 (m, 12H), 3.60 − 3.54 (m, 4H), 3.50 (dd, J = 8.3,

5.1 Hz, 1H), 3.45 (t, J = 6.7 Hz, 4H), 2.50 (t, J = 7.6 Hz, 2H), 2.15 − 2.03 (m, 1H), 1.91 − 1.80 (m, 1H), 1.64 (s, 2H), 1.60 − 1.51 (m, 4H), 1.41 − 1.29 (m, 4H), 0.91 (t, J = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 175.64 (C=O), 173.20 (C=O), 71.33 (CH$_2$ × 2), 70.81 (CH$_2$), 70.74 (CH$_2$), 70.72 (CH$_2$), 70.19 (CH$_2$), 69.22 (CH$_2$), 69.12 (CH$_2$), 64.13 (CH$_2$), 63.75 (CH$_2$), 53.88 (NH$_2$-CH), 31.83 (CH$_2$ × 2), 30.66 (CH$_2$), 29.68 (CH$_2$), 19.40 (CH$_2$ × 2), 14.04 (CH$_3$ × 2). IR (NaCl, neat, cm^{-1}): 3384 (w, amine N-H), 3318 (w, amine N-H), 2957 (s, alkane C-H), 2933 (s, alkane C-H), 2870 (s, alkane C-H), 1736 (s, ester C=O), 1607 (w, amine N-H bending), 1180 (s, ester C-O), 1115 (s, ether C-O). HRMS (*m/z*): calcd for C$_{25}$H$_{50}$NO$_{10}$, 524.3429; found, 524.3406 [M+H]$^+$.

Preparation of 2a-f

These amidations were carried out following the general procedure by Heyl and Fessner. [44]

Preparation of 1,5-dibutyl (2S)-2-(3-{[(2S)-1,5-dibutoxy-1,5-dioxopentan-2-yl]carbamoyl}prop-2-ynamido)pentanedioate (2a)

To a solution of acetylenedicarboxylic acid (286.2 mg, 2.509 mmol) in NMP (5 mL) at 0 °C was added a solution dropwise of amine **1a** (1.553 g, 5.988 mmol) in NMP (2.5 mL). After 10 min, DMTMM (2.006 g, 7.249 mmol) was added. The reaction mixture was stirred at 0 °C for 5 h. The mixture was partitioned between ethyl acetate (50 mL) and water (50 mL). The organic layer was washed with brine (50 mL), sat. NaHCO$_3$ (50 mL), 1M HCl (50 mL), and brine (50 mL × 2). The organic layer was dried over MgSO$_4$ and concentrated *in vacuo*. The residue was dissolved in a minimum amount of refluxing THF, cooled to room temperature, then stored at -20 °C overnight. The byproduct (6-dimethoxy-1,3,5-triazin-2(1H)-one) was crystallized from the THF solution and removed by filtration. The solution was concentrated *in vacuo* and further purified by column chromatography (SiO$_2$, hexanes/ethyl acetate, 7/3). The product was obtained as an amorphous white solid (1.220 g, 2.045 mmol, 81.51%). R_f: 0.25 (SiO$_2$, hexanes/ethyl acetate, 7/3). Melting point: 62-63 °C. ^{1}H NMR (500 MHz,

CDCl$_3$, δ, ppm): 7.10 (d, J = 8.0 Hz, 2H), 4.68 (td, J = 7.9, 5.0 Hz, 2H), 4.17 (td, J = 6.7, 2.8 Hz, 4H), 4.09 (t, J = 6.7 Hz, 4H), 2.48 – 2.33 (m, 4H), 2.29 – 2.20 (m, 2H), 2.04 (dtd, J = 14.3, 8.1, 6.4 Hz, 2H), 1.69 – 1.57 (m, 8H), 1.44 – 1.33 (m, 8H), 0.94 (t, J = 7.5 Hz, 6H), 0.93 (t, J = 7.3 Hz, 6H). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 172.71 (C=O), 171.01 (C=O), 151.13 (C=O), 76.84 (C-alkyne), 66.12 (CH$_2$), 64.94 (CH$_2$), 52.28 (CH), 30.74 (CH$_2$), 30.62 (CH$_2$), 30.25 (CH$_2$), 27.35 (CH$_2$), 19.25 (CH$_2$), 19.16 (CH$_2$), 13.83 (CH$_3$), 13.78 (CH$_3$). IR (KBr Pellet, cm^{-1}): 3279 (s, amine N-H), 2960 (s, alkane C-H), 2934 (s, alkane C-H), 2874 (s, alkane C-H), 1744 (s, ester C=O), 1728 (s, ester C=O), 1650 (s, amide C=O), 1538 (s, amide N-H bending), 1176 (s, ester C-O). HRMS (m/z): Calcd for C$_{30}$H$_{49}$N$_2$O$_{10}$, 597.3382; found, 597.3384 [M+H]$^+$.

Preparation of 1,5-dihexyl (2S)-2-(3-{[(2S)-1,5-bis(hexyloxy)-1,5-dioxopentan-2-yl] carbamoyl}prop-2-ynamido)pentanedioate (2b)

To a solution of acetylenedicarboxylic acid (1.134 g, 9.942 mmol) in NMP (20 mL) at 0 °C was added a solution dropwise of amine **1b** (9.677 g, 30.68 mmol) in NMP (10 mL). After 10 min, DMTMM (7.783 g, 28.13 mmol) was added. The reaction mixture was stirred at 0 °C for 5 h. The mixture was partitioned between ethyl acetate (200 mL) and water (200 mL). The organic layer was washed with brine (200 mL), sat. NaHCO$_3$ (200 mL), 1M HCl (200 mL), and brine (200 mL × 2). Then the organic layer was dried over MgSO$_4$ and concentrated *in vacuo*. The residue was dissolved in a minimum amount of refluxing THF, cooled to room temperature, and then stored at -20 °C overnight. The byproduct (6-dimethoxy-1,3,5-triazin-2(1H)-one) was crystallized from the THF solution and removed by filtration. The solution was concentrated *in vacuo* and further purified by column chromatography (SiO$_2$, hexanes/ethyl acetate, 75/25). The product was obtained as an amorphous white solid (3.160 g, 4.457 mmol, 44.83%). R_f: 0.43 (SiO$_2$, hexanes/ethyl acetate, 75/25). Melting point: 60-62 °C. ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 6.80 (d, J = 7.8 Hz, 2H), 4.66 (td, J = 7.6, 5.0 Hz, 2H), 4.17 (td, J = 6.8, 3.7 Hz, 4H), 4.08 (t, J = 6.8 Hz, 4H), 2.50 – 2.30 (m, 4H), 2.29 – 2.19 (m, 2H), 2.05 (dp, J = 14.4, 7.3, 6.7 Hz, 2H), 1.71 – 1.57 (m, 8H), 1.41 – 1.22 (m, 24H), 0.97 – 0.81 (m, 12H). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 172.67 (C=O), 171.03 (C=O), 151.14 (C=O), 76.85 (C-alkyne), 66.41 (O-CH$_2$), 65.23 (O-CH$_2$), 52.26 (NH$_2$-CH), 31.56 (CH$_2$), 31.47 (CH$_2$), 30.24 (CH$_2$), 28.66 (CH$_2$), 28.55 (CH$_2$), 27.35 (CH$_2$), 25.69 (CH$_2$), 25.57 (CH$_2$), 22.66 (CH$_2$), 22.63 (CH$_2$), 14.13 (CH$_3$), 14.10 (CH$_3$). IR (KBr Pellet, cm^{-1}): 3269 (s, amine N-H), 2958 (s, alkane C-H), 2932 (s, alkane C-H), 2860 (s, alkane C-H), 1739 (s, ester C=O), 1646 (s, amide C=O), 1540 (s, amide N-H bending), 1190 (s, ester C-O). HRMS (m/z): Calcd for C$_{38}$H$_{65}$N$_2$O$_{10}$, 709.4634; found, 709.4628 [M+H]$^+$.

Preparation of 1,5-dis(2-ethylhexyl) (2S)-2-(3-{[(2S)-1,5-bis[(2-ethylhexyl)oxy]-1,5-dioxopentan-2-yl]carbamoyl}prop-2-ynamido)pentanedioate (2c)

To a solution of acetylenedicarboxylic acid (286.6 mg, 2.513 mmol) in NMP (5 mL) at 0 °C was added a solution dropwise of amine **1c** (2.538 g, 6.831 mmol) in NMP (2.5 mL). After 10 min, DMTMM (2.005 g, 7.246 mmol) was added. The reaction mixture was stirred at 0 °C for 5 h. The mixture was partitioned between ethyl acetate (50 mL) and water (50 mL). The organic layer was washed with brine (50 mL), sat. NaHCO$_3$ (50 mL), 1M HCl (50 mL), and brine (50 mL × 2). Then the organic layer was dried over MgSO$_4$ and concentrated *in vacuo*. The residue was dissolved in a minimum amount of refluxing THF, cooled to room temperature, and then stored at -20 °C overnight. The byproduct (6-dimethoxy-1,3,5-triazin-2(1H)-one) was crystallized from the THF solution and removed by filtration. The solution was concentrated *in vacuo* and further purified by column chromatography (SiO$_2$, hexanes/ethyl acetate, 80/20). The product was obtained as an amorphous white solid (1.528 g, 1.861 mmol, 74.05%). R_f: 0.37 (SiO$_2$, hexanes/ethyl acetate, 80/20). Melting point: 49-53 °C. ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 6.84 (d, J = 7.8 Hz, 2H), 4.68 (td, J = 7.6, 4.9 Hz, 2H), 4.15 – 4.05 (m, 4H), 4.05 – 3.96 (m, 4H), 2.49 – 2.31 (m, 4H), 2.29 – 2.21 (m, 2H), 2.09 – 2.01 (m, 2H), 1.66 – 1.55 (m, 4H),

1.43 – 1.18 (m, 32H), 1.04 – 0.74 (m, 24H). ^{13}C NMR (126 MHz, CDCl$_3$ δ, ppm): 172.72 (C=O), 171.10 (C=O), 151.09 (C=O), 76.81 (C-alkyne), 68.61 (O-CH$_2$), 68.58 (O-CH$_2$), 67.48 (O-CH$_2$), 52.28 (NH$_2$-CH), 38.83 (CH), 38.79 (CH), 30.47 (CH$_2$), 30.41 (CH$_2$), 30.37 (CH$_2$), 30.24 (CH$_2$), 29.05 (CH$_2$), 29.00 (CH$_2$), 28.98 (CH$_2$), 27.41 (CH$_2$), 23.86 (CH$_2$), 23.81 (CH$_2$), 23.79 (CH$_2$), 23.09 (CH$_2$), 23.06 (CH$_2$), 23.05 (CH$_2$), 14.18 (CH$_3$), 14.15 (CH$_3$), 11.09 (CH$_3$), 11.05 (CH$_3$), 11.02 (CH$_3$). IR (KBr Pellet, cm^{-1}): 3291 (s, amine N-H), 2959 (s, alkane C-H), 2931 (s, alkane C-H), 2874 (s, alkane C-H), 2860 (s, alkane C-H), 1742 (s, ester C=O), 1731 (s, ester C=O), 1651 (s, amide C=O), 1641 (s, amide C=O), 1533 (s, amide N-H bending), 1179 (s, ester C-O). HRMS (m/z): Calcd for C$_{46}$H$_{81}$N$_2$O$_{10}$, 821.5886; found, 821.5890 [M+H]$^+$.

Preparation of 1,5-dis(decyl) (2S)-2-(3-{[(2S)-1,5-bis(decyloxy)-1,5-dioxopentan-2-yl] carbamoyl}prop-2-ynamido)pentanedioate (2d)

To a solution of acetylenedicarboxylic acid (1.378 g, 12.08 mmol) in NMP (24 mL) at 0 °C was added a solution dropwise of amine **1d** (12.74 g, 29.79 mmol) in NMP (12 mL). After 10 min, DMTMM (9.300 g, 33.61 mmol) was added. The reaction mixture was stirred at 0 °C for 5 h. The mixture was partitioned between ethyl acetate (200 mL) and water (200 mL). The organic layer was washed with brine (200 mL), sat. NaHCO$_3$ (200 mL), 1M HCl (200 mL), and brine (200 mL × 2). The organic layer was then dried over MgSO$_4$ and concentrated *in vacuo*. The residue was dissolved in a minimum amount of refluxing THF, cooled to room temperature, and then stored at -20 °C overnight. The byproduct (6-dimethoxy-1,3,5-triazin-2(1H)-one) was crystallized from the THF solution and removed by filtration. The solution was concentrated *in vacuo* and further purified by column chromatography (SiO$_2$, hexanes/ethyl acetate, 80/20). The product was obtained as an amorphous white solid (7.818 g, 8.376 mmol, 69.34%). R_f: 0.40 (SiO$_2$, hexanes/ethyl acetate, 80/20). Melting point: 50-51 °C. ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 6.79 (d, J = 7.7 Hz, 2H), 4.66 (td, J = 7.6, 5.1 Hz, 2H), 4.21 – 4.11 (m, 4H), 4.08 (t, J = 6.8 Hz, 4H), 2.49

– 2.30 (m, 4H), 2.24 (dq, J = 13.5, 7.2 Hz, 2H), 2.04 (dq, J = 14.5, 7.5 Hz, 2H), 1.71 – 1.57 (m, 8H), 1.39 – 1.18 (m, 58H), 0.88 (t, J = 6.8 Hz, 12H). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 172.67 (C=O), 171.02 (C=O), 151.13 (C=O), 76.80 (C-alkyne), 66.42 (O-CH$_2$), 65.24 (O-CH$_2$), 52.26 (NH$_2$-CH), 32.02 (CH$_2$ × 2), 30.23 (CH$_2$), 29.68 (CH$_2$), 29.67 (CH$_2$ × 2), 29.63 (CH$_2$), 29.44 (CH$_2$ × 2), 29.40 (CH$_2$), 29.34 (CH$_2$), 28.71 (CH$_2$), 28.60 (CH$_2$), 27.36 (CH$_2$), 26.03 (CH$_2$), 25.91 (CH$_2$), 22.81 (CH$_2$ × 2), 14.24 (CH$_3$ × 2). IR (KBr Pellet, cm^{-1}): 3307 (s, amine N-H), 2955 (s, alkane C-H), 2922 (s, alkane C-H), 2854 (s, alkane C-H), 1746 (s, ester C=O), 1733 (s, ester C=O), 1648 (s, amide C=O), 1643 (s, amide C=O), 1528 (s, amide N-H bending), 1199 (s, ester C-O). HRMS (m/z): Calcd for C$_{54}$H$_{97}$N$_2$O$_{10}$, 933.7138; found, 933.7143 [M+H]$^+$.

Preparation of 5-[2-(2-butoxyethoxy)ethyl] 1-{2-[2-(2-methoxyethoxy)ethoxy]ethyl} (2S)-2-(3-{[(2S)-1,5-bis({2-[2-(2-methoxyethoxy) ethoxy]ethoxy})-1,5-dioxopentan-2-yl] carbamoyl}prop-2-ynamido)pentanedioate (2e)

To a solution of acetylenedicarboxylic acid (0.8424 g, 7.386 mmol) in NMP (15 mL) at 0 °C was added a solution dropwise of amine **1e** (9.055 g, 20.60 mmol) in NMP (7.5 mL). After 10 min, DMTMM (5.180 g, 18.72 mmol) was added. The reaction mixture was stirred at 0 °C for 5 h. The mixture was partitioned between ethyl acetate (150 mL) and water (150 mL). The organic layer was washed with brine (150 mL), sat. NaHCO$_3$ (150 mL), 1M HCl (150 mL), and brine (150 mL × 2). The organic layer was dried over MgSO$_4$ and concentrated *in vacuo*. The residue was dissolved in a minimum amount of refluxing THF, cooled to room temperature, and then stored at -20 °C overnight. The byproduct (6-dimethoxy-1,3,5-triazin-2(1H)-one) was crystallized from the THF solution and then removed by filtration. The solution was concentrated *in vacuo* and further purified by column chromatography (SiO$_2$, CH$_2$CH$_2$/MeOH, 95/5). The product was obtained as a clear oil (5.104 g, 5.333 mmol, 72.20%). R_f: 0.38 (SiO$_2$, CH$_2$CH$_2$/MeOH, 95/5). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 7.54 (d, J = 8.1 Hz, 2H), 4.67 (td, J = 8.1, 5.1 Hz, 2H), 4.31 (dt, J = 10.9, 6.1 Hz, 4H), 4.28 –

4.18 (m, 4H), 3.70 (t, J = 4.9 Hz, 8H), 3.67 (s, 7H), 3.66 − 3.61 (m, 17H), 3.58 − 3.52 (m, 8H), 3.37 (d, J = 2.5 Hz, 12H), 2.53 − 2.36 (m, 4H), 2.24 (dtd, J = 14.6, 7.4, 5.1 Hz, 2H), 2.06 (dq, J = 14.8, 7.6 Hz, 2H). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 172.54 (C=O), 170.64 (C=O), 151.25 (C=O), 76.78 (C-alkyne), 72.07 (CH$_2$), 72.03 (CH$_2$), 70.80 (CH$_2$), 70.71 (CH$_2$ × 2), 70.65 (CH$_2$), 70.63 (CH$_2$), 69.06 (CH$_2$), 68.86 (CH$_2$), 64.85 (CH$_2$), 64.00 (CH$_2$), 59.11 (CH$_3$ × 2), 52.22 (NH$_2$-CH), 30.38 (CH$_2$), 27.10 (CH$_2$). IR (NaCl, neat, cm^{-1}): 3260 (s, amine N-H), 2878 (s, alkane C-H), 1736 (s, ester C=O), 1665 (s, amide C=O), 1535 (s, amide N-H bending), 1199 (s, ester C-O), 1104(s, ether C-O). HRMS (*m/z*): Calcd for C$_{42}$H$_{73}$N$_2$O$_{22}$, 957.4649; found, 957.4652 [M+H]$^+$.

Preparation of 1,5-bis({2-[2-(2-butoxyethoxy)ethyl]ethyl}) (2S)-2-(3-{[(2S)-1,5-bis({2-[2-(2-butoxyethoxy)ethoxy]ethoxy})-1,5-dioxopentan-2-yl]carbamoyl}prop-2-ynamido)pentanedioate (2f)

To a solution of acetylenedicarboxylic acid (0.7922 g, 6.945 mmol) in NMP (15 mL) at 0 °C was added a solution dropwise of amine **1f** (12.47 g, 23.81 mmol) in NMP (7.5 mL). After 10 min, DMTMM (5.430 g, 19.62 mmol) was added. The reaction mixture was stirred at 0 °C for 5 h. The mixture was partitioned between ethyl acetate (150 mL) and water (150 mL). The organic layer was washed with brine (150 mL), sat. NaHCO$_3$ (150 mL), 1M HCl (150 mL), and brine (150 mL × 2). The organic layer was dried over MgSO$_4$ and concentrated *in vacuo*. The residue was dissolved in a minimum amount of refluxing THF, cooled to room temperature, and then stored at -20 °C overnight. The byproduct (6-dimethoxy-1,3,5-triazin-2(1H)-one) was crystallized from the THF solution and removed by filtration. The solution was concentrated *in vacuo* and further purified by column chromatography (SiO$_2$, CH$_2$CH$_2$/MeOH, 96/4). The product was obtained as a clear oil (3.520g, 3.128mmol, 45.04%). R_f: 0.28 (SiO$_2$, CH$_2$CH$_2$/MeOH, 96/4). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 7.38 (d, J = 8.0 Hz, 2H), 4.68 (td, J = 7.9, 5.1 Hz, 2H), 4.37 − 4.29 (m, 4H), 4.29 − 4.18 (m, 4H), 3.75 − 3.69 (m, 8H), 3.67 (s, 7H), 3.66 − 3.61

(m, 17H), 3.61 − 3.55 (m, 8H), 3.46 (td, J = 6.7, 2.9 Hz, 8H), 2.55 − 2.36 (m, 4H), 2.25 (dtd, J = 14.7, 7.3, 5.2 Hz, 2H), 2.07 (dq, J = 14.7, 7.5 Hz, 2H), 1.61 − 1.51 (m, 8H), 1.41 − 1.30 (m, 8H), 0.91 (t, J = 7.4 Hz, 12H). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 172.55 (C=O), 170.65 (C=O), 151.16 (C=O), 76.77 (C-alkyne), 71.35 (CH$_2$), 71.34 (CH$_2$), 70.81 (CH$_2$ × 2), 70.78 (CH$_2$ × 2), 70.74 (CH$_2$ × 2), 70.20 (CH$_2$), 70.17 (CH$_2$), 69.08 (CH$_2$), 68.87 (CH$_2$), 64.91 (CH$_2$), 64.04 (CH$_2$), 52.27 (NH$_2$-CH), 31.83 (CH$_2$ × 2), 30.34 (CH$_2$), 27.13 (CH$_2$), 19.41 (CH$_2$ × 2), 14.07 (CH$_3$ × 2). IR (NaCl, neat, cm^{-1}): 3270 (m, amine N-H), 2975 (s, alkane C-H), 2933 (s, alkane C-H), 2871 (s, alkane C-H), 1740 (s, ester C=O), 1668 (s, amide C=O), 1534 (m, amide N-H bending), 1198 (s, ester C-O), 1119 (s, ether C-O). HRMS (*m/z*): Calcd for C$_{54}$H$_{97}$N$_2$O$_{22}$, 1125.6527; found, 1125.6523 [M+H]$^+$.

Preparation of 1-azidomethyl-4-tert-butylbenzene (3)

Caution: sodium azide and organic azide can be toxic **and explosive**. Guidelines for safe organic azides should follow (N_C + N_O) / N_N ≥ 3 and N_C > N_N (N = number of atoms).[45] *t*-Butylbenzylic azide and PVC-azide (4.4% and 12.0%) were found safe to manipulate in lab. Special care is still needed when handling organic azides.

Preparation of Amberlite-N$_3$[46]: To a 250 mL beaker was added 40.00 g Amberlite IPA-400 and a solution of 15.00 g NaN$_3$ in 80 ml water. The mixture was left to stir for 1 h. The mixture was filtered and washed with water (100 mL × 2). The charged Amberlite-N$_3$ was then charged a second time with a new solution of 15 g NaN$_3$ in 80 mL water for 1 h. After the second charge, Amberlite-N$_3$ was filtered and washed with water (100 mL × 3), followed by methanol (100 mL), ether (50 mL × 2), and then dried under vacuum for 20 mins.

To a 100 ml round bottom flask was added 1-bromomethyl-4-*tert*-butylbenzene (1.650 g, 7.264 mmol), acetonitrile (30 mL), and Amberlite-N$_3$ (12.83 g). The reaction was stirred at room temperature for 18 h. The reaction went to completion as monitored by TLC. The reaction mixture was filtered, then dried over MgSO$_4$,

filtered again and concentrated. The product was obtained as a clear oil (1.356 g, 7.165 mmol, 98.64%). R_f: 0.57 (SiO$_2$, hexanes/ethyl acetate, 95/5). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): δ 7.41 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 7.8 Hz, 2H), 4.31 (s, 2H), 1.33 (s, 9H).

Preparation of 1,5-dibutyl (2S)-2-({1-[(4-tert-butylphenyl)methyl]-4-{[(2S)-1,5-dibutoxy-1,5-dioxopentan-2-yl]carbamoyl}-1H-1,2,3-triazol-5-yl}formamido)pentanedioate (4)

To a solution of benzylic azide **3** (94.3 mg, 0.498 mmol) in 2 mL acetonitrile-d_6 was added alkyne **2a** (282.4 mg, 0.4733 mmol). The reaction was heated to 60 °C for 22 h. The reaction mixture was concentrated *in vacuo* and further purified by column chromatography (SiO$_2$, hexanes/ethyl acetate, 8/2). The product was obtained as a clear oil (290.2 mg, 0.3692 mmol, 74.14%). R_f: 0.41 (SiO$_2$, hexanes/ethyl acetate, 8/2). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 11.36 (d, J = 7.3 Hz, 1H), 8.19 (d, J = 8.5 Hz, 1H), 7.32 (s, 4H), 6.12(AB, J = 13.9 Hz, 1H), 6.07 (AB, J = 13.9 Hz, 1H), 4.85 (td, J = 8.0, 5.0 Hz, 1H), 4.71 (td, J = 7.6, 5.4 Hz, 1H), 4.24 − 4.10 (m, 4H), 4.10 − 3.99 (m, 4H), 2.53 − 2.23 (m, 6H), 2.20 - 2.07 (m, 2H), 1.69 − 1.55 (m, 9H), 1.44 − 1.31 (m, 8H), 1.27 (s, 9H), 0.99 − 0.84 (m, 12H). By NOESY NMR: amide H (**k**) at δ 8.19 ppm is in close proximity to benzylic AB protons (**a**), while amide H (**j**) at δ 11.36 ppm is in close proximity to methine H (**e**) at δ 4.71 ppm, see supporting Information (Figure S2). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 172.53 (C=O), 172.51 (C=O), 171.19 (C=O), 170.90 (C=O), 161.41 (C=O), 156.69 (C=O), 151.49 (triazole ring C=C), 138.57 (triazole ring C=C), 132.33 (benzene ring C), 130.48 (benzene ring C), 128.42 (benzene ring CH), 125.73 (benzene ring CH), 65.89 (CH$_2$), 65.53 (CH$_2$), 64.81 (CH$_2$), 64.64 (CH$_2$), 54.12 (CH$_2$), 52.37 (CH), 51.89 (CH), 34.68 (C), 31.37 (CH$_3$ × 3), 30.77 (CH$_2$), 30.71 (CH$_2$), 30.65 (CH$_2$), 30.64 (CH$_2$), 30.48 (CH$_2$), 30.37 (CH$_2$), 27.74 (CH$_2$), 27.33 (CH$_2$), 19.24 (CH$_2$), 19.22 (CH$_2$), 19.16 (CH$_2$ × 2), 13.83 (CH$_3$), 13.80 (CH$_3$), 13.78 (CH$_3$), 13.76 (CH$_3$). IR (neat): 3346 (w, amide N-H), 2961 (s, alkane C-H), 2936 (s, alkane C-H), 2874 (m, alkane C-H), 1739 (s, ester C=O), 1678 (s, amide C=O), 1654 (m, amide C=O), 1582 (m, amide N-H bending), 1552 (s, amide N-H bending), 1180 (s, ester C-O). HRMS (*m/z*): Calcd for C$_{41}$H$_{64}$N$_5$O$_{10}$, 786.4648; found, 786.4618 [M+H]$^+$.

Preparation of PVC-azide[36,42,47]

Purification of PVC
PVC (25.00 g, 400 mmol) was dissolved in THF (250 mL). The solution was precipitated in MeOH (1 L). The precipitates were filtered, dissolved in THF, precipitated in MeOH another two times. The precipitate was then dried over house vaccum for three days.

Preparation of 4.4 mol % PVC-N3 (5)
To a solution of purified PVC (12.03 g, 19.24 mmol) in DMF (120 mL) was slowly added sodium azide (11.95 g, 18.38 mmol). The reaction mixture was stirred at 62 °C for 30 min. After cooling to room temperature, the reaction mixture was filtered to remove insoluble salt. The filtrate was precipitated in 1.2 L of MeOH. The mixture was stirred with a stir bar for 10 mins. The precipitates were filtered and dried under vacuum to remove the majority of MeOH. The precipitated was then dissolved in 120 mL of THF and precipitated in 600 mL of MeOH/water (3/1). Precipitates were filtered, washed with MeOH, then dissolved in 120 mL of THF. The solution was then precipitated in MeOH (900 mL). Precipitates were filtered and dried under vacuum for 3 days. 4.4 mol % PVC-N$_3$ was obtained as a white solid (8.153 g). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): δ 4.77 − 4.54 (br, s), 4.54 − 4.37 (br, s), 4.37 − 4.23 (br, s), 4.22 − 4.13 (br, s), 4.13 − 4.01 (br, s), 2.53 − 2.23 (br, m), 2.23 − 1.92 (br, m), 1.92 − 1.72 (br, m). Elemental analysis: C, 39.23; H, 5.12; N, 3.02.

Preparation of 12.0 mol % PVC-N3 (5')
To a solution of PVC (20.00 g, 32.00 mmol) in DMF (200 mL) was slowly added sodium azide (20.00 g, 30.76 mmol). The reaction mixture was stirred to 62 °C for 2 h. The workup procedure was the same as for the 4.4 mol % PVC sample above. 12.0 mol % PVC-N$_3$ was obtained as a white solid (12.61 g). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): δ 4.68 − 4.53 (br, s), 4.53 − 4.38 (br, s), 4.38

– 4.22 (br, s), 4.22 – 4.12 (br,s), 4.12 – 4.01 (br,s), 2.52 – 2.23 (br, m), 2.23 – 1.95 (br, m), 1.95 – 1.65 (br, m). Elemental analysis: C, 38.69; H, 5.22; N, 8.17.

Preparation of internally plasticized PVC[42]

Preparation of PVC-4.4%-nBu (6a)

To a 50 mL round bottom flask was added PVC-4.4%-N$_3$ **5** (805.2 mg, 12.88 mmol), alkyne **2a** (384.3 mg, 0.6440 mmol), and 3-pentanone (8 mL). The reaction mixture was heated to 90 °C for 48 h. The resulting polymer was purified via precipitation in 100 mL of MeOH three times. The polymer was filtered and dried to give a white solid (750.0 mg). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): δ 11.66 – 11.23 (br, m), 8.42 – 8.16 (br, m), 6.77 – 6.34 (br, m), 4.95 – 4.82 (br, s), 4.82 – 4.67 (br, s), 4.67 – 4.54 (br, m), 4.54 – 4.39 (br, m), 4.36 – 4.24 (br, m), 4.24 – 4.13 (br, m), 4.13 – 4.01 (br, m), 3.90 – 3.62 (br, m), 2.99 – 2.57 (br, m), 2.57 –2.23 (br, m), 2.23-1.73 (br, m), 1.73 – 1.45 (br, m), 1.45 – 1.15 (br, m), 1.00 – 0.74 (br, m). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 172.52 (C=O), 171.03 (C=O), 170.91 (C=O), 161.20 (C=O), 156.55 (C=O), 132.17 (Triazole -C=C-), 65.93 (-CH$_2$-O-), 65.59 (-CH$_2$-O-), 64.84 (-CH$_2$-O-), 64.64 (-CH$_2$-O-), 57.11 - 55.02 (PVC -CH-Cl- and PVC -CH-triazole), 52.43 (-NH-CH-), 52.01 (-NH-CH-), 47.40 - 44.94 (Family of CH$_2$ PVC peaks), 30.75 (CH$_2$), 30.71(CH$_2$), 30.65 (CH$_2$), 30.62 (CH$_2$), 30.49 (CH$_2$), 30.40 (CH$_2$), 27.69 (CH$_2$), 27.31 (CH$_2$), 19.24 (CH$_2$), 19.17 (CH$_2$), 13.87 (CH$_3$), 13.84 (CH$_3$), 13.78 (CH$_3$). IR (NaCl, thin film, cm^{-1}): 3384 (w, amide N-H), 2962 (s, alkane C-H), 2934 (s, alkane C-H), 2873 (m, alkane C-H), 1736 (s, ester C=O), 1677 (s, amide C=O), 1655 (m, amide C=O), 1579 (m, amide N-H bending), 1552 (m, amide N-H bending), 1255 (s, ester C-O), 1199 (s, ester C-O), 615 (m, C-Cl).

Preparation of PVC-12.0%-nBu (6'a)

To a 15 mL round bottom flask was added PVC-12.0%-N$_3$ **5'** (217.5 mg, 3.480 mmol), alkyne **2a** (780.1 mg, 1.307 mmol), and 3-pentanone (3.5 mL). The reaction mixture was heated to 90 °C for 48 h. The resulting polymer was purified via precipitation in 40 mL of MeOH three times. The

polymer was filtered and dried to give a pale yellow solid (297.4 mg). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 11.69 – 11.07 (br, m), 8.59 – 8.10 (br, m), 6.73 – 6.11 (br, m), 4.94 – 4.80 (br, s), 4.80 – 4.66 (br, s), 4.66 – 4.52 (br, m), 4.52 – 4.33 (br, m), 4.33 – 4.24 (br, s), 4.24 – 4.09 (br, m), 4.09 – 3.98 (br, m), 3.89 – 3.50 (br, m), 3.08 – 2.58 (br, m), 2.57 – 2.22 (br, m), 2.22 – 1.81 (br, m), 1.73 – 1.50 (br, m), 1.49 – 1.09 (br, m), 1.04 – 0.70 (br, m). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 172.52 (C=O), 170.98 (C=O), 161.19 (C=O), 156.52 (C=O), 138.62 (Triazole -C=C-), 132.03 (Triazole -C=C-), 65.91 (-CH$_2$-O-), 65.57 (-CH$_2$-O-), 64.82 (-CH$_2$-O-), 64.62 (-CH$_2$-O-), 57.04 - 54.95 (PVC -CH-Cl- and PVC -CH-triazole), 52.43 (-NH-CH-), 52.01 (-NH-CH-), 47.40 - 45.37 (Family of CH$_2$ PVC peaks), 30.75 (CH$_2$), 30.71 (CH$_2$), 30.64 (CH$_2$), 30.62 (CH$_2$), 30.47 (CH$_2$), 30.39 (CH$_2$), 27.69 (CH$_2$), 27.29 (CH$_2$), 19.23 (CH$_2$), 19.16 (CH$_2$), 13.86 (CH$_2$), 13.82 (CH$_3$), 13.77 (CH$_3$). IR (NaCl, thin film, cm^{-1}): 3378 (w, amide N-H), 2961 (s, alkane C-H), 2935 (s, alkane C-H), 2874 (m, alkane C-H), 1737 (s, ester C=O), 1677 (s, amide C=O), 1655 (m, amide C=O), 1579 (m, amide N-H bending), 1551 (s, amide N-H bending), 1259 (s, ester C-O), 1199 (s, ester C-O), 616 (w, C-Cl).

Preparation of PVC-4.4%-nHex (6b)

To a 25 mL round bottom flask was added PVC-4.4%-N$_3$ **5** (1.001 g, 16.02 mmol), alkyne **2b** (1.155 g, 1.629 mmol), and 3-pentanone (8 mL). The reaction mixture was heated to 90 °C for 48 h. The resulting polymer was purified via precipitation in 100 mL of MeOH three times. The polymer was filtered and dried to give a pale yellow solid (902.3 mg). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 11.65 – 11.19 (br, m), 8.53 – 8.15 (br, m), 6.77 – 6.25 (br, m), 4.93 – 4.81 (br, m), 4.81 – 4.66 (br, s), 4.66 – 4.52 (br, m), 4.52 – 4.37 (br, m), 4.37 – 4.22 (br, m), 4.22 – 4.10 (br, m), 4.10 – 4.00 (br, m), 3.90 – 3.60 (br, m), 3.05 – 2.59 (br, m), 2.59 – 2.22 (br, m), 2.22 – 1.78 (br, m), 1.74 – 1.52 (br, m), 1.46 – 1.15 (br, m), 1.03 – 0.71 (br, m). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 172.51 (C=O), 171.03 (C=O), 161.18 (C=O), 156.54 (C=O), 138.69 (Triazole -C=C-), 132.18 (Triazole -C=C-), 66.24 (-CH$_2$-O-), 65.89 (-CH$_2$-O-), 65.14 (-CH$_2$-O-), 64.95 (-CH$_2$-O-), 57.12 - 55.02 (PVC -CH-Cl- and

PVC -CH-triazole), 52.44 (-NH-CH-), 51.99 (-NH-CH-), 47.41 - 44.94 (Family of CH_2 PVC peaks), 31.54 (CH_2), 31.49 (CH_2), 31.46 (CH_2), 30.49 (CH_2), 30.38 (CH_2), 28.68 (CH_2), 28.65 (CH_2), 28.57 (CH_2), 27.74 (CH_2), 27.34 (CH_2), 25.68 (CH_2), 25.58 (CH_2), 22.66 (CH_2), 22.62 (CH_2), 14.15 (CH_3). IR (NaCl, thin film, cm^{-1}): 3383 (w, amide N-H), 2957 (s, alkane C-H), 2931 (s, alkane C-H), 2859 (m, alkane C-H), 1736 (s, ester C=O), 1677 (m, amide C=O), 1654 (m, amide C=O), 1578 (m, amide N-H bending), 1551 (m, amide N-H bending), 1255 (s, ester C-O), 1196 (s, ester C-O), 615 (w, C-Cl).

Preparation of PVC-12.0%-nHex (6′b)

To a 25 mL round bottom flask was added PVC-12.0%-N$_3$ **5′** (399.1 mg, 6.386 mmol), alkyne **2b** (1.701 g, 2.399 mmol), and 3-pentanone (6.4 mL). The reaction mixture was heated to 90 °C for 48 h. The resulting polymer was purified via precipitation in 40 mL of MeOH three times. The polymer was filtered and dried to give a pale yellow solid (824.2 mg). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 11.64 – 11.03 (br, m), 8.56 – 8.09 (br, m), 6.71 – 6.10 (br, m), 4.98 – 4.80 (br, m), 4.80 – 4.65 (br, m), 4.65 – 4.51 (br, m), 4.51 – 4.33 (br, m), 4.33 – 4.22 (br, m), 4.22 – 4.09 (br, m), 4.09 – 3.98 (br, m), 3.87 – 3.41 (br, m), 3.07 – 2.58 (br, m), 2.56 – 2.22 (br, m), 2.22 – 1.81 (br, m), 1.74 – 1.50 (br, m), 1.45 – 1.10 (br, m), 1.03 – 0.71 (br, m). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 172.50 (C=O), 170.99 (C=O), 161.21 (C=O), 156.54 (C=O), 138.51 (Triazole -C=C-), 132.14 (Triazole -C=C-), 66.21 (-CH$_2$-O-), 65.86 (-CH$_2$-O-), 65.25 (-CH$_2$-O-), 65.12 (-CH$_2$-O-), 64.92 (-CH$_2$-O-), 57.07 - 55.00 (PVC -CH-Cl- and PVC -CH-triazole), 52.42 (-NH-CH-), 51.97 (-NH-CH-), 47.41 - 45.38 (Family of CH$_2$ PVC peaks), 31.54 (CH$_2$), 31.52 (CH$_2$), 31.47 (CH$_2$), 31.44 (CH$_2$), 30.47 (CH$_2$), 30.36 (CH$_2$), 28.66 (CH$_2$), 28.63 (CH$_2$), 28.55 (CH$_2$), 27.72 (CH$_2$), 27.30 (CH$_2$), 25.66 (CH$_2$), 25.56 (CH$_2$), 22.63 (CH$_2$), 22.60 (CH$_2$), 14.12 (CH$_3$), 14.10 (CH$_3$). IR (NaCl, thin film, cm^{-1}): 3378 (w, amide N-H), 2957 (s, alkane C-H), 2931 (s, alkane C-H), 2859 (m, alkane C-H), 1737 (s, ester C=O), 1676 (s, amide C=O), 1655 (s, amide C=O), 1579 (s, amide N-H bending), 1551 (s, amide N-H bending), 1255 (s, ester C-O), 1195 (s, ester C-O), 615 (w, C-Cl).

Preparation of PVC-4.4%-2EtHex (6c)

To a 15 mL round bottom flask was added PVC-4.4%-N$_3$ **5** (615.0 mg, 9.840 mmol), alkyne **2c** (1.037 g, 1.263 mmol), and 3-pentanone (10 mL). The reaction mixture was heated to 90 °C for 48 h. The resulting polymer was purified via precipitation in 100 mL of MeOH/hexanes (70/30) three times. The polymer was filtered and dried to give a pale yellow solid (786.9 mg). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 11.65 – 11.15 (br, m), 8.38 – 8.14 (br, m), 6.72 – 6.16 (br, m), 4.93 – 4.83 (br, m), 4.83 – 4.67 (br, s), 4.67 – 4.53 (br, m), 4.53 – 4.37 (br, m), 4.37 – 4.16 (br, m), 4.16 – 4.04 (br, m), 4.04 – 3.89 (br, m), 3.89 – 3.49 (br, m), 3.00 – 2.59 (br, m), 2.59 – 2.23 (br, m), 2.23 – 1.73 (br, m), 1.73 – 1.45 (br, m), 1.45 – 1.07 (br, m), 1.07 – 0.69 (br, m). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 172.53 (C=O), 171.10 (C=O), 170.96 (C=O), 161.13 (C=O), 156.58 (C=O), 138.60 (Triazole -C=C-), 132.16 (Triazole -C=C-), 68.39 (-CH$_2$-O-), 68.02 (-CH$_2$-O-), 67.40 (-CH$_2$-O-), 67.19 (-CH$_2$-O-), 57.11 - 55.02 (PVC -CH-Cl- and PVC -CH-triazole), 52.46 (-NH-CH-), 52.01 (-NH-CH-), 47.41 - 44.94 (Family of CH$_2$ PVC peaks), 38.80 (CH), 38.75 (CH), 30.54 (CH$_2$), 30.45 (CH$_2$), 30.41 (CH$_2$), 30.36 (CH$_2$), 29.03 (CH$_2$), 28.99 (CH$_2$), 27.75 (CH$_2$), 27.42 (CH$_2$), 23.86 (CH$_2$), 23.84 (CH$_2$), 23.81 (CH$_2$), 23.09 (CH$_2$), 23.08 (CH$_2$), 23.05 (CH$_2$), 23.04 (CH$_2$), 14.21 (CH$_3$), 14.19 (CH$_3$), 11.11 (CH$_3$), 11.09 (CH$_3$), 11.07 (CH$_3$). IR (neat): 3382 (w, amide N-H), 2960 (s, alkane C-H), 2930 (s, alkane C-H), 2873 (m, alkane C-H), 2861 (s, alkane C-H), 1736 (s, ester C=O), 1677 (s, amide C=O), 1655 (m, amide C=O), 1578 (m, amide N-H bending), 1551 (m, amide N-H bending), 1256 (s, ester C-O), 1199 (s, ester C-O), 615 (w, C-Cl).

Preparation of PVC-12.0%-2EtHex (6′c)

To a 15 mL round bottom flask was added PVC-12.0%-N$_3$ (**5′**) (198.3 mg, 3.173 mmol), alkyne **2c** (987.2 mg, 1.202 mmol), and 3-pentanone (3.2 mL). The reaction mixture was heated to 90 °C for 48 h. The resulting polymer was purified via precipitation in 100 mL of MeOH/hexanes (70/30) three times. The polymer was filtered and dried to give a pale yellow solid (115.8 mg). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 11.69 – 11.16 (br, m), 8.54 – 8.11 (br, m), 6.75 – 6.08 (br, m),

4.98 – 4.83 (br, m), 4.83 – 4.68 (br, s), 4.68 – 4.52 (br, m), 4.52 – 4.33 (br, m), 4.33 – 4.19 (br, m), 4.19 – 4.04 (br, m), 4.04 – 3.86 (br, m), 3.86 – 3.44 (br, m), 3.00 – 2.60 (br, m), 2.60 – 2.23 (br, m), 2.23 – 1.77 (br, m), 1.71 – 1.46 (br, m), 1.46 – 1.07 (br, m), 1.06 – 0.66 (br, m). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 172.53 (C=O), 170.98 (C=O), 161.18 (C=O), 156.57 (C=O), 138.68 (Triazole -C=C-), 132.19 (Triazole -C=C-), 68.37 (-CH$_2$-O-), 68.01 (-CH$_2$-O-), 67.38 (-CH$_2$-O-), 67.17 (-CH$_2$-O-), 57.05 - 55.00 (PVC -CH-Cl- and PVC -CH-triazole), 52.45 (-NH-CH-), 52.00 (-NH-CH-), 47.42 – 45.42 (Family of CH$_2$ PVC peaks), 38.80 (CH), 30.45 (CH$_2$), 30.41 (CH$_2$), 29.02 (CH$_2$), 28.99 (CH$_2$), 27.75 (CH$_2$), 27.40 (CH$_2$), 23.86 (CH$_2$), 23.84 (CH$_2$), 23.07 (CH$_2$), 23.05 (CH$_2$), 14.18 (CH$_3$), 11.08 (CH$_3$), 11.05 (CH$_3$). IR (neat): 3379 (w, amide N-H), 2960 (s, alkane C-H), 2931 (s, alkane C-H), 2873 (m, alkane C-H), 2861 (s, alkane C-H), 1737 (s, ester C=O), 1677 (s, amide C=O), 1655 (s, amide C=O), 1579 (s, amide N-H bending), 1551 (s, amide N-H bending), 1259 (s, ester C-O) , 1198 (s, ester C-O), 616 (w, C-Cl).

Preparation of PVC-4.4%-nDec (6d)

To a 50 mL round bottom flask was added PVC-4.4%-N$_3$ **5** (1.024 g, 16.38 mmol), alkyne **2d** (1.912 g, 2.048 mmol), and 3-pentanone (8 mL). The reaction mixture was heated to 90 °C for 48 h. The resulting polymer was purified via precipitation in 100 mL of MeOH/hexanes (70/30) three times. The polymer was filtered and dried to give a pale yellow solid (1.207 g). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 11.54 – 11.21 (br, m), 8.42 – 8.14 (br, m), 6.70 – 6.25 (br, m), 4.95 – 4.81 (br, m), 4.81 – 4.67 (br, m), 4.67 – 4.53 (br, m), 4.53 – 4.37 (br, m), 4.37 – 4.22 (br, m), 4.22 – 4.10 (br, m), 4.10 – 3.89 (br, m), 3.89 – 3.43 (br, m), 3.17 – 2.60 (br, m), 2.60 – 2.23 (br, m), 2.23 – 1.80 (br, m), 1.80 – 1.48 (br, m), 1.48 – 1.06 (br, m), 1.04 – 0.71 (br, m). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 172.48 (C=O), 171.03 (C=O), 170.91 (C=O), 161.13 (C=O), 156.54 (C=O), 138.51 (Triazole -C=C-), 132.13 (Triazole -C=C-), 66.23 (-CH$_2$-O-), 65.88 (-CH$_2$-O-), 65.12 (-CH$_2$-O-), 64.93 (-CH$_2$-O-), 57.11 - 55.01 (PVC -CH-Cl- and PVC -CH-triazole), 52.41 (-NH-CH-), 51.96 (-NH-CH-), 47.38 - 44.93 (Family of CH$_2$ PVC peaks),

31.99 (CH$_2$), 30.46 (CH$_2$), 30.35 (CH$_2$), 29.67 (CH$_2$), 29.65 (CH$_2$), 29.63 (CH$_2$), 29.59 (CH$_2$), 29.41 (CH$_2$), 29.37 (CH$_2$), 29.34 (CH$_2$), 29.30 (CH$_2$), 28.72 (CH$_2$), 28.68 (CH$_2$), 28.60 (CH$_2$), 27.73 (CH$_2$), 27.31 (CH$_2$), 26.00 (CH$_2$), 25.90 (CH$_2$), 22.79 (CH$_2$), 14.25 (CH$_3$). IR (neat): 3381 (w, amide N-H), 2954 (s, alkane C-H), 2926 (s, alkane C-H), 2855 (m, alkane C-H), 1737 (s, ester C=O), 1677 (m, amide C=O), 1657 (m, amide C=O), 1580 (m, amide N-H bending), 1551 (m, amide N-H bending), 1255 (s, ester C-O) , 1199 (s, ester C-O), 616 (w, C-Cl).

Preparation of PVC-12.0%-nDec (6'd)

To a 50 mL round bottom flask was added PVC-12.0%-N$_3$ (**5'**) (919.1 mg, 14.71 mmol), alkyne **2d** (5.100 g, 5.464 mmol), and 3-pentanone (14.7 mL). The reaction mixture was heated to 90 °C for 48 h. The resulting polymer was purified via precipitation in 100 mL of MeOH/hexanes (70/30) three times. The polymer was filtered and dried to give a pale yellow solid (1.489 g). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 11.63 – 11.05 (br, m), 8.57 – 8.06 (br, m), 6.83 – 6.07 (br, m), 4.97 – 4.80 (br, s), 4.80 – 4.66 (br, s), 4.66 – 4.52 (br, s), 4.52 – 4.33 (br, m), 4.33 – 4.23 (br, s), 4.23 – 4.08 (br, m), 4.08 – 3.86 (br, s), 3.86 – 3.34 (br, m), 3.16 – 2.59 (br, m), 2.59 – 2.21 (br, m), 2.21 – 1.83 (br, m), 1.81 – 1.50 (br, m), 1.50 – 1.03 (br, m), 1.03 – 0.60 (br, m). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 172.48 (C=O), 170.97 (C=O), 161.15 (C=O), 156.55 (C=O), 138.57 (Triazole -C=C-), 132.03 (Triazole -C=C-), 66.21 (-CH$_2$-O-), 65.87 (-CH$_2$-O-), 65.12 (-CH$_2$-O-), 64.93 (-CH$_2$-O-), 57.02 - 54.99 (PVC -CH-Cl- and PVC -CH-triazole), 52.42 (-NH-CH-), 51.96 (-NH-CH-), 47.42 - 45.41 (Family of CH$_2$ PVC peaks), 32.01 (CH$_2$), 30.46 (CH$_2$), 30.35 (CH$_2$), 29.67 (CH$_2$), 29.65 (CH$_2$), 29.61 (CH$_2$), 29.42 (CH$_2$), 29.38 (CH$_2$), 29.35 (CH$_2$), 29.31 (CH$_2$), 28.73 (CH$_2$), 28.70 (CH$_2$), 28.62 (CH$_2$), 27.75 (CH$_2$), 27.32 (CH$_2$), 26.01 (CH$_2$), 25.92 (CH$_2$), 22.80 (CH$_2$), 14.24 (CH$_3$). IR (neat): 3379 (w, amide N-H), 2955 (s, alkane C-H), 2926 (s, alkane C-H), 2855 (m, alkane C-H), 1739 (s, ester C=O), 1676 (s, amide C=O), 1655 (m, amide C=O), 1579 (m, amide N-H bending), 1551 (s, amide N-H bending), 1259 (s, ester C-O) , 1198 (s, ester C-O), 616 (w, C-Cl).

Preparation of PVC-4.4%-TEGMe (6e)

To a 50 mL round bottom flask was added PVC-4.4%-N$_3$ (**5**) (1.064 g, 17.02 mmol), alkyne **2e** (2.036 g, 2.127 mmol), and 3-pentanone (17 mL). The reaction mixture was heated to 90 °C for 48 h. The resulting polymer was purified via precipitation in 100 mL of MeOH four times. The polymer was filtered and dried to give a pale yellow solid (1.159 g). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 11.71 – 11.14 (br, m), 8.44 – 8.19 (br, m), 6.70 – 6.29 (br, m), 4.98 – 4.82 (br, s), 4.82 – 4.67 (br, s), 4.67 – 4.52 (br, m), 4.52 – 4.37 (br, m), 4.37 – 4.09 (br, m), 3.85 – 3.58 (br, m), 3.58 – 3.45 (br, m), 3.36 (s), 2.95 – 2.61 (br, m), 2.61 – 2.46 (br, m), 2.46 – 2.22 (br, m), 2.22 – 1.68 (br, m). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 172.47 (C=O), 172.37 (C=O), 170.95 (C=O), 170.77 (C=O), 162.32 (C=O), 161.19 (C=O), 156.53 (C=O), 138.63 (Triazole -C=C-), 132.02 (Triazole -C=C-), 72.54 (-CH$_2$-O-), 72.00 (-CH$_2$-O-), 71.95 (-CH$_2$-O-), 70.70 (-CH$_2$-O-), 70.67 (-CH$_2$-O-), 70.63 (-CH$_2$-O-), 69.13 (-CH$_2$-O-), 69.09 (-CH$_2$-O-), 68.87 (-CH$_2$-O-), 64.88 (-CH$_2$-O-), 64.60 (-CH$_2$-O-), 63.97 (-CH$_2$-O-), 63.80 (-CH$_2$-O-), 61.81 (-CH$_2$-O-), 59.11 (CH$_3$), 57.10 - 55.00 (PVC -CH-Cl- and PVC -CH-triazole), 52.31 (-NH-CH-), 51.92 (-NH-CH-), 47.36 - 44.90 (Family of CH$_2$ PVC peaks), 30.17 (CH$_2$), 27.35 (CH$_2$), 27.06 (CH$_2$). IR (neat): 3380 (w, amide N-H), 2911 (s, alkane C-H), 2877 (s, alkane C-H), 1739 (s, ester C=O), 1676 (s, amide C=O), 1653 (m, amide C=O), 1579 (m, amide N-H bending), 1552 (s, amide N-H bending), 1254 (s, ester C-O), 1199 (s, ester C-O), 1105 (s, ether C-O), 615 (w, C-Cl).

Preparation of PVC-12.0%-TEGMe (6'e)

To a 25 mL round bottom flask was added PVC-12.0%-N$_3$ **5'** (285.1 mg, 4.562 mmol), alkyne **2e** (1.642 g, 1.716 mmol), and 3-pentanone (4.6 mL). The reaction mixture was heated to 90 °C for 48 h. The resulting polymer was purified via precipitation in 40 ml of MeOH 4 times. The polymer was filtered and dried to give a pale yellow solid (550.8 mg). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 11.71 – 11.13 (br, s), 8.59 – 8.20 (br, s), 6.70 – 6.13 (br, m), 5.02 – 4.81 (br, s), 4.81 – 4.67 (br, s), 4.67 – 4.51 (br, m), 4.51 – 4.09 (br, m), 3.92 – 3.55 (br, m), 3.57 – 3.43 (br, m), 3.42 – 3.27 (br, s), 2.95 – 2.42 (br, m), 2.44 – 1.70 (br,

m). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 172.49 (C=O), 170.96 (C=O), 161.37 (C=O), 156.54 (C=O), 132.10 (Triazole -C=C-), 72.58 (-CH$_2$-O-), 72.04 (-CH$_2$-O-), 70.70 (-CH$_2$-O-), 70.66 (-CH$_2$-O-), 69.12 (-CH$_2$-O-), 68.88 (-CH$_2$-O-), 64.89 (-CH$_2$-O-), 64.62 (-CH$_2$-O-), 63.99 (-CH$_2$-O-), 63.82 (-CH$_2$-O-), 61.86 (-CH$_2$-O-), 59.14 (CH$_3$), 57.10 - 56.00 (PVC -CH-Cl- and PVC -CH-triazole), 51.93 (-NH-CH-), 47.39 - 45.81 (Family of CH$_2$ PVC peaks), 30.18 (CH$_2$), 27.10 (CH$_2$). IR (neat): 3334 (m, amide N-H), 2881 (s, alkane C-H), 1736 (s, ester C=O), 1676 (s, amide C=O), 1542 (m, amide N-H bending), 1254 (s, ester C-O), 1199 (s, ester C-O), 1108 (s, ether C-O), 612 (w, C-Cl).

Preparation of PVC-4.4%-TEGBu (6f)

To a 50 mL round bottom flask was added PVC-4.4%-N$_3$ (**5**) (1.008 g, 16.13 mmol), alkyne **2f** (2.270 g, 2.017 mmol), and 3-pentanone (15 mL). The reaction mixture was heated to 90 °C for 72 h. The resulting polymer was purified via precipitation in 100 mL of MeOH four times. The polymer was filtered and dried to give a pale yellow solid (974.5 mg). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 11.53-11.04 (br, s), 8.44 – 8.19 (br, s), 6.68-6.62 (br, m), 4.99 – 4.82 (br, s), 4.82 – 4.68 (br, s), 4.66 – 4.52 (br, m), 4.52 – 4.36 (br, m), 4.38 – 4.06 (br, m), 3.87 – 3.65 (br, m), 3.66 – 3.59 (br, m), 3.60 – 3.52 (br, m), 3.44 (t, *J* = 6.7 Hz), 2.97 – 2.62 (br, m), 2.62 – 2.47 (br, m), 2.48 – 2.22 (br, m), 2.22 – 1.81 (br, m), 1.61 – 1.48 (br, m), 1.44 – 1.29 (br, m), 0.90 (t, *J* = 7.4 Hz). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 172.49 (C=O), 170.94 (C=O), 161.57 (C=O), 156.55 (C=O), 138.67 (Triazole -C=C-), 71.30 (-CH$_2$-O-), 70.78 (-CH$_2$-O-), 70.71 (-CH$_2$-O-), 70.66 (-CH$_2$-O-), 70.16 (-CH$_2$-O-), 69.13 (-CH$_2$-O-), 68.90 (-CH$_2$-O-), 64.92 (-CH$_2$-O-), 64.62 (-CH$_2$-O-), 64.01 (-CH$_2$-O-), 63.84 (-CH$_2$-O-), 57.11 - 55.01 (PVC -CH-Cl- and PVC -CH-triazole), 52.35 (-NH-CH-), 51.94 (-NH-CH-), 47.38 - 44.93 (Family of CH$_2$ PVC peaks), 31.82 (CH$_2$), 30.18 (CH$_2$), 27.02 (CH$_2$), 19.39 (CH$_2$), 14.07 (CH$_3$). IR (neat): 3326 (m, amide N-H), 2958 (s, alkane C-H), 2934 (s, alkane C-H), 2872 (s, alkane C-H), 1739 (s, ester C=O), 1672 (s, amide C=O), 1536 (s, amide N-H bending), 1254 (s, ester C-O), 1195 (s, ester C-O), 1119 (s, ether C-O), 615 (w, C-Cl).

Preparation of PVC-12.0%-TEGBu (6'f)

To a 25 mL round bottom flask was added PVC-12.0%-N_3 (**5'**) (294.0 mg, 4.704 mmol), alkyne **2f** (2.008 g, 1.784 mmol), and 3-pentanone (4.7 mL). The reaction mixture was heated to 90 °C for 48 h. The resulting polymer was purified via precipitation in 40 mL of MeOH four times. The polymer was filtered and dried to give a pale yellow solid (513.2 mg). ^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 11.52 – 11.09 (br, s), 8.58 – 8.16 (br, s), 6.51 (br, m), 5.03 – 4.82 (br, s), 4.82 – 4.68 (br, s), 4.68 – 4.53 (br, m), 4.53 – 4.05 (br, m), 3.86 – 3.51 (br, s), 3.45 (s), 2.95 – 2.61 (br, m), 2.61 – 2.42 (br, m), 2.42 – 2.24 (br, m), 2.24 – 1.77 (br, m), 1.72 – 1.46 (br, m), 1.46 – 1.23 (br, m), 1.09 – 0.72 (br, m). ^{13}C NMR (126 MHz, CDCl$_3$, δ, ppm): 172.46 (C=O), 170.93 (C=O), 170.76 (C=O), 161.33 (C=O), 161.13 (C=O), 156.60 (C=O), 139.68 (Triazole -C=C-), 138.62 (Triazole -C=C-), 77.41 (-CH$_2$-O-), 77.16 (-CH$_2$-O-), 76.91 (-CH$_2$-O-), 71.28 (-CH$_2$-O-), 70.77 (-CH$_2$-O-), 70.72 (-CH$_2$-O-), 70.70 (-CH$_2$-O-), 70.66 (-CH$_2$-O-), 70.15 (-CH$_2$-O-), 69.11 (-CH$_2$-O-), 68.88 (-CH$_2$-O-), 64.89 (-CH$_2$-O-), 64.60 (-CH$_2$-O-), 63.81 (-CH$_2$-O-), 61.72 (-CH$_2$-O-), 57.08 - 54.98 (PVC -CH-Cl- and PVC -CH-triazole), 52.31 (-NH-CH-), 51.91 (-NH-CH-), 47.37 - 44.92 (Family of CH$_2$ PVC peaks), 31.81 (CH$_2$), 30.17 (CH$_2$), 27.41 (CH$_2$), 27.06 (CH$_2$), 19.38 (CH$_2$), 14.05 (CH$_3$). IR (neat): 3380 (m, amide N-H), 2957 (s, alkane C-H), 2933 (s, alkane C-H), 2871 (s, alkane C-H), 1739 (s, ester C=O), 1677 (s, amide C=O), 1653 (m, amide C=O), 1579 (m, amide N-H bending), 1552 (s, amide N-H bending), 1254 (s, ester C-O), 1195 (s, ester C-O), 1116 (s, ether C-O), 614 (w, C-Cl).

RESULTS AND DISCUSSION

The first example of an electron poor alkyne, **2a,** bearing four *n*-butyl esters, was prepared in two steps (Scheme 1). Glutamate ester **1a** was synthesized by reaction of L-glutamic acid with *n*-butanol via Fischer esterification.[43] Esterification and amidation of acetylenedicarboxylic acid can be particularly difficult, due to competing Michael addition, especially when employing traditional coupling agents. For example, use of the conventional reagent DCC results only in an undesired intramolecular Michael addition to form the 1,3,5-trisubstituted hydantoin.[48,49] Heyl and Fessner developed the coupling reagent DMTMM (4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride), which allows direct amidification of acetylenedicarboxylic acid with amines.[44] DMTMM in NMP as solvent was used to achieve synthesis of the acetylenediamide **2a** with amine **1a** in 82% yield.
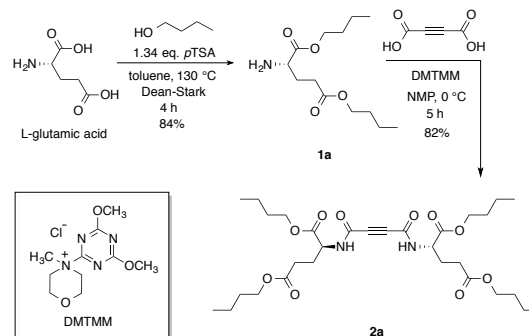

SCHEME 1 Synthesis of acetylenediamide tetraester **2a** based on glutamic acid as a branched linker

In order to test the thermal reactivity of the alkyne diamide **2a** with an organoazide prior to applying the cycloaddition to azidized PVC, a small model molecule, benzylic azide **3** was synthesized from 1-bromomethyl-4-*tert*-butylbenzene using Amberlite IRA-400 ion-exchange resin pre-charged with aqueous NaN$_3$.[46] Reaction of alkyne **2a** with the model azide **3** gave triazole **4** as a well-defined molecule in 74% yield (Scheme 2).
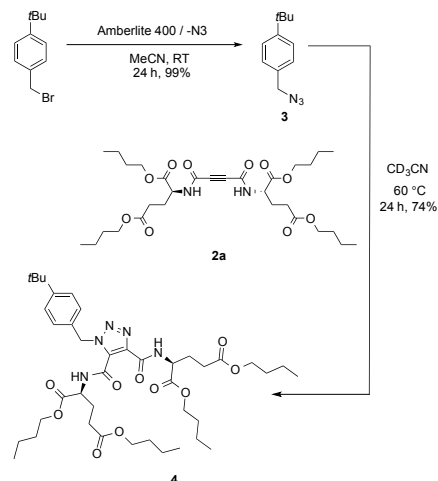
SCHEME 2 Model reaction: cycloaddition of small molecule azide with acetylenediamide tetraester **2a**.

A series of glutamate ester diamide alkynes **2b-f** bearing a variety of terminal ester groups were synthesized using analogus reactions to that of **2a** (Scheme 3). PVC-azide (4.4% azide **5** and 12.0% azide **5'**) was prepared using NaN$_3$ in an S$_N$2 displacement of chlorine atoms on PVC in DMF. Thermal azide-alkyne dipolar cycloaddition was then carried out to form the triazole attachments bearing tetraesters at 90 °C, to give PVC functionalized at 4% of the original chlorine sites (polymer **6a-f**), and at 12% (polymers **6'a-f**).
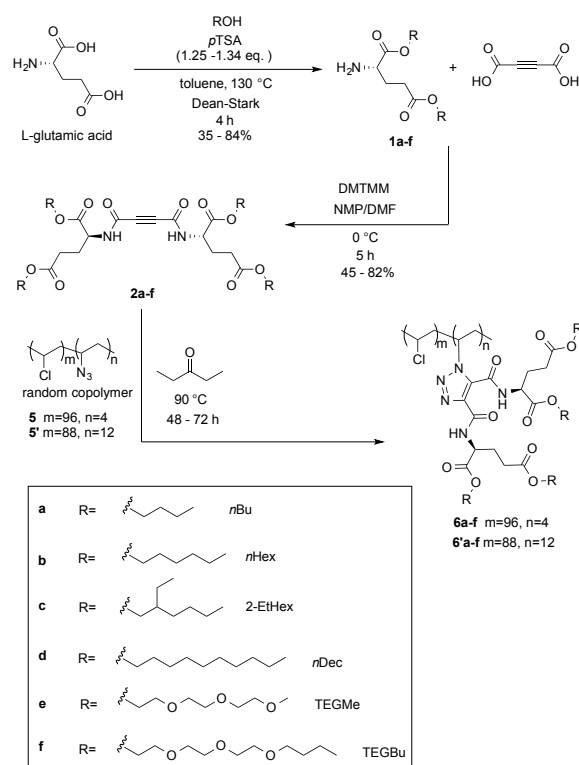
SCHEME 3 Preparation of tetraester alkynes and introduction to PVC via azide/alkyne cycloaddition.

IR spectroscopy was effective at evaluating triazole formation on the polymer by monitoring the disappearance of the azide peak at 2114 cm^{-1} (Figure 2a). Comparison of the IR spectra of diglutamate ester functionalized PVC **6'a** and small molecule triazole **4** (Figures 2b and 2c) revealed very similar peaks. For both the model

compound **4** and the diglutamate ester triazole functionalized PVC **6'a**, the broad amide N-H stretch was found near 3350 cm^{-1}. Similarly, the ester C=O stretch was seen at 1737 cm^{-1} for functionalized PVC **6'a** and at 1739 cm^{-1} for model **4**. The amide C=O stretch and N-H bend were observed for both the internally plasticized PVC **6'a** and model **4** at 1677 and 1678 cm^{-1} (amide C=O stretching, amide I band) and at 1551 and 1552 cm^{-1} (amide NH bending, amide II band), respectively.

Internally plasticized 12% *n*Bu tetraester PVC **6'a** was further characterized by comparing the ^{1}H NMR spectrum of the polymer **6'a** to spectra of PVC-12%-azide **5'** and model triazole **4** (Figure 3). Comparing the ^{1}H NMR spectra of PVC-12%-azide **5'** (Figure 3a) with that of polymer **6'a** (Figure 3b), it is clear that both feature protons from the PVC backbone: CH-Cl methane protons of the PVC backbone have a chemical shift of δ 4.7-4.2 ppm; -CH$_2$- methylene protons from the PVC have a chemical shift of δ 2.5-1.6 ppm. Peaks from the tetraester triazole polymer **6'a** were corelated to model triazole **4**. For both, there are two types of amide proton peaks, appearing at δ 11.3 and 8.3 ppm. Conjugation of the carbonyl amides to the triazole aromatic group[50] results in downfield shifts of the amide protons. The differences between the ^{1}H chemical shifts of the two amides likely arises from intramolecular H-bonding[51] of the more downfield amide proton **j** at δ 11.3 ppm. The proton peaks of **6'a** at δ 1.6, 1.4, and 0.9 (labeled **g**, **h**, and **i** in Figure 3c) ppm come from the *n*-butyl chains of the diglutamate tetraester. Likewise, the ^{13}C NMR spectra of **6'a** and **4** clearly corroborate the attachment of the triazole tetraester (see supporting information, Figure S1).

The thermal properties of diglutamate tetraester functionalized PVC samples were measured using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The DSC data show specific heat capacities and heat flow during the second heating cycle for both 4 and 12 mol % samples (Figure 4). For PVC bearing 12 mol % internal plasticizer, the T$_g$ values of the alkyl

esters are all higher than those of the PEG esters,

longer alkyl ester chains result in lower T_g values
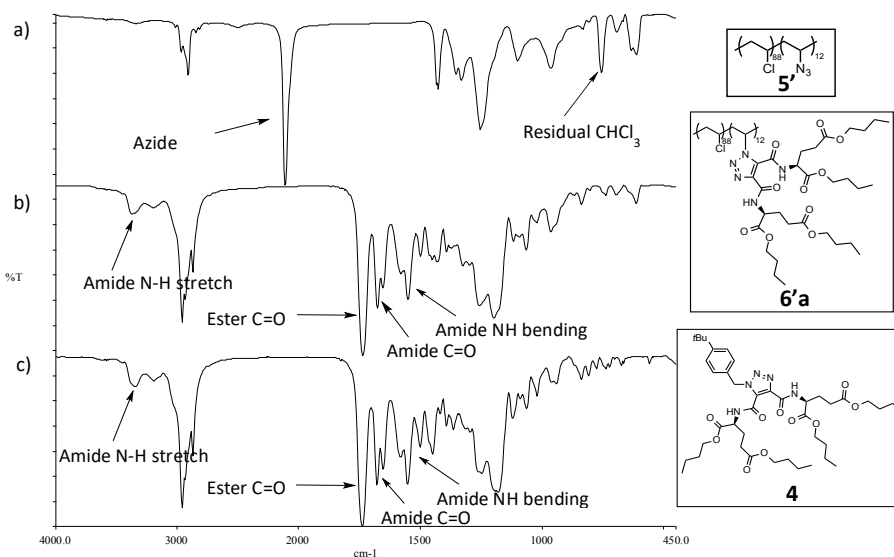
even though the *n*Dec and TEGMe esters are exactly the same length. Within the alkyl esters,

than shorter chains. Adding an *n*-butyl group at the end of the PEG ester in place of the methyl

FIGURE 2 IR spectra comparing a) PVC-12%-azide **5'**, b) PVC-12%-*n*Bu **6'a**, and c) model triazole **4**

FIGURE 3 ^{1}H NMR spectra (in CDCl$_3$) of a) PVC-12%-N$_3$ **5'**, b) PVC-12%-*n*Bu **6'a**, and c) model compound **4** Note: in spectrum c), peak **a** is an AB quartet.

group at the end of the PEG ester makes very little difference, giving only a slight depression of the T_g value at 12% substitution. Collected T_g values of the second heating cycle are given in Table 1. More extensive T_g data indicating the first heating and cooling cycles, and the more significant second heating cycle are available in

Table S1 in the Supporting Information. The lowest T_g value obtained is -1 °C for the tetra(TEGBu) ester diglutamate triazole functionalized PVC, indicating excellent internal plasticization.

TGA was performed in order to evaluate the stability of these functionalized polymers (Figure
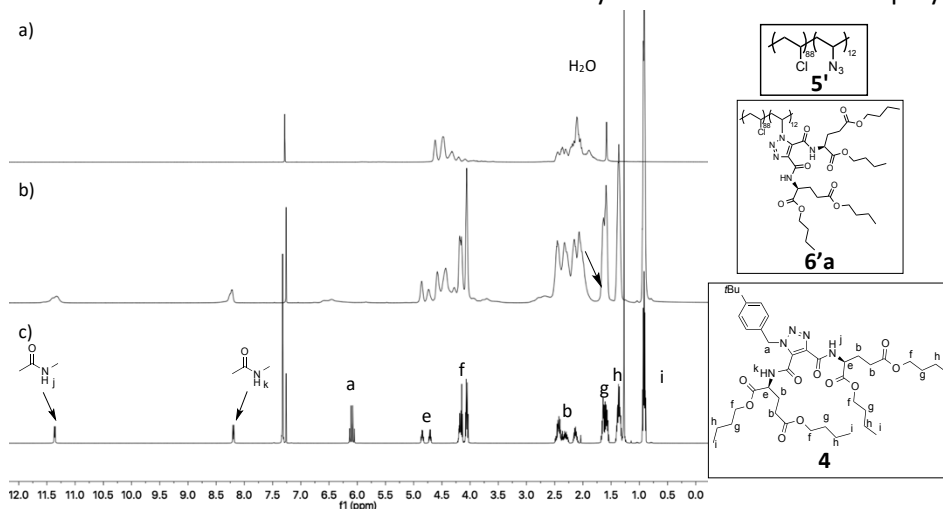
5, Table 2). For the alkyl chain tetraester diglutamates, the sample weight stays relatively unchanged until an onset temperature is reached. For most of the polymers tested, this onset temperature is greater than 200 °C, and is directly correlated with the alkyl ester chain length. Focusing on the 12 mol % polymers, a successive increase in decomposition onset temperatures is observed from *n*Bu to *n*Hex to *n*Dec diglutamate functionalized PVC. The decomposition onset temperature are higher for the 12 mol % substituted series compared to the 4 mol % polymers. Compared to pure PVC, the decomposition onset temperatures of the alkyl

6a 4% *n*Bu	62	**6'a** 12% *n*Bu	41
6b 4% *n*Hex	53	**6'b** 12% *n*Hex	28
6c 4% 2EtHex	47	**6'c** 12% 2EtHex	21
6d 4% *n*Dec	39	**6'd** 12% *n*Dec	18
6e 4% TEGMe	40	**6'e** 12% TEGMe	3
6f 4% TEGBu	41	**6'f** 12% TEGBu	-1

[a] T_g is from the 2nd heating cycle

tetraester diglutamate functionalized PVC samples are similar, suggesting that this type of internal plasticizer is relatively stable, even under significant thermal stress. Examining the triethylene glycol ester diglutamate esters (TEGMe and TEGBu), the sample weights decrease at moderate temperatures, starting at approximately 150 °C. The observed temperatures of thermal decomposition for the triethylene glycol esters are consistent with previous reports of typical poly(ethylene glycol) thermal degradation.[52-54] The slope of the initial decrease is small, followed by a sharper decline. This suggests that the polyethers initially undergo a slow decomposition process under thermal stress before undergoing rapid decomposition at higher temperatures. TGA data measured under nitrogen show higher
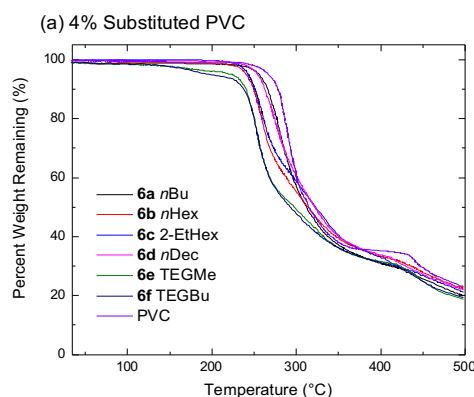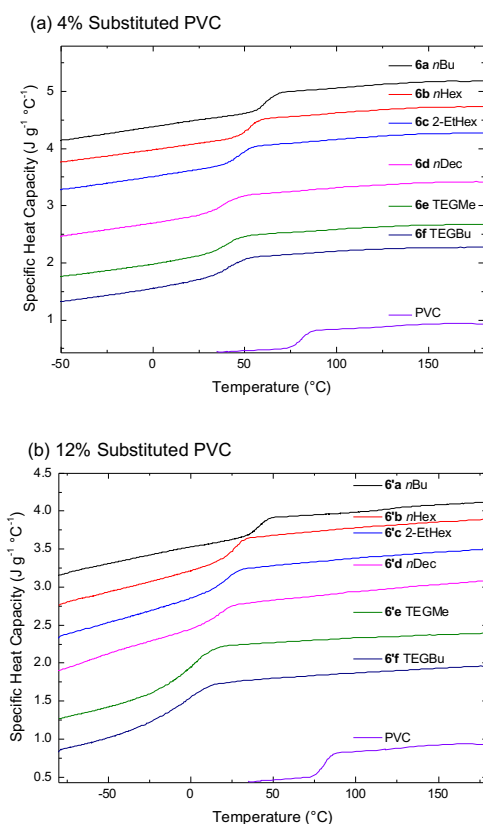
(a) 4% Substituted PVC

(b) 12% Substituted PVC

FIGURE 4 DSC (2nd heat cycle) of internally plasticized PVC

TABLE 1 DSC T_g values for PVC bearing 4 mol % and 12 mol % glutamic ester-derived branched internal plasticizers

Polymer	T_g (°C)[a]	Polymer	T_g (°C)[a]
PVC	81		

(a) 4% Substituted PVC

(b) 12% Substituted PVC

Legend:
- 6'a nBu
- 6'b nHex
- 6'c 2-EtHex
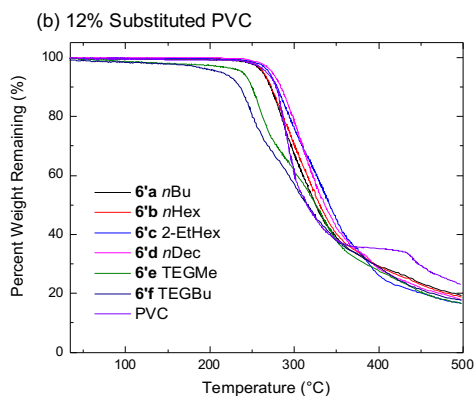- 6'd nDec
- 6'e TEGMe
- 6'f TEGBu
- PVC

FIGURE 5 TGA data (open to air) illustrating percent weight remaining versus temperature for functionalized and unfunctionalized PVC

**TABLE 2** TGA temperatures at 5% weight loss

Polymer	T_5 (°C)[a]	Polymer	T_5 (°C)[a]
PVC	267		
6a 4% nBu	256	**6'a** 12% nBu	262
6b 4% nHex	240	**6'b** 12% nHex	263
6c 4% 2EtHex	243	**6'c** 12% 2EtHex	270
6d 4% nDec	254	**6'd** 12% nDec	274
6e 4% TEGMe	224	**6'e** 12% TEGMe	239
6f 4% TEGBu	197	**6'f** 12% TEGBu	214

[a] T_5 = temperature at 5% weight loss, TGA measured open to air

onset temperatures in comparison with data measured under air; otherwise, no significant differences were observed (see Supporting Information).

To examine the effect of doubling the density of ester plasticizing moieties using this branched linker, a comparison with TEGMe dieaters plasticizers **7** and **7'** from previous work in the Braslau lab[42] is useful (Scheme 4). For 4 mol % PVC samples, the T_g value of diester **7** = 61 °C, whereas for the tetraester **6e** the T_g = 40 °C. Even more pronounced, for the more densely substituted PVC sample **7'**, the diester plasticizer showed a T_g = 42 °C compared to the tetraester **6'e** at T_g = 3 °C. Thus doubling the number of

esters from two to four for each triazole linkage gives significantly enhanced plasticization. However, the diesters was synthesized in only two steps: one step less compared to the synthesis of the diglutamate tetraesters functionalized PVC samples **6e** and **6'e** in this work.

	T_g(°C)		T_g(°C)
4%	**7** 61	**6e** 40
12%	**7'** 42	**6'e** 3

7 m=96, n=4
7' m=88, n=12

6e m=96, n=4
6'e m=88, n=12
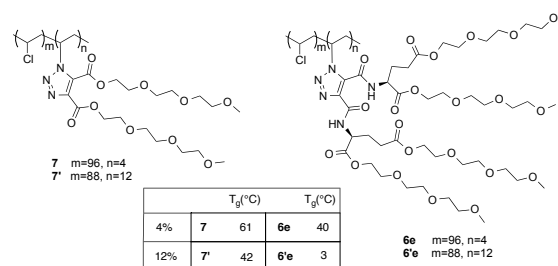
SCHEME 4 Comparison of glass transition temperatures between previous TEGMe diesters and branched TEGMe tetraesters.

(a) T_g as a Function of wt% Plasticizer

Legend:
- DEHP-PVC Standard
- 4% Substituted PVC
- 12% Substituted PVC
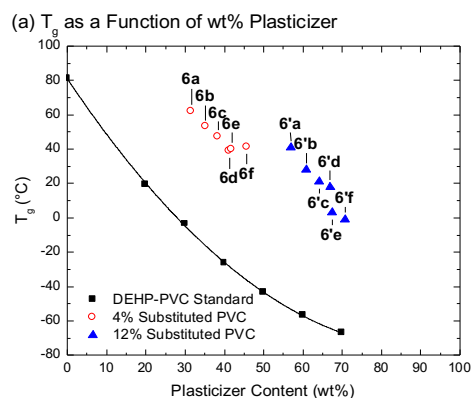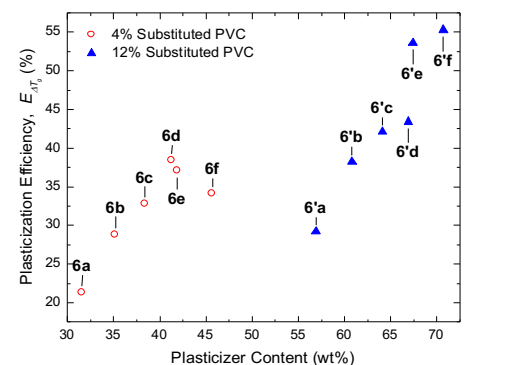
(b) Plasticization Efficiency as a Function of wt% Plasticizer

Legend:
- 4% Substituted PVC
- 12% Substituted PVC

FIGURE 6 a) Plot of T_g versus Plasticizer Content of DEHP-PVC Standard, 4% Substituted PVC **6a-f**, and 12% Substituted PVC **6'a-6'f**, b) Plot of

Plasticization Efficiency of 4% Substituted PVC **6a-f** and 12% Substituted PVC **6'a-6'f**

In order to evaluate the efficacy of plasticization, the T_g values of these branched internally plasticized PVC samples were compared to that of externally plasticized DEHP-PVC[42] as a function of plasticizer content by weight percent (Figure 6a). The trend shows that use of traditional DEHP plasticizer is more effective than internal plasticization. Among the internally plasticized samples, the T_g values are correlated with the degree of PVC substitution, and T_g values below 0 °C can be achieved by 12% TEGBu substituted PVC. Plasticization efficiency[42,55] increases with increasing plasticizer weight percent. There is also a subtle dependence of plasticization efficiencies on the ester functional group: polyether esters lead to higher plasticization efficiency than alkyl esters at a similar plasticizer weight percent (**6'd** = nDec, 66.9 wt% of plasticizer, T_g = 18 °C; **6'e** = TEGMe, 67.4 wt% of plasticizer, T_g = 3 °C). Also, 4% TEGBu substituted PVC **6f** gives a higher plasticization efficiency (34%) than 12% nBu substituted PVC **6'a** (29%), thus the use of polyethers overrides the lower degree of substitution on PVC. Although DEHP-PVC is more effective as a plasticizer, but the migratory issue makes the traditional phthalate approach less satisfactory considering the durability of the PVC products and the health issues ensuing from phthalate contamination.

CONCLUSIONS

Internal plasticization of PVC bearing triazoles with branched glutamic acid linkers displaying four ester groups per triazole has been investigated. A facile 3-step synthesis involving Fischer esterification, DMTMM amide coupling, and thermal 3+2 azide/alkyne cycloaddition was employed. By varying the ester substituents and examining the effects on the glass transition temperatures, longer length substituents correlate with lower T_g values for both alkyl and triethylene glycol esters. Polyether esters are more effective at depressing the T_g values compared to alkyl esters. In summary, by TGA

the triethylene glycol esters degrade at lower temperatures than the alkyl esters. In summary, non-migratory plasticization was successfully achieved, with impressive T_g values and plasticizing efficiencies greater than 50% for tetra(polyether) esters at 12% substitution of the chlorine atoms on the PVC chain.

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