### Title

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### Authors

Earla, Aruna
Li, Longbo
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# Phthalate Plasticizers Covalently Linked to PVC *via* Copper-Free or Copper Catalyzed Azide-Alkyne Cycloadditions

Aruna Earla,[a] Longbo Li,[a] Philip Costanzo,[b] and Rebecca Braslau*,[a]

[a] Department of Chemistry and Biochemistry, University of California, Santa Cruz, CA 95064, USA

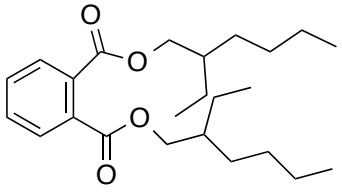
[b] Department of Chemistry and Biochemistry, California Polytechnic State University, San Luis Obispo, CA 93407, USA

ABSTRACT: Plasticization of PVC was carried out by covalently linking phthalate derivatives via copper-free (thermal) or copper catalyzed azide-alkyne cycloadditions. Di(2-ethylhexyl) phthalate derivatives (DEHP-ether and DEHP-ester) were synthesized and appended to PVC at two different densities. The glass transition temperatures of the modified PVC decreased with increasing content of plasticizer. PVC-DEHP-ether gave lower glass transition temperatures than PVC-DEHP-ester, reflecting the enhanced flexibility of the ether versus ester linker.

Keywords: Internal Plasticizer; Phthalate Diester; Huisgen azide-alkyne cycloaddition

## 1. Introduction

Polyvinyl chloride (PVC) is one of the most widely used and economically important thermoplastics. Global annual consumption in 2012 for PVC was 37.4 million tons, and is expected to continue to grow [1]. Pure PVC is a rigid, brittle solid requiring a large amount of plasticizer to obtain flexibility and moldability. The most common plasticizer class currently in use are phthalate esters, accounting for 70% of the global plasticizer demand in 2014 [2], with the (2-ethylhexyl) phthalate diester DEHP **1 (Fig. 1)** being the most popular. However, the adverse developmental [3,4], reproductive [5,6], neurological [7] and immune [8] health effects of many phthalates has led to a search for alternative plasticizers.



**1**

Di(2-ethylhexyl) phthalate (DEHP)

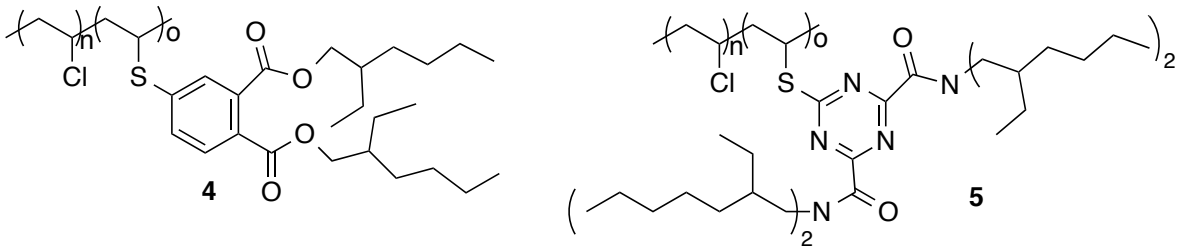
**Fig. 1. Structure of the Most Common Phthalate Plasticizer: DEHP**

Other common small molecule plasticizers include terphthalates, 1,2-cyclohexane-dicarboxylic acid di*iso*nonyl ester (Hexamoll® DINCH®), epoxidized vegetable oils, citrates, mellitates, adipates, benzoates, maleates, succinates, sebacates, phosphates, *iso*sorbide esters. Because these plasticizers are not covalently linked to PVC, they can migrate within the material and leach out when the plastic comes into contact with air [9], liquid [10-17]or some absorbent solid materials [18-20]. Some polymeric plasticizers such as poly(ε-caprolactone), poly(butylene adipate), and poly(epichlorohydrin) are also utilized. The most effective approach to avoid migration of plasticizer from the PVC matrix is to covalently attach the plasticizer to the polymer. Historically, the first example of internal plasticization of PVC was the work of Michel et al [21] using nucleophilic substitution of the chlorine atoms with 2-ethylhexyl esters of *o*-mercaptobenzoic acid **2** and thioglycolic acid **3** (**Fig. 2**). The glass transition temperatures decreased as the degree of substitution increased. The plasticizing power of the thioglycolic ester is greater than that of the ethylhexyl ester of *o*-mercaptobenzoic acid. Likewise, Reinecke et al [22]. demonstrated the internal plasticization of PVC, initially via thiolate nucleophilic substitution of some of the chlorine atoms with two phthalate-based thiol derivatives: di(2-ethylhexyl) 5-mercaptophthalate (DEHP-SH) **4** and di(2-ethylhexyl) 5-mercaptoisophthalate (*iso*DEHP-

SH). The degree of functionalization obtained was 23 mol% for DEHP-SH and 30 mol% for *iso*DEHP-SH. This group has expanded this chemistry to include a variety of aromatic and heteroaromatic sulfides [23,24] bearing esters, amides, ureas, urethanes, sulfonate esters and sulfornamides, often bearing 2-ethylhexyl groups or Jeffamines to give impressive low $T_g$ values at 20% or 40% weight sulfide.

**Sulfide, Thiolester Linked Internal Plasticizers:**


Michel's 1986 Sulfide and Thiolester

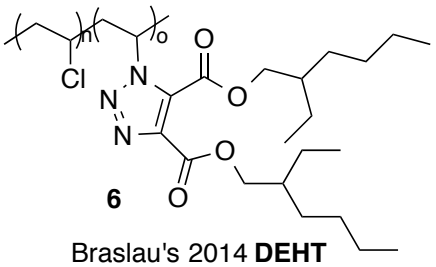



examples of Reinecke's Aromatic and Heteroaromatic Sulfides

**Fig. 2. Internal Plasticizers Prepared by Sulfur Nucleophile Displacement of Chloride on PVC**

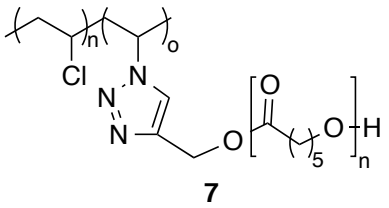
Aromatic sulfides such as PVC-DEHP-SH **4** and substituted triazine sulfides **5** show good plasticization, zero migration and no elimination, a high loading (typically 40%) of the plasticizer is required to lower the $T_g$ to desirable temperatures. The longterm stability of these aryl and heteroaryl sulfide derivatives is a concern; oxidation products are expected as the material ages in air; elimination becomes a possibility. Cycloadditions of azides and alkynes in a (3+2) fashion to form triazoles [25,26] have become widely popular due to both the chemoselectivity and mild reaction conditions. Inspired by the structural similarity between phthalate esters and 4,5-diester 1,2,3-triazoles, we recently demonstrated the covalent attachment of the phthalate mimics using thermal Huisgen cycloaddition of PVC-azide with electron-poor di(2-ethylhexyl) acetylenedicarboxylate [27].

**Triazole Linked Internal Plasticizers:**



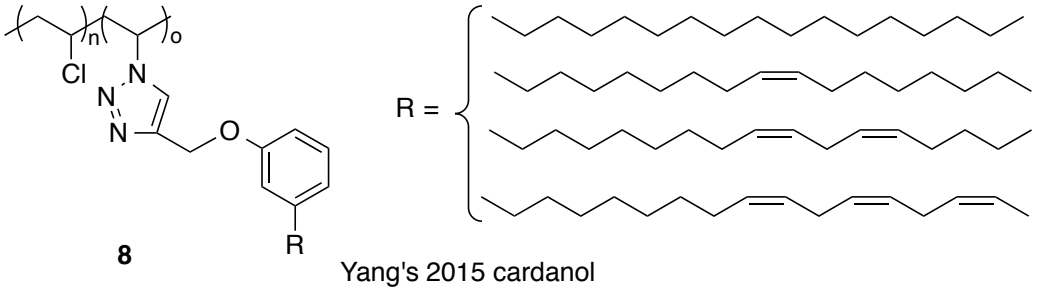
**6**

Braslau's 2014 **DEHT**
Di(2-ethylhexyl)-1H-triazole-4,5-dicarboxylate



**7**

Tasdelen's 2015 **PCL** polycaprolactone



**8**

Yang's 2015 cardanol

**Fig. 3. Internal Plasticizers by Azide Displacement of Chloride on PVC followed by Triazole Formation**

Experimental values for the glass transition temperatures ($T_g$) of pure PVC, 15% displacement of chlorine by azide (15% PVC-Azide), and 15% plasticized PVC bearing 2-ethylhexyl triazole diester (15% PVC-DEHT) **6** were 83 °C, 76 °C, and 65 °C, respectively, indicating plasticization by the phthalate mimic (**Fig. 3**). However, the $T_g$ of 15% PVC-DEHT is way too high for most commercial applications. This only moderate reduction in $T_g$ may be due to the restricted rotation of the plasticizer mimic attached directly to the PVC polymer chain. A flexible linker between the triazole ring and the plasticizer would provide additional degrees of rotation. Following our triazole phthalate plasticizer mimic publication, similar triazole cycloadditions to form internally plasticized PVC have been published. Recently, Tasdelen et al [28] synthesized graft copolymers by photoinduced copper-mediated azide-alkyne cycloaddition (CuAAC) of alkyne terminated poly(ε-caprolactone) (PCL) and PVC-azide. The single $T_g$ = 76 °C for PVC-g-PCL **7** indicates that PCL is miscible with PVC, but imparts little plasticization. Yang et al [29] carried out covalent modification of PVC by CuAAC of PVC-azide with an alkyne tethered to naturally abundant cardanol. The modified polymer PVC-cardanol **8** exhibited a decreased $T_g$ = 51 °C, thermal stability and no migration. Herein are reported phthalate (2-ethylhexyl) diesters covalently linked to PVC by two different rotationally flexible tethers. These internal plasticizers are attached either by using mild, copper-free thermal Huisgen cycloaddition, or by copper-catalyzed azide-alkyne cycloadditions. Specifically, phthalate diesters bearing a terminal alkyne were designed with either an ester or ether linkage, with triazole formation as the chemoselective attachment strategy, to form PVC-DEHP-ether **9** and PVC-DEHP-ester **10** (**Fig. 4**). The synthesis of phthalate-based terminal alkynes DEHP-ether and DEHP-ester and their covalent attachment to PVC, and the resulting plasticization as reflected by the $T_g$ values of the resulting materials is described.

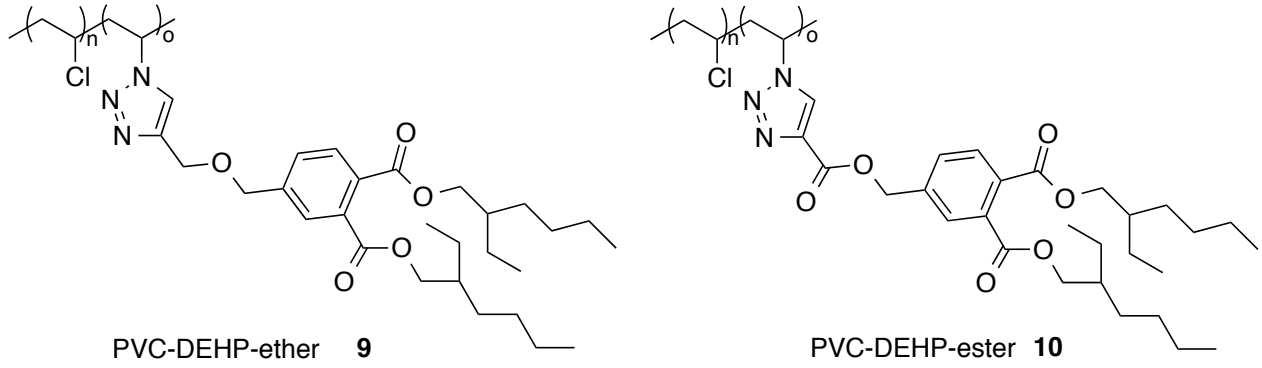
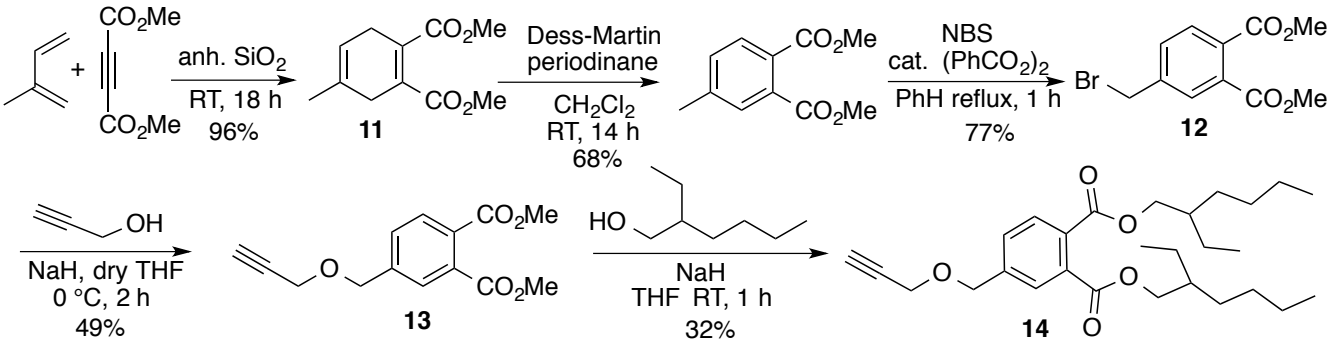


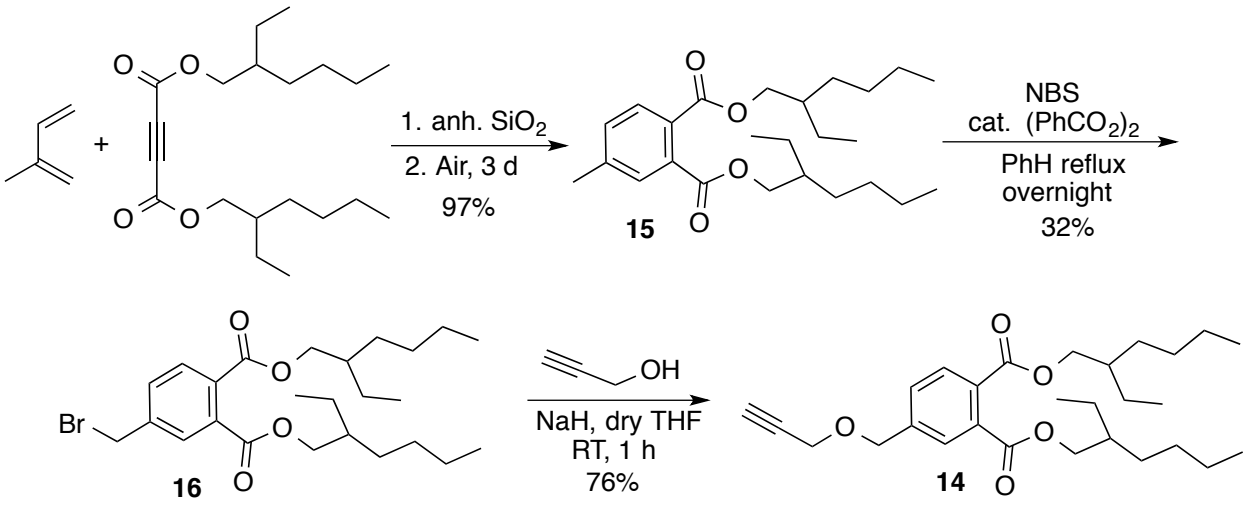

**Fig. 4. Internally Plasticized PVC-DEHP Derivatives 9 and 10 with Flexible Tethers**

## 2. Results and discussion

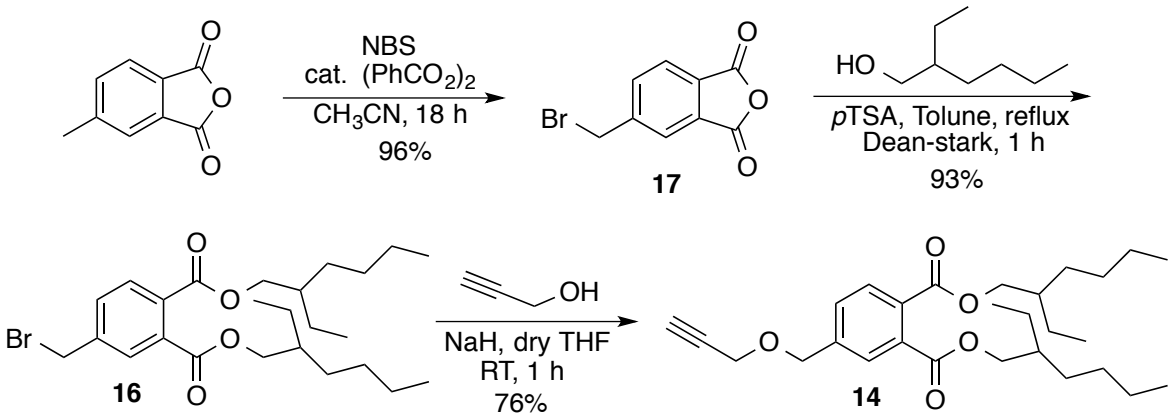
For the preparation of DEHP-ether, three synthetic routes were explored. The first approach (**Scheme 1**) involved Diels-Alder reaction of isoprene and dimethylacetylene dicarboxylate catalyzed by anhydrous silica gel [30] to give cyclohexadiene dicarboxylate **11** in 96% yield. Oxidation using Dess-Martin periodinane gave dimethyl-4-methylphthalate in 68% yield. Benzylic bromination using *N*-bromosuccinimide (NBS) and catalytic benzoyl peroxide in refluxing benzene for 1h afforded dimethyl-4-bromomethylphthalate **12** in 77% yield. Williamson ether synthesis of benzyl bromide **12** with propargyl alcohol in the presence of sodium hydride gave the respective ether **13** in 49% yield. Transesterification with deprotonated 2-ethylhexanol afforded the key terminal alkyne DEHP ether **14** in 32%.




**Scheme 1. First Diels-Alder Route to DEHP-ether 14**

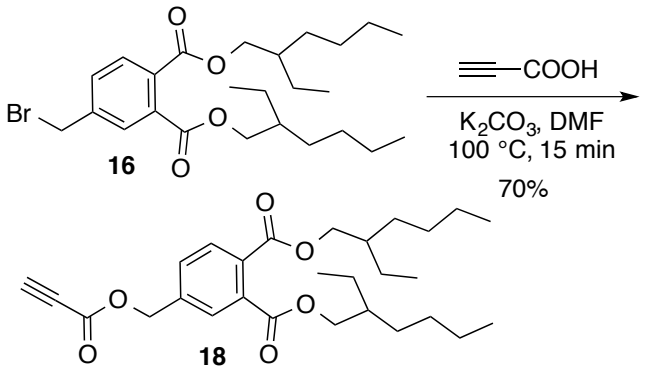



**Scheme 2. Second, More Convergent Diels-Alder Route to DEHP-ether 14**



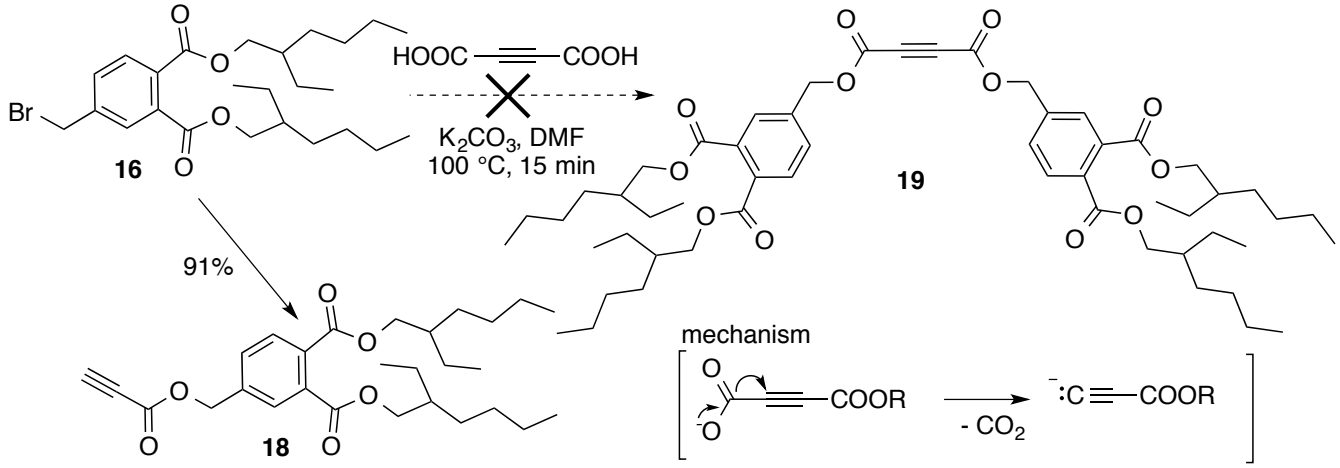

**Scheme 3. 4-Methylphthalic Anhydride Route to DEHP-ether 14**

In the second, more convergent approach (**Scheme 2**), Diels-Alder reaction of di(2-ethylhexyl) acetylene dicarboxylate and isoprene was carried out in the presence of activated anhydrous silica gel [30] to give di(2-ethylhexyl) 4-methylphthalate **15** in 97% yield. Benzylic bromination using NBS and catalytic benzoyl peroxide gave di(2-ethylhexyl) 4-(bromomethyl)-phthalate **16** in 32% yield. The $S_N2$ reaction with sodium propargylate afforded ether **14** in 76% yield. The third and the most efficient method to synthesize propargyl ether **14** started with commercially available 4-methylphthalic anhydride (**Scheme 3**). Switching to refluxing acetonitrile, bromination using NBS gave the benzylic bromide **17** in 96% yield. Esterification with 2-ethylhexanol using catalytic *p*-toluenesulfonic acid in toluene and azeotropic removal of water gave the diester **16** in 93% yield, followed by etherification to **14** in 76% yield, with an overall yield of 68% yield over the three steps. Di(2-ethylhexyl) 4-(bromomethyl) phthalate **16** served as a precursor to a second phthalate derivative with an ester linkage: DEHP-ester **18**. Benzylic bromide **16** was treated with propiolic acid and potassium carbonate in dimethylformamide for 15 minutes at 100 °C. The terminal alkyne DEHP-ester **18** was obtained in 70% yield after purification by silica gel column chromatography (**Scheme 4**).



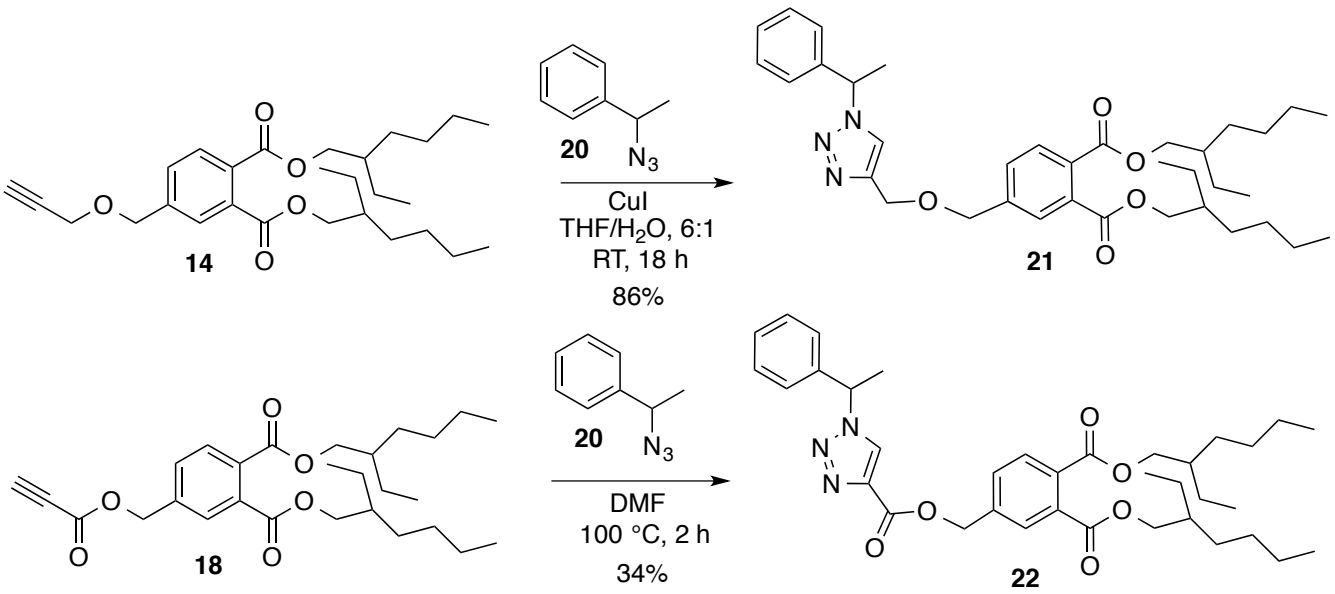

**Scheme 4. Synthesis of DEHP-ester 18**

An attempt to prepare the symmetrical DEHP-diester **19** by the reaction of benzylic bromide **16** with acetylenedicarboxylic acid under similar conditions was not successful (**Scheme 5**). Instead, monodecarboxylation ensued under the basic conditions, to form the stabilized acetylenic anion. Upon acidic workup, DEHP-ester **18** was unexpectedly obtained.

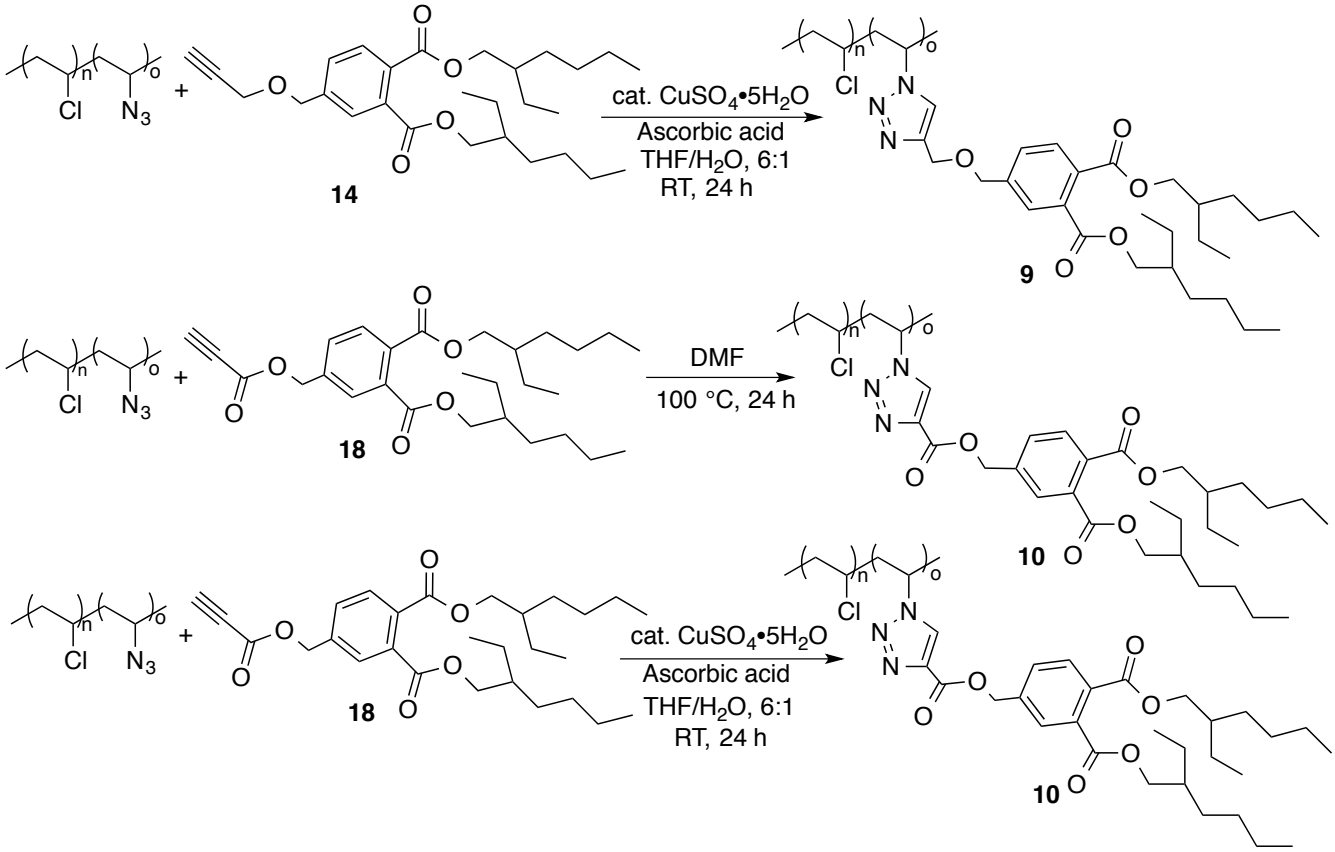



**Scheme 5. Attempted Synthesis of Phthalate Derivative DEHP-Diester 19**

Synthetic modification of commercial PVC results in polydisperse products, which are not amenable to easy characterization by $^1$H NMR, $^{13}$C NMR, or mass spectroscopy. Therefore, (1-azidoethyl) benzene [27] was investigated as a model compound to confirm the viability of azide/alkyne cycloaddition reactions with these newly synthesized phthalate derivatives. For the unactivated ether derivative **14**, copper catalyzed cycloaddition was utilized at room temperature to form the triazole **21**. Thus cycloaddition of DEHP-ether **14** with benzyl azide **20** using catalytic copper iodide in a 6:1 mixture of tetrahydrofuran and water produced triazole **21** in 86% yield (**Scheme 6**). The disappearance of the terminal alkyne peak at 2120 cm$^{-1}$ and the azide peak at 2116 cm$^{-1}$ followed by the appearance of a peak at 1547 cm$^{-1}$ is indicative of the formation of the triazole. In the $^1$H NMR spectrum, the benzylic proton of (1-azidoethyl) benzene shifted from δ 4.58 to δ 5.81 ppm in the triazole. The thermal Huisgen reaction is facilitated by electron poor substituents on the alkyne, which lower the alkyne HOMO. Using the electron-poor ester substituted alkyne, DEHP-ester **18** underwent thermal 1,3-dipolar cycloaddition with (1-azidoethyl) in benzene at 100 °C for 2 hours to give triazole **22** isolated in 34% yield as a single regioisomer.




**Scheme 6. Model Reactions: Copper Catalyzed and Thermal Huisgen Cycloadditions of Terminal Alkyne DEHP Derivatives with a Small Molecule Azide**




**Scheme 7. Attachment of DEHP-ether and DEHP-ester to Form Internally Plasticized PVC Triazoles with Ether 9 and Ester 10 Tethers**

These two complimentary conditions were then applied to modify PVC. Azide functional groups were incorporated into PVC by nucleophilic substitution of some of the chlorines [27]. PVC with 5% or 15% substituted

azide was used in the cycloaddition reactions with phthalates tethered to terminal alkynes. The degree of azidation was determined by elemental analysis. The cycloaddition of PVC-azide with DEHP-ether **14** using copper iodide in 6:1 mixture of tetrahydrofuran and water gave a blue colored solid polymer after precipitation in methanol. To avoid coloration of the PVC, the copper iodide was replaced by copper sulfate/ascorbic acid to catalyze the cycloaddition of PVC-azide with DEHP-ether **14**. The reaction was carried out for 24 hours at room temperature, resulting in the PVC bearing the ether-tethered phthalate **9** as a white solid after precipitation in methanol (**Scheme 7**)**.** Thermal cycloaddition of DEHP-ester **18** with the small molecule model (1-azidoethyl) benzene (**Scheme 6**) in dimethylformamide at 100 °C went to completion in 2 h. However, under these same thermal conditions, the reaction of 15% PVC-azide (with a six-fold excess of terminal alkyne **18** per azide) required 24 hours. Alternatively, the same PVC triazole **10** was obtained in 24 hours at room temperature when copper sulfate/ascorbic acid was used with only 1.5 equivalent of alkyne **18** per azide (**Scheme 8**). The conversion of azides into triazoles pendant to the PVC was conveniently monitored by FTIR spectroscopy (**Fig. 5**). The shrinking of the diagnostic azide band at 2100-2000 $cm^{-1}$, with concomitant appearance of the ester C=O band at 1725-1635 $cm^{-1}$ and the C-N band at 1550-1500 $cm^{-1}$ is indicative of the formation of the triazoles tethered to phthalate esters. The glass transition temperatures of unmodified PVC, 5% and 15% PVC-azide and the covalently plasticized PVC samples were determined by using differential Scanning Calorimetry (DSC) and compared with non-covalent mixtures of 5% PVC-DEHP and 15% PVC-DEHP. To obtain the non-covalent PVC-phthalate samples, a mixture of PVC (purified by the method of Rusen [31]) with either 5 wt% DEHP or 15 wt% DEHP was mechanically stirred at 120 °C for 4 h. The extent of $T_g$ reduction in the presence of plasticizer is used as a parameter to assess the plasticizing efficiency. For each run, the calorimeter was equilibrated at 20 °C with a temperature ramp of 20 °C/min to 150 °C and then held at isothermal conditions at 150 °C for 5 minutes before ending cycle 1. The sample was then cooled to 50 °C at a rate of 10 °C/min and held at 50 °C under isothermal conditions to end cycle 2. For cycle 3, the sample was heated at a rate of 10 °C/min to 150 °C. The first cycle of heating is carried out to erase the pre-existing thermal history of the polymer. Mechanical and thermal properties of a polymer are affected by a number of variables such as chemical composition and molecular weight, as well as thermally induced phenomena such as crystallization and physical aging, all of which contribute to the microstructure [32]. The covalent modification of PVC-DEHT, PVC-DEHP-ether, PVC-DEHP-ester, and formation of the non-covalent DEHP samples were carried out under different reaction conditions, imparting different thermal histories to the polymer samples. Thus by heating and rapid cooling each of the PVC samples during cycles 1 and 2 of the DSC analysis, the thermal histories are erased. As shown in **Table 1**, for most samples, two $T_g$ values were obtained in cycle 1, reflecting several polymeric regimes.

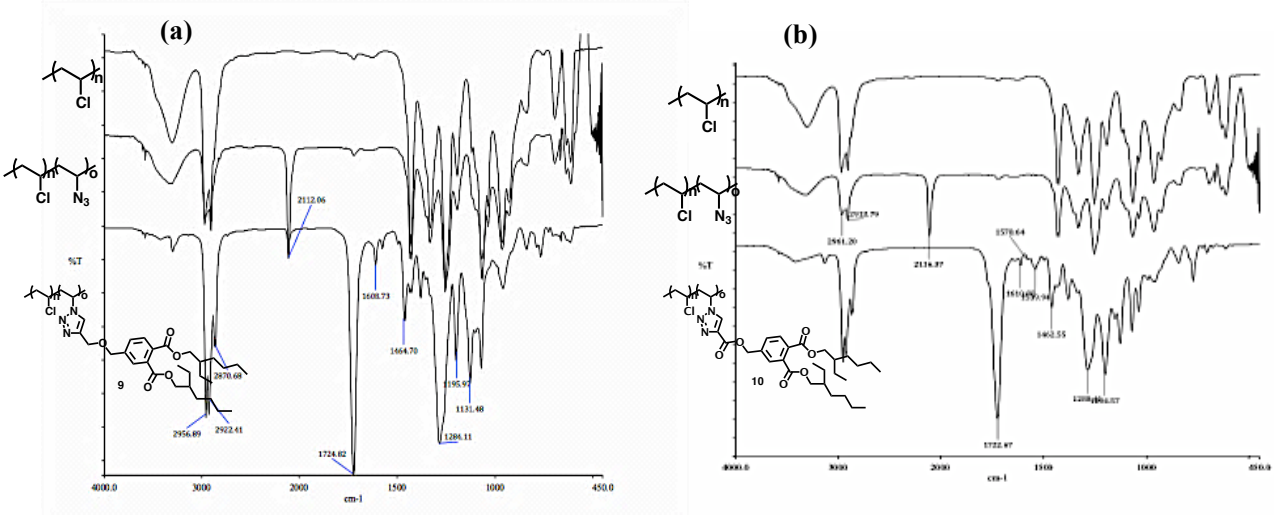



**Fig. 5. Stacked FTIR Spectra: (a) PVC, 15% PVC-Azide, and 15% PVC-DEHP-ether Triazole (b) PVC, 15% PVC-Azide, and 15% PVC-Azide-ester Triazole prepared by CuAAC**

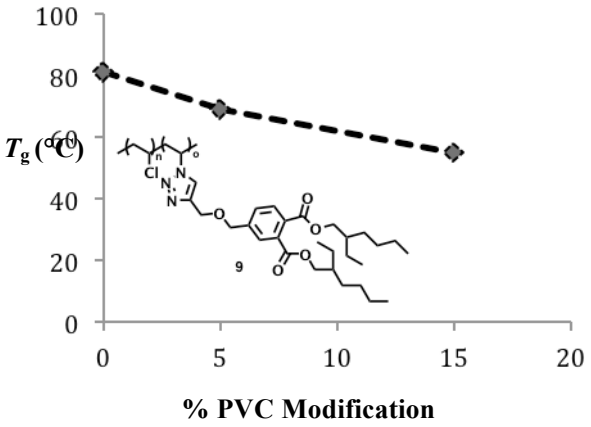
**Table 1. Glass Transition Temperatures from Cycles 1 and 3 by DSC**

The polydispersity index of the commercial PVC used in these experiments is 1.95, reflecting a realistic approach to internal plasticization on non-homogeneous PVC samples. One can envision that

| Sample | $T_g$ (°C) | | |
|---|---|---|---|
| | Cycle 1 | | Cycle 3 |
| | $T_{g1}$ | $T_{g2}$ | $T_g$ |
| PVC (purified following Rusen's procedure)[29] | 83 | | 82 |
| 5% PVC-Azide | 84 | | 84 |
| 15% PVC-Azide | 60 | 75 | 75 |
| 5% PVC-DEHT **6** | 61 | | 61 |
| 15% PVC-DEHT **6** | 64 | | 65 |
| 5% PVC-DEHP-ether **9** | 45 | 68 | 69 |
| 15% PVC-DEHP-ether **9** | 58 | | 55 |
| 5% PVC-DEHP-ester **10** (Cu cat.) | 58 | 71 | 69 |
| 15% PVC-DEHP-ester **10** (Cu cat.) | 59 | 83 | 60 |
| 5% PVC-DEHP-ester **10** (thermal) | 67 | 79 | 77 |
| 15% PVC-DEHP-ester **10** (thermal) | 31 | 61 | 60 |
| 5% PVC-DEHP conventional non-covalent mixture | 87 | | 74 |
| 15%PVC-DEHP conventional non-covalent mixture | 83 | | 75 |

low molecular weight PVC chains might undergo azidation faster than the high molecular weight polymers, and certainly different triads of stereoisomers are expected to show different reactivities to azide substitution within the PVC samples, giving rise to multiple $T_g$s. An examination of the DSC thermograms of these internally plasticized PVC samples indicates that the $T_g$ values decrease with increasing substitution of the chlorine atoms in PVC with azide and subsequently with tethered DEHP derivatives. **Fig. 6** clearly illustrates this trend: increasing the load of these phthalate derivatives is reflected in enhanced plasticization. The nucleophilic substitution of 15% of the chlorine atoms of PVC with simple azide decreases the glass transition temperature of the polymer from 82 °C to 75 °C. The $T_g$s were further reduced to 69 °C and 55 °C for 5% and 15% PVC-DEHP-ether **9**, respectively (Figure 5). For 5% and 15% PVC-DEPH-ester **10**, the $T_g$s were observed at 69 °C and 60 °C, respectively (Figure 4). In the case of PVC-DEHT **8**, the glass transition temperature *increased* from 61 °C for 5% PVC-DEHT to 65 °C for 15% PVC-DEHT. It is possible that direct attachment of aromatic DEHT to the polymer chain imparts some crystallinity to the otherwise flexible PVC backbone, thus increasing the $T_g$s with increasing triazole substitution.

As described by Millán [33], certain regions of PVC undergo nucleophilic substitution more readily than others. These regions are associated with tacticity-specific microstructure within PVC. For the nucleophile sodium benzenethiolate [34,35] at up to 20% substitution, $T_g$ is related to preferential substitution at the mmr triad of isotactic sequences and the rmr triad located at the end of syndiotactic sequences. During the early stages of nucleophilic substitution, the TGTG or the GTTG conformation of the mmr isotactic tetrads are converted into nucleophile-substituted tetrads with a highly rigid TTTT conformation, thus increasing the glass transition temperature of PVC. When the mmr isotactic tetrads are depleted, the less reactive rrm syndiotactic tetrads then take part in nucleophilic substitution. This results in the shortening of the syndiotactic sequences, exchanging them for sequences of reduced rigidity, and thus decreasing the glass transition temperature. At conversions higher than 20%, neither mmr nor rrm triads are associated with isotactic or syndiotactic sequences. Therefore no significant change in the tacticity-induced microstructure is expected, and the results of variation of $T_g$ are due to the progressive substitution for chlorine atoms by the nucleophile. The stereochemical structure of



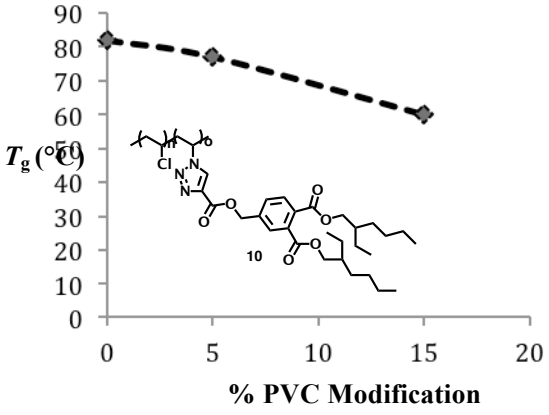



**Fig. 6. Variation of Glass Transition Temperatures of PVC-DEHP-ether 9 and PVC-DEHP-ester 10 with Increasing Internal Plasticizer Content (note: the dashed line is provided as an aid to the eye. It does not represent a fit of the data.)**

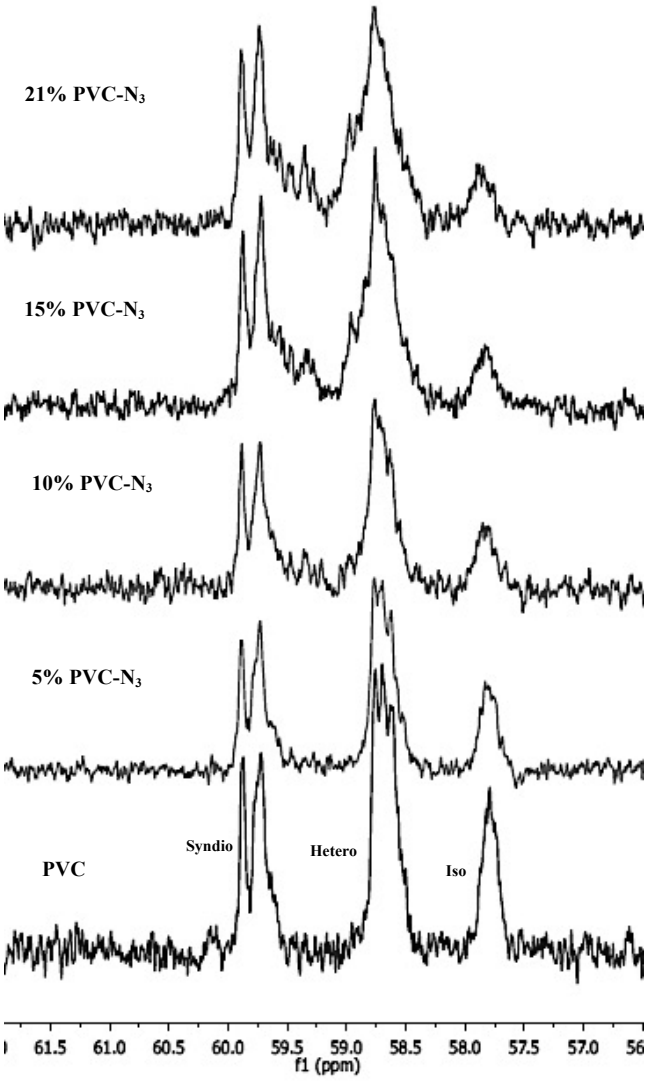



**Fig. 7. $^{13}$C NMR Spectra of PVC and PVC substituted with Azide in DMF-$d_6$**

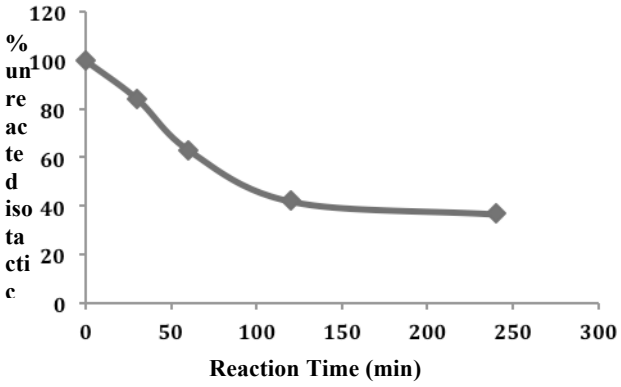



**Fig. 8. Participation of Isotactic Chlorines of PVC in Nucleophilic Subsitution with Azides**

azide substituted PVC was studied by $^{13}$C NMR in deuterated DMF-$d_6$ (**Fig. 7**.). In unmodified PVC, the resonances from 57.5 to 60.0 ppm are those of the methine carbons bearing chlorine atoms. The peaks of isotactic, heterotactic, and syndiotactic tetrads [33,36] are clearly shown in **Fig 7**. With increasing azidation, the isotactic peaks get smaller with concurrent increase in the two downfield regions. At low levels of azidation, chlorines from the isotactic tetrads undergo preferential substitution. The peaks associated with methine carbons bearing azide come below 58.4 ppm for all three tetrads. After a certain point there is no change in the isotactic region, implying that nucleophilic substitution by azide is occurring at the other tetrads (**Fig. 8**).

## 3. Conclusion

In summary, PVC was modified with pendant triazoles bearing a derivative of the most common phthalate plasticizer DEHP by two different flexible linkers: an ether and an ester (PVC-DEHP-ether **9** and PVC-DEHP-ester **10**). The synthesis of these tethered phthalates was developed, and the glass transition temperatures measured to assess the plasticizing efficacy. The reduction in glass transition temperature of PVC, from 83 °C to 55 °C for 15% PVC-DEHP-ether **9**, and to 60 °C for 15% PVC-DEHP-ester **10**, indicates successful plasticization of PVC by covalently attaching phthalate derivatives. Comparison of glass transition temperatures shows that PVC-DEHP-ether **9** is more effective in imparting plasticization than the ester analogue **10**. This makes sense, because the ether linkage is more flexible than the ester linkage, which has several preferred conformations. Both 15% covalent ether and ester linkages were more effective than thermally incubating non-covalent DEHP at 15% weight with PVC. However, even 15% PVC-DEHP-ether showed only a moderate decline in $T_g$, indicating that substitution higher than 15% of the chlorine atoms of PVC will be required to achieve desirable plasticization for most commercial applications.

## 4. Experimental

Commercial bulk polymerized PVC (Mw = 43,000) was purchased from Sigma-Aldrich and was purified by following the procedure of Rusen [29]. PVC (5.003 g) was dissolved in 60 mL of tetrahydrofuran (THF) at room temperature, followed by precipitation with 180 mL of methanol. PVC-azide (5% and 15%) was prepared according to our previously published procedure

[27]. For 21% PVC-azide, 2.019 g of PVC and 2.006 g of sodium azide were stirred in 20 mL of DMF at 60 °C for 4 h. The % azidation of all PVC-$N_3$ samples were determined by elemental analysis. Tetrahydrofuran (Fisher Scientific) was dried over sodium and benzophenone when anhydrous conditions were required. Acetonitrile (Fisher Scientific) and toluene (Fisher Scientific) were obtained from a PureSolv solvent purification system manufactured by Innovative Technologies, Inc. when anhydrous conditions were required. Anhydrous silica gel (grade 60, 40 - 75 mesh, Sorbent Technologies) was activated by heating at 200 °C for 24 h under nitrogen and stored in a desiccator upon cooling. All other chemicals were used as received. The following chemicals were purchased from Sigma-Aldrich: sodium azide (99.5%), 2-ethylhexanol (99%), sodium hydride (60% in mineral oil), *N*-bromosuccinamide (NBS), benzoyl peroxide, propiolic acid (95%), and anhydrous dimethyformamide. The following chemicals were purchased from Acros Organics: dimethyl acetylenedicarboxylate (98%), 4-methyl-phthalic anhydride (96%), Dess-Martin periodinane (97%), and *p*-toluenesulfonic acid monohydrate (99%). The following chemicals were purchased from Alfa Aesar: acetylenedicarboxylic acid, and dimethylacetylene dicarboxylate (95%). Silica gel column chromatography was performed on a Biotage Isolera™ Prime automated flash purification system. NMR spectra were recorded at ambient temperature on a Varian 500 MHz spectrometer or INOVO 500 MHz in $CDCl_3$ as solvent unless otherwise noted. The spectra were recorded with the residual $CHCl_3$ peak (δ 7.27 ppm) as internal standard for $^1$H NMR and $CDCl_3$ triplet (δ 77.27 ppm) for $^{13}$C NMR. FTIR spectra were recorded on a Perkin-Elmer spectrometer as a neat film on a KBr cell. High resolution mass spectra (HRMS) were recorded either on a benchtop Mariner electrospray ionization time-of-flight (ESITOF) mass spectrometer or on LTQ Orbitrap. A TA Instruments DSC Q1000 was utilized to measure glass transition temperatures and other thermal endotherms. All samples underwent a 5 min isotherm at 50 °C and were then heated to 150 °C at a heating rate of 20 °C/min followed by a 5 min isotherm before cooling to 50 °C at a cooling rate of 10 °C/min. Finally, samples were heated to 150 °C at a heating rate of 10 °C/min to record thermal transitions. The typical sample masses were approximately 8 mg, which were sealed in aluminum hermetic pans.

**Preparation of dimethyl 4-methylcyclohexa-1,4-diene-1,2-dicarboxylate (11) [**37]. Following the procedure of Smit et al [28] a mixture of dimethylacetylene dicarboxylate (3.468 g, 24.40 mmol), isoprene (14.7 mL, 146 mmol), and activated silica gel (40.13 g) was stirred at room temperature for 18 h. The reaction flask was equipped with a Findenser™ to minimize the evaporation of isoprene. Diethyl ether (100 mL) was added to the reaction mixture, and then filtered. The filtrate was concentrated *in vacuo* to give the title compound as a yellow oil (4.932 g, 96.14% yield).

TLC: 75:25 hexanes/ethyl acetate, *p*-anisaldehyde stain, $R_f$: 0.50.

$^1$H NMR (500 MHz, $CDCl_3$): δ 5.36 – 5.34 (m, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 2.98 – 2.92 (m, 2H), 2.87 – 2.82 (m, 2H), 1.67 (s, 3H).

$^{13}$C NMR (125 MHz, $CDCl_3$, DEPT): δ 168.7 ( C=O), 168.5 ( C=O), 132.9 (4°), 132.4 (4°), 129.7 (4°), 116.7 (CH), 52.2 ($O\underline{C}H_3$), 32.1 ($CH_2$), 28.6 ($CH_2$), 22.5 ($CH_3$).

FTIR: 2953 (C-H stretch), 1727 (C=O stretch), 1655 (C=C stretch), 1435 (C-H scissoring), 1250 (C-O stretch) $cm^{-1}$.

**Preparation of dimethyl 4-methylphthalate [**35]. To a stirred solution of dimethyl 4-methylcyclohexa-1,4-diene-1,2-dicarboxylate **11** (2.816 g, 13.39 mmol) in 50 mL of dichloromethane was added Dess-Martin periodinane (5.682 g, 13.39 mmol) and stirred at room temperature for 14 h. The reaction mixture was concentrated *in vacuo*, diluted with 100 mL of hexanes, and then filtered. The filtrate was concentrated *in vacuo* to give the title compound as a yellow oil (1.891 g, 67.76% yield).

TLC: 75:25 hexanes/ethyl acetate, *p*-anisaldehyde stain, $R_f$: 0.47.

$^1$H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, $J$ = 8.0 Hz, 1H), 7.48 (d, $J$ = 1.7 Hz, 1H), 7.33 (dd, d, $J$ = 8.0, 1.7 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 2.42 (s, 3H).

$^{13}$C NMR (125 MHz, $CDCl_3$, DEPT): δ 168.8 (C=O), 167.9 ( C=O), 142.2 (4°), 132.8 (4°), 131.5 (CH), 129.4 (CH), 129.3 (CH), 128.5 (4°), 52.7 ($CH_3$), 52.5 ($CH_3$), 21.3 ($CH_3$).

FTIR: 2959 (C-H stretch), 1728 (C=O stretch), 1463 (C-H scissoring), 1288 (C-O stretch) $cm^{-1}$.

**Preparation of dimethyl 4-(bromomethyl)phthalate (12) [**38]. To a stirred solution of dimethyl 4-methylphthalate **11** (1.891 g, 9.082 mmol) and *N*-bromosuccinimide (1.617 g, 9.082 mmol) in 20 mL of benzene was added benzoyl peroxide (0.0391 g, 0.2738 mmol) and the reaction mixture was refluxed for 3 h. The reaction was allowed to cool to room temperature, diluted with 100 mL of hexanes, and then filtered. The filtrate was concentrated *in vacuo*. The resulting crude yellow oil (3.124 g) was purified by Biotage gradient chromatography using hexanes/ethyl acetate as eluent to give the title compound as a pale yellow oil (1.995 g, 76.78% yield).

TLC: 75:25 hexanes/ethyl acetate, *p*-anisaldehyde stain, $R_f$: 0.42.

$^1$H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, $J$ = 1.0 Hz, 1H), 7.70 (d, $J$ = 8.0 Hz, 1H), 7.55 (dd, $J$ = 8.0 Hz, 1.0 Hz, 1H), 4.48 (s, 2H), 3.91 (s, 3H), 3.89 (s, 3H).

$^{13}$C NMR (125 MHz, $CDCl_3$, DEPT): δ 167.7 ( C=O), 167.6 ( C=O), 141.2 (4°), 132.7 (4°), 131.7 (4°), 131.7 (CH), 129.7 (CH), 129.5 (CH), 52.8 ($CH_3$), 52.7 ($CH_3$), 31.3 ($CH_2$).

FTIR: 2953 (C-H stretch), 1728 (C=O stretch), 1435 (C-H scissoring), 1294 (C-O stretch) $cm^{-1}$.

**Preparation of dimethyl 4-((prop-2-yn-1-yloxy)-methyl)phthalate (13).** To a stirred solution of dimethyl 4-(bromomethyl)phthalate **12** (1.228 g, 4.294 mmol) and propargyl alcohol (0.4798 g, 8.564 mmol) in 20 mL of anhydrous tetrahydrofuran was added sodium hydride(0.0961 g, 1.713 mmol, 60% suspension in mineral oil) in portions over 10 minutes at 0 °C. The reaction mixture was stirred for 2 h and then quenched with 10 mL of saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted three times with 50 mL of ethyl acetate. The combined organic layer was washed two times with 20 mL of brine, dried over $MgSO_4$ and concentrated *in vacuo*. The resulting red oil (2.325 g) was purified by silica gel column chromatography with 75:25 hexanes/ethyl acetate as eluent to give the title compound as a pale yellow oil (0.5515 g, 48.97% yield).

TLC: 75:25 hexanes/ethyl acetate, *p*-anisaldehyde stain, $R_f$: 0.33.

$^1$H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 1.5 Hz, 1H), 7.53 (dd, *J* = 7.9, 1.5 Hz, 1H), 4.67 (s, 2H), 4.21 (d, *J* = 2.5 Hz, 2H), 3.41 (s, 3H), 3.40 (s, 3H), 2.76 (t, *J* = 2.5 Hz, 1H).

$^{13}$C NMR (125 MHz, $CDCl_3$, DEPT): δ 168.2 ( C=O), 167.8 (C=O), 141.1 (4°), 132.5 (4°), 131.1 (4°), 130.0 (CH), 129.3 (CH), 127.9 (CH), 79.2 (CH), 75.3 (4°), 70.4 ($CH_2$), 57.7 ($CH_2$), 52.8 ($CH_3$), 52.7 ($CH_3$).

FTIR: 2931 (aliphatic C-H stretch), 2120 (alkyne C-C stretch), 1727 (C=O stretch), 1462 (aromatic C=C stretch), 1287 (C-O stretch) $cm^{-1}$

**Preparation of bis(2-ethylhexyl) 4-((prop-2-yn-1-yloxy)methyl)phthalate (14).** To a stirred solution of 2-ethylhexanol (0.4398 g, 3.377 mmol) in 5 mL of anhydrous tetrahydrofuran was added sodium hydride (0.3402 g, 7.091 mmol, 60% suspension in mineral oil) at room temperature and stirred for 5 minutes. A solution of dimethyl 4-((prop-2-yn-1-yloxy)methyl) phthalate **13** (0.4428 g, 1.688 mmol) in 5 mL of anhydrous tetrahydrofuran was added at room temperature, and stirred for 1 h. The reaction mixture was cooled to 0 °C, and then quenched with 3 mL of saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted three times with 10 mL of chloroform. The combined organic layer was washed two times with 10 mL of brine, dried over $MgSO_4$ and concentrated *in vacuo*. The resulting red oil (0.8178 g) was purified by silica gel column chromatography with 75:25 hexanes/ethyl acetate as eluent, to give the title compound as a pale yellow oil (0.2414 g, 31.18% yield).

TLC: 75:25 hexanes/ethyl acetate, *p*-anisaldehyde, $R_f$: 0.77.

$^1$H NMR (500 MHz, $CDCl_3$, two diastereomers): δ 7.72 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 1.7 Hz, 1H), 7.52 (dd, *J* = 7.9, 1.7 Hz, 1H), 4.67 (s, 2H), 4.31 - 4.11 (m, 6H), 2.49 (t, *J* = 2.5 Hz, 1H), 1.68 (m, 2H), 1.47 - 1.20 (m, 16H), 0.99 - 0.81 (m, 12H).

$^{13}$C NMR (125 MHz, $CDCl_3$, DEPT, two diastereomers): δ 167.9 ( C=O), 167.5 (C=O), 141.1 (4°), 133.1 (4°), 131.6 (4°), 129.9 (CH), 129.3 (CH), 127.9 (CH), 79.2 (CH), 75.2 (4°), 70.4 ($CH_2$), 68.3 ($CH_2$), 68.2 ($CH_2$), 57.6 ($CH_2$), 38.8 (CH), 31.9 ($CH_2$), 30.4 ($CH_2$), 28.9 ($CH_2$), 23.7 ($CH_2$), 23.0 ($CH_2$), 14.1 ($CH_3$), 11.0 ($CH_3$).

FTIR: 2931 (aliphatic C-H stretch), 2120 (alkyne C-C stretch), 1727 (C=O stretch), 1462 (aromatic C=C stretch), 1287 (C-O stretch) $cm^{-1}$.

HRMS: calcd. for $C_{28}H_{42}O_5$ $[M+H]^+$: 459.3105: found 459.3075.

**Preparation of bis(2-ethylhexyl) 4-methylphthalate (15).** Following the procedure of Smit et al. [30] a mixture of 2-ethylhexylacetylene dicarboxylate (1.739 g, 4.746 mmol), anhydrous silica gel (20.13 g), and isoprene (5.8 mL, 58 mmol) was stirred at room temperature for 18 h. The reaction flask was equipped with a Findenser™ to minimize evaporation of isoprene. Dichloromethane (200 mL) was added to the reaction mixture, and then filtered. The filtrate was concentrated *in vacuo* and bubbled with air for 3 d to give the title compound as a yellow oil (2.011, 96.14% yield).

TLC: 90:10 hexanes/ethyl acetate, *p*-anisaldehyde stain, $R_f$: 0.66.

$^1$H NMR (500 MHz, $CDCl_3$, two diastereomers): δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 1.7 Hz, 1H), 7.31 (dd, *J* = 8.0, 1.7 Hz, 1H), 4.25 – 4.11 (m, 4H), 2.42 (s, 3H), 1.75 – 1.49 (m, 2H), 1.51 – 1.18 (m, 16H), 1.02 – 0.77 (m, 12H).

$^{13}$C NMR (125 MHz, $CDCl_3$, DEPT, two diastereomers): δ 168.5 ( C=O), 167.5 ( C=O), 141.9 (4°), 133.3 (4°), 131.3 (CH), 129.9 (CH), 129.3 (4°), 67.9 ($CH_2$), 67.6 ($CH_2$), 38.8 (CH), 38.7 (CH), 30.4 ($CH_2$), 30.2 ($CH_2$), 28.8 ($CH_2$), 28.7 ($CH_2$), 23.7 ($CH_2$), 23.5 ($CH_2$), 21.3 ($CH_3$), 14.1 ($CH_3$), 11.0 ($CH_3$).

FTIR: 2953 (C-H stretch), 1728 (C=O stretch), 1435 (C-H scissoring), 1294 (C-O stretch) $cm^{-1}$.

**Preparation of bis(2-ethylhexyl) 4-(bromomethyl)-phthalate (16).** To a stirred solution of bis(2-ethylhexyl) 4-methylphthalate **15** (0.3681 g, 0.9098 mmol) and *N*-bromosucinimide (0.1943 g, 0.0273 mmol) in 10 mL of benzene was added benzoyl peroxide (0.0039 g, 1.991 mmol) at room temperature. The reaction mixture was refluxed for 3 d using a Dean-Stark apparatus. The reaction mixture was concentrated *in vacuo* to evaporate benzene. The resulting yellow oil (0.2221 g) was puri fied by Biotage gradient chromatography using hexanes/ethyl acetate as eluent, to give the title compound as a pale yellow oil (0.1511 g, 32.29% yield).

TLC: 90:10 hexanes/ethyl acetate, *p*-anisaldehyde stain, $R_f$: 0.40.

$^1$H NMR (500 MHz, $CDCl_3$, two diastereomers): δ 7.69 (d, *J* = 1.8 Hz, 1H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.55 (dd, *J*= 7.5, 1.8 Hz, 1H), 4.49 (s, 2H), 4.29 - 4.12 (m, 4H), 1.68 (m, 2H), 1.48 - 1.18 (m, 16H), 0.81 - 0.91 (m, 12H).

$^{13}$C NMR (125 MHz, $CDCl_3$, DEPT, two diastereomers): δ 167.8 ( C=O), 167.7 (C=O), 141.4 (4°), 133.7 (4°), 132.6 (4°), 131.9 (CH), 129.9 (CH), 129.8 (CH), 68.9 ($CH_2$), 68.7 ($CH_2$), 39.12 (CH), 31.9 ($CH_2$), 30.8 ($CH_2$), 29.3 ($CH_2$), 24.2 ($CH_2$), 23.4 ($CH_2$), 14.5 ($CH_3$), 11.4 ($CH_3$).
FTIR: 2930 (C-H stretch), 1728 (C=O stretch), 1463 (C-H scissoring), 1288 (C-O stretch) cm$^{-1}$.

was allowed to cool to room temperature and 20 mL of saturated sodium bisulfite solution was added. The reaction mixture was concentrated *in vacuo*. The aqueous layer was extracted three times with 100 mL of diethyl ether. The combined organic layer was washed with 100 mL of brine, dried over $MgSO_4$, and then concentrated *in vacuo*. The resulting yellow viscous oil (7.027 g, 92.64%) was used in the next step without purification.
$^1$H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, *J* = 1.5 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.92 (dd, *J* = 7.8, 1.5 Hz, 1H), 4.59 (s, 2H).
$^{13}$C NMR (125 MHz, $CDCl_3$, DEPT): δ 162.2 (C=O), 162.1 (C=O), 146.9 (4°), 136.9 (4°), 136.8 (CH), 126.2 (CH), 125.9 (CH), 125.5 (4°), 30.5 ($CH_2$).
FTIR: 2953 (C-H stretch), 1701 (C=O stretch, anhydride), 1423 (C-H scissoring), 1289 (C-O stretch) cm$^{-1}$.
HRMS: calcd. for $C_9H_5BrO_2$ $[M+H]^+$: 240.9495: found 240.9476.

**Preparation of bis(2-ethylhexyl) 4-(bromomethyl)-phthalate by anhydride opening (16).** To a stirred solution of 4-bromomethyl-phthalic anhydride **17** (7.997 g, 33.18 mmol) and 2-ethylhexanol (8.641 g, 66.35 mmol) in 50 mL of toluene was added *p*-toluenesulfonic acid (0.3786 g, 1.991 mmol). The reaction mixture was refluxed for 2 h using a Dean-Stark apparatus, then cooled and concentrated *in vacuo*. The resulting yellow oil (0.2221 g) was purified by silica gel column chromatography using 90:10 hexanes/ethyl acetate as eluent, to give the title compound as a pale yellow oil (12.12 g, 75.17% yield).

**Preparation of bis(2-ethylhexyl) 4-((prop-2-yn-1-yloxy)methyl)phthalate (14).** To a stirred solution of bis(2-ethylhexyl) 4-(bromomethyl)phthalate **16** (3.084 g, 6.391 mmol) and propargyl alcohol (0.4297 g, 7.669 mmol) in 60 mL of dry tetrahydrofuran was added sodium hydride (0.6282 g, 26.18 mmol, 60% suspension in mineral oil) in portions over 10 minutes at 0 °C. The reaction mixture was warmed to room temperature and stirred for 22 h, then cooled to 0 °C and quenched with 10 mL of saturated ammonium chloride solution. The organic layer was separated and the aqueous layer was extracted three times with 50 mL of ethyl acetate. The combined organic layer was washed two times with 20 mL of brine, dried over $MgSO_4$ and concentrated *in vacuo*. The resulting red oil (3.325 g) was purified by silica gel column chromatography with 90:10 hexanes/ethyl acetate as eluent, to give the title compound as a pale yellow oil (2.111 g, 72.03% yield).

**Preparation of bis(2-ethylhexyl) 4-((propioloyloxy)-**

HRMS: calcd. for $C_{29}H_{35}BrO_4$ [M-H]: 481.1958: found 481.1955.

**Preparation of 4-bromomethylphthalic anhydride (17).** To a stirred solution of 4-methylphthalic anhydride and *N*-bromosuccinimide (5.601 g, 31.47 mmol) in 100 mL of acetonitrile was added dibenzoyl peroxide (0.1345 g, 0.9441 mmol) at room temperature. The reaction mixture was refluxed for 24 h. The reaction mixture

**methyl)phthalate (18).** To a stirred solution of bis(2-ethylhexyl) 4-(bromomethyl)phthalate **16** (4.311 g, 8.935 mmol) and propiolic acid (0.6706 g, 8.935 mmol) in 10 mL of anhydrous dimethylformamide was added potassium carbonate (3.705 g, 26.81 mmol) at room temperature. The reaction mixture was heated to 100 °C and stirred for 15 minutes, then allowed to come to room temperature and diluted with 100 mL of water. The aqueous layer was extracted three times with 100 mL of chloroform. The combined organic layer was washed three times with 100 mL of brine, dried over $MgSO_4$ and concentrated *in vacuo*. The resulting red oil (4.123 g) was purified by silica gel column chromatography using 90:10 hexanes/ethyl acetate as eluent, to give the title compound as a pale yellow oil (2.985 g, 70.63% yield).
TLC: 75:25 hexanes/ethyl acetate, *p*-anisaldehyde stain, $R_f$: 0.24.
$^1$H NMR (500 MHz, $CDCl_3$, two diastereomers): δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.69 (s, 1H), 7.53 (m, 1H), 5.26 (s, 2H), 4.21 (m, 4H), 2.94 (s, 1H), 1.75 – 1.60 (m, 2H), 1.36 (m, 16H), 1.02 – 0.79 (m, 12H).
$^{13}$C NMR (125 MHz, $CDCl_3$, DEPT, two diastereomers): δ 167.3 ( C=O), 167.1 (C=O), 152.2 (C=O), 137.7 (4°), 132.9 (4°), 132.4 (4°), 130.3 (CH), 129.3 (CH), 128.3 (CH), 75.7 (CH), 74.1 (4°), 68.3 ($CH_2$), 68.2 ($CH_2$), 66.4 ($CH_2$), 38.7 (CH), 38.6 (CH), 30.4 ($CH_2$), 30.3 ($CH_2$), 28.9 ($CH_2$), 23.7 ($CH_2$), 22.9 ($CH_2$), 14.0 ($CH_3$), 10.9 ($CH_3$).
IR (neat): 2959 (aliphatic C-H stretch), 2020 (alkyne C-C stretch), 1725 (C=O stretch), 1461 (aromatic C=C stretch), 1286 (C-O stretch) cm$^{-1}$.
HRMS: calcd. for $C_{28}H_{41}O_6$ $[M+H]^+$: 473.2898: found 473.2875.

**Preparation of bis(2-ethylhexyl) 4-(((1-(1-phenylethyl)-1*H*-1,2,3-triazol-4-yl)methoxy)methyl)-phthalate (21).** To a stirred solution of bis(2-ethylhexyl) 4-((prop-2-yn-1-yloxy)methyl)phthalate **14** (0.0876 g, 0.1910 mmol) and 1-phenylethyl azide (0.0637 g, 0.4331 mmol) in 10 mL of 6:1 THF:$H_2O$ was added copper iodide (0.0521 g, 0.2736 mmol) at room temperature and stirred for 18 h. The reaction mixture was diluted with 50 mL of diethyl ether. The organic layer was separated and washed three times with 10 mL of saturated sodium carbonate solution, one time with 10 mL of brine, dried over $MgSO_4$ and concentrated *in vacuo* to give a yellow oil (0.1041 g, 86.03% yield).
TLC: 75:25 hexanes/ethyl acetate, *p*-anisaldehyde stain, $R_f$: 0.19.

$^1$H NMR (500 MHz, $CDCl_3$, multiple diastereomers): δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.63 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.45 (s, 1H), 7.38 – 7.10 (m, 3H), 7.29 – 7.26 (m, 2H), 5.80 (q, *J* = 7.0 Hz, 1H), 4.68 (s, 2H), 4.64 (s, 2H), 4.30 – 4.09 (m, 4H), 1.97 (d, *J* = 7.0 Hz, 3H), 1.67 (m, 2H), 1.47 – 1.20 (m, 16H), 0.90 (m, 12H).

$^{13}$C NMR (125 MHz, $CDCl_3$, DEPT, multiple diastereomers): δ 168.1 (C=O), 167.5 (C=O), 144.8 (4°), 141.6 (4°), 139.6 (4°), 133.2 (4°), 131.4 (4°), 129.8 (CH), 129.3 (CH), 128.9 (CH), 128.7 (CH), 127.7 (CH), 126.7 (CH), 121.5 (CH), 71.5 ($CH_2$), 68.3 ($CH_2$), 68.2 ($CH_2$), 64.2 ($CH_2$), 60.4 (CH), 38.8 (CH), 38.7 (CH), 30.4 ($CH_2$), 30.3 ($CH_2$), 29.0 ($CH_2$), 23.8 ($CH_2$), 23.7 ($CH_2$), 23.0 ($CH_2$), 21.6 ($CH_3$), 14.1 ($CH_3$), 11.0 ($CH_3$).

IR (neat): 2959 (aliphatic C-H stretch), 1726 (C=O stretch), 1576 (C-N stretch), 1458 (aromatic C=C stretch), 1286 (C-O stretch) $cm^{-1}$.

HRMS: calcd. for $C_{36}H_{51}N_3O_5$ $[M+H]^+$: 606.3902: found 606.3848.

**Preparation of bis(2-ethylhexyl) 4-(((1-(1-phenylethyl)-1*H*-1,2,3-triazole-4-carbonyl)oxy)methyl)-phthalate (22).** A solution of bis(2-ethylhexyl) 4-((propioloyloxy)methyl)phthalate **18** (0.4865 g, 0.1029 mmol) and 1-phenylethyl azide (0.1514 g, 0.1029 mmol) in 3 mL of dimethylformamide was stirred at 100 °C for 2 h. The reaction mixture was allowed to come to room temperature, and then diluted with 20 mL of dichloromethane. The organic layer was washed three times with 10 mL of brine, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting yellow oil (0.5432 g) was purified by silica gel column chromatography using 3:1 hexanes/ethyl acetate as eluent, to give the title compound as a colorless oil (0.2155 g, 33.78% yield).

TLC: 75:25 hexanes/ethyl acetate, *p*-anisaldehyde stain, $R_f$: 0.24.

$^1$H NMR (500 MHz, $CDCl_3$, multiple diastereomers): δ 7.96 (s, 1H), 7.75 – 7.62 (m, 2H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.28 (m, 3H), 7.28-7.17 (m, 2H), 5.84 (q, *J* = 7.1 Hz, 1H), 5.37 (s, 2H), 4.22 - 4.10 (m, 4H), 1.96 (d, *J* = 7.1 Hz, 3H), 1.65 - 1.58 (m, 2H), 1.45 – 1.15 (m, 16H), 0.94 - 0.76 (m, 12H).

$^{13}$C NMR (125 MHz, $CDCl_3$, DEPT, multiple diastereomers): δ 167.5 (C=O), 167.2 (C=O), 160.3 (C=O), 139.4 (4°), 138.8 (4°), 138.7 (4°), 132.9 (4°), 132.1 (4°), 130.5 (CH), 129.2 (CH), 129.1 (CH), 128.9 (CH), 128.4 (CH), 126.6 (CH), 126.5 (CH), 68.3 ($CH_2$), 68.1 ($CH_2$), 65.4 ($CH_2$), 60.8 (CH), 38.7 (CH), 38.6 (CH), 30.3 ($CH_2$), 30.2 ($CH_2$), 28.9 ($CH_2$), 23.7 ($CH_2$), 23.6 ($CH_2$), 22.9 ($CH_2$), 21.2 ($CH_3$), 14.1 ($CH_3$), 11.0 ($CH_3$).

IR (neat): 2959 (aliphatic C-H stretch), 1726 (C=O stretch), 1541 (C-N stretch), 1458 (aromatic C=C stretch), 1286 (C-O stretch) $cm^{-1}$.

HRMS: calcd. for $C_{36}H_{49}N_3O_6$ $[M+H]^+$: 620.3695: found 620.3644.

**Preparation of 5% PVC-DEHP-ether (9).** To a stirred solution of 5% PVC-azide (1.511 g, 22.22 mmol) and DEHP-ether **14** (0.7642 g, 1.667 mmol) in 70 mL of 6:1, THF:$H_2O$ was added $CuSO_4$•$5H_2O$ (0.5548 g, 2.272 mmol) and ascorbic acid (0.6783 g, 5.677 mmol). The reaction mixture was stirred at room temperature for 24 h, and then filtered. The filtrate was poured into 200 mL of methanol. The precipitated solid was filtered, washed one time with 25 mL of water, one time with 25 mL of methanol and dried to give yellow solid (1.236 g). The cycloaddition of 15% PVC-azide sample was carried out in a similar fashion with three times more of DEHP-ether **14**.

IR (neat): 2959 (aliphatic C-H stretch), 1723 (C=O stretch), 1541 (C-N stretch), 1462 (aromatic C=C stretch), 1284 (C-O stretch) $cm^{-1}$.

**Preparation of 5% PVC-DEHP-ester (10) by Cu catalyzed route.** To a stirred solution of 5% PVC-azide (1.031 g, 15.16 mmol) and DEHP-ester **18** (0.5338 g, 1.129 mmol) in 70 mL of 6:1, THF:$H_2O$ was added $CuSO_4$•$5H_2O$ (0.5673 g, 2.272 mmol) and ascorbic acid (0.6783 g, 3.851 mmol). The reaction mixture was stirred at room temperature for 24 h, and then filtered. The filtrate was poured into 200 mL of methanol and filtered. The cake was washed one time with 25 mL of water, one time with 25 mL of methanol and dried to give yellow solid (1.012 g). The cycloaddition of 15% PVC-azide sample was carried out in a similar fashion with three times more of DEHP-ester **18**.

IR (neat): 2959 (aliphatic C-H stretch), 1725 (C=O stretch), 1578 (C-N stretch), 1459 (aromatic C=C stretch), 1287 (C-O stretch) $cm^{-1}$.

**Preparation of 5% PVC-DEHP-ester (10) by thermal route.** To a stirred solution of 5% PVC-azide (0.3479 g, 5.116 mmol) in 10 mL of dimethylformamide was added DEHP-ester **18** (0.7254 g, 1.535 mmol) and stirred at 100 °C for 24 h. The reaction mixture was allowed to cool to room temperature and then poured into 100 mL of methanol, and filtered. The cake was washed three times with 20 mL of methanol and dried to give white solid (0.3256 g). The cycloaddition of 15% PVC-azide sample was carried out in a similar fashion with three times more of DEHP-ester **18**.

## Associated content

$^1$H NMR, $^{13}$C NMR, DEPT, FTIR, and DSC thermograms. The Supporting Information is available free of charge on the ACS Publications website.

## Author information


### Corresponding Author

Prof. Rebecca Braslau
Department of Chemistry and Biochemistry
University of California, Santa Cruz,
Santa Cruz, California, 95064, USA.
Telephone: (831) 459-3087
Email: rbraslau@ucsc.edu



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