



Phthalate plasticizers covalently linked to PVC via copper-free or copper catalyzed azide-alkyne cycloadditions



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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.

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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.

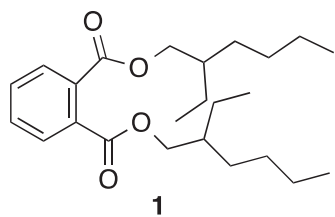
Other common small molecule plasticizers include terphthalates, 1,2-cyclohexane-dicarboxylic acid diisononyl ester (Hexamoll[®] DINCH[®]), epoxidized vegetable oils, citrates, mellitates, adipates, benzoates, maleates, succinates, sebacates, phosphates, isosorbide esters. Because these plasticizers are 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 sulfonamides, often bearing 2-ethylhexyl groups or Jeffamines to give impressive low T_g values at 20% or 40% weight sulfide.

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

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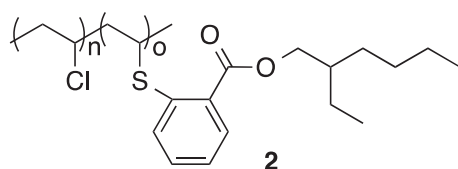


1
Di(2-ethylhexyl) phthalate (DEHP)

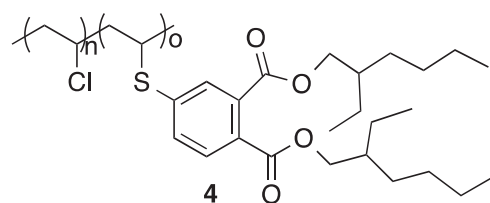
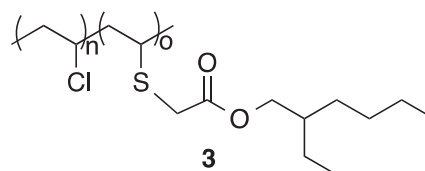
Fig. 1. Structure of the most common phthalate plasticizer: DEHP.

with an alkyne tethered to naturally abundant cardanol. The modified polymer PVC-cardanol **8** exhibited a decreased $T_g = 51^\circ\text{C}$, 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**

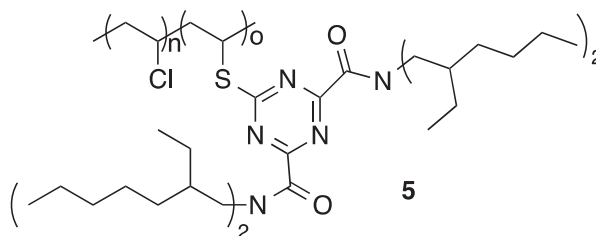
Sulfide, Thiolester Linked Internal Plasticizers:



2
Michel's 1986 Sulfide and Thiolester



4



5

examples of Reinecke's Aromatic and Heteroaromatic Sulfides

Fig. 2. Internal plasticizers prepared by sulfur nucleophile displacement of chloride on PVC.

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].

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 $T_g = 76^\circ\text{C}$ 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

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.

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%.

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

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