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https://escholarship.org/uc/item/9306g72f

Journal

Polymer Reviews, 62(3)

ISSN

0736-6574

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Publication Date

2022-07-03

DOI

10.1080/15583724.2021.1986066

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Peer reviewed

Internal Plasticization of PVC

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Abstract

Polyvinyl Chloride (PVC) is among the most abundant plastics worldwide. PVC is inherently brittle: to impart flexibility, small molecule plasticizers are usually added to the PVC matrix. This use of external plasticizers (often phthalates) has raised numerous health concerns due to their tendency to migrate out of PVC, where they can be ingested or contaminate the environment. Internal plasticization, in which a plasticizer is covalently bound to the PVC backbone, offers a solution to the problem of plasticizer migration. This comprehensive review covers the preparation of internally plasticized PVC in the literature. Strategies fall into three main categories: nucleophilic substitution of chlorine atoms on PVC; graft polymerization using plasticizing monomers, usually from defect sites in the PVC backbone; and copolymerization of vinyl chloride with monomers bearing plasticizing species. Minimizing cost and number of synthetic steps are important considerations when designing plasticizers for this large-scale commodity plastic.

Key Words

Polyvinyl chloride, self-plasticization, covalent attachment, phthalate, non-migratory

Introduction

Polyvinyl Chloride (PVC) is one of the most common thermoplastics in the world, making up 17% of the global plastic market[1] amounting to over 44 million metric tons in 2018.[2]

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Applications range from building materials, toys, credit cards, automotive components and clothing to medical devices. Due to the low cost, optical clarity, and facile sterilization, 40% of plastic medical devices are made of PVC.[3]

PVC as a pure material is a brittle solid. For most applications, it must be mixed with a plasticizer to impart flexibility. Traditionally, plasticizers are mixed with PVC as "external plasticizers," without covalent attachment. This leads to plasticizer migration, where the plasticizer diffuses out of PVC into adjacent materials for example: into the air, water or other liquids, food, soil or onto the skin of a person who touches a PVC product. Plasticizer migration degrades the properties of the material, contaminates the environment, and exposes people to often harmful plasticizers.[4]

The most commonly used plasticizer is di(2-ethylhexyl)phthalate (DEHP, note: DOP, dioctyl phthalate, is the same as DEHP. DEHP is used throughout, regardless as to which acronym was used in the original literature).[5] The toxicity of DEHP and its subsequent metabolites has been extensively investigated, and has been recently reviewed.[6] Given these toxicity concerns, development of less-toxic small-molecule plasticizers has been an active area of research.[3] Even more attractive are non-migratory plasticizers, as this not only avoids toxicity but also allows the PVC to retain its physical properties over time.

There are several strategies for preventing plasticizer migration. (1) Polymeric plasticizers with high molecular weights have a greatly reduced tendency to migrate. (2) The surface of the PVC material may be crosslinked by radiation or chemical treatment to inhibit plasticizer leaching. (3) The plasticizer may be covalently bound to the PVC polymer chain: "internal plasticization." In Moulay's landmark 2010 review article "Chemical modification of poly(vinyl chloride)—Still on the run,"[7] a scholarly overview of chemical transformations was presented up through 2009.

Since that time, many researchers have explored covalent bonding of potential plasticizers to PVC. Although a few reviews have addressed covalent attachment in the overall context of PVC plasticization,[3,8,9,10] these discussions have been limited to a subset of internal plasticization strategies. Herein we present a comprehensive review of internal plasticization of PVC.

This overview will first cover covalent linkage of plasticizing species to PVC via nucleophilic substitution of chlorine atoms on the PVC chain, in the order of sulfur nucleophiles, followed by nitrogen (amine and azide) nucleophiles. Nucleophiles which are also effective bases suffer from competing elimination, which is sometimes acknowledged, but often ignored by workers in this field. Graft polymerization from PVC, dominated by reaction from allylic and tertiary defect sites inherent in the PVC chain, is then reviewed. In the last section, copolymerization of vinyl chloride monomer with monomers that afford internal plasticization is covered, starting with linear random copolymerization, and then block copolymerization. Lastly, two examples are presented of complex polymer architectures designed to compatibilize plasticizing polymer subunits with PVC.

1 Covalent Attachment of Plasticizers via Nucleophilic Substitution on PVC

1.1 *Sulfide Linkages*

The first example of internally plasticized PVC by nucleophilic substitution was reported in 1981 by Marian and Levin.[11] Sodium 2-(2'-butoxyethoxy)ethyl thiolate was added to PVC, replacing some of the chloride groups (**Scheme 1.1**). T_g values were not measured, however, all modified polymers showed a decrease in tensile modulus and tensile strength, and an increase in elongation at break, indicating enhanced flexibility. Increasing the thiol substitution from 10% to

25% (as determined by elemental analysis) further decreased both modulus and tensile strength, and further increased elongation.

[Scheme 1.1]

In 1986 Michel *et al.*[12] used sodium thiolates to covalently bond the 2-ethylhexyl ester of *o*-mercaptobenzoic acid and of the similar ester of thioglycolic acid to PVC (**Scheme 1.2**). The T_g values of the polymer decreased with increasing amounts of sulfide substitution. T_g is the glass transition temperature: the temperature at which a polymer changes from a glassy state to a rubbery state. As a result, materials with low T_g values are increasingly flexible. The T_g of commercially available PVC is around 81 °C.[13] The 2-ethylhexyl ester of thioglycolic acid showed better plasticization efficiency compared to the 2-ethylhexyl ester of *o*-mercaptobenzoic acid. The lowest T_g achieved in this work was 56 °C with 15 mol% of covalently linked 2-ethylhexyl ester of thioglycolic acid.

In 1997, del Val et al. also performed substitutions with the 2-ethylhexyl ester of thioglycolic acid (**Scheme 1.2**).[14] A similar T_g value of 56 °C was observed at 20 wt% of plasticizer. This internal plasticizer was less efficient than a non-bound mixture of PVC and 2-ethylhexyl thioglycolate with the same stoichiometry.

[Scheme 1.2]

Millan et al. substituted PVC chlorines with sodium phenylthiolate (**Scheme 1.3**), and measured the resulting T_g depression in a study of tacticity.[15,16] This nucleophilic substitution occurs preferentially at isotactic portions of PVC, and converts these segments from a gauche/*trans* mixture to an all-*trans* configuration. This has the effect of straightening the polymer chain, counteracting some of the plasticization. Conditions that decreased this selectivity therefore increased plasticization. Running the reaction at higher temperatures (60 vs 25 °C) or in a very

polar solvent such as *N*-methylpyrrolidone or hexamethylphosphoramide led to enhanced plasticization. T_g values ranged from 80 °C for unmodified PVC to 62 °C for PVC with 50% of the chlorine atoms replaced with aryl sulfides under polar conditions. López and Mijangos studied the same reaction; reacting PVC in the melt (160 °C) gave more efficient plasticization than in butanone, tetrahydrofuran (THF), or dimethylmalonate solvents.[17] T_g values around 60 °C were observed at 55% phenylthiolate substitution.

[Scheme 1.3]

In 2002, the Reinecke group studied similar chlorine atom substitution with thiophenols containing various *para*- substituents (**Scheme 1.4**).[18] Substituents that can participate in hydrogen bonding greatly increased the T_g (antiplasticizing), while those that do not hydrogen bond were somewhat plasticizing, lowering the T_g values to around 70 °C. The density of all modified polymers decreased, indicating a disruption in chain packing. Notably, side reactions including both crosslinking and chloride elimination from PVC were investigated. When a thiol containing an aliphatic amine was used, elimination (dehydrochlorination) was observed, however no dehydrochlorination was observed for aromatic amines. When a thiophenol bearing a carboxylic acid functionality was used, crosslinked polymers were obtained.

[Scheme 1.4]

The use of halogenated thiophenols was also investigated by the Reinecke group (**Scheme 1.5**).[19] T_g values ranged from 85 °C for perfluorothiophenol to 54 °C for 4-fluorothiophenol at 55% substitution.

[Scheme 1.5]

In 2010, the Reinecke group synthesized several regioisomers of thiol-substituted 2-ethylhexyl phthalates in three steps, and covalently linked them to PVC by nucleophilic

substitution (**Scheme 1.6**). [20]   The lowest T_g obtained was around 0 °C. Di(2-ethylhexyl) 4-mercaptophthalate has higher plasticization efficiency than that of di(2-ethylhexyl) 5-mercaptoisophthalate. This is the first example of directly attaching the phthalate motif to PVC.

[Scheme 1.6]

In 2016, the Reinecke group developed two additional strategies to attach plasticizers via aromatic (**Scheme 1.7**) or heteroaromatic thiols (**Scheme 1.8**).[21] Both strategies require 4-5 synthetic steps. For the first strategy, T_g values for PVC bearing 14 to 39 wt% plasticizer range from 28 to 62 °C (**Scheme 1.7**). The second strategy uses trichlorotriazine (TCTA) as the starting material (**Scheme 1.8**). Two chlorines on TCTA were replaced either by amines or alcohols. The third chlorine was then converted to the sodium thiolate using nucleophilic aromatic substitution with thiourea followed by hydrolysis with NaOH to reveal the aryl thiolate. Reaction with the PVC backbone at 85 °C for 2 hours appended these triazines to PVC. For samples bearing 40 wt% of these heteroaromatic thiol-based plasticizers, T_g values range from 35 to 55 °C.

[Scheme 1.7]

[Scheme 1.8]

In 2016 and 2017, the Reinecke group[22,23] used high molecular weight plasticizers to achieve plasticization with less chlorine substitution (**Scheme 1.9**). They also explored the influence of the compatibility of the covalently attached plasticizers on T_g by changing the ratio of PVC-miscible polyethylene glycol (PEG) and PVC-immiscible polypropylene oxide (PPO) making use of commercially available Jeffamines®. Compared to previous studies, these new PEG-PPO trichlorotriazine (TCTA) derivatives exhibit low T_g values. For example, when R_1=(PO)$_3$(EG)$_{19}$, R_2=H, R_3=(PO)$_3$(EG)$_{19}$, R_4=H (M_w=2100 g/mol), the T_g value is -18 °C with 45 wt% of plasticizer, and the T_g is -41 °C with 73 wt% of plasticizer. Amines containing more

ethylene glycol repeat units demonstrate higher plasticization efficiency compare to amines with more propylene oxide repeat units. Comparing traditional non-covalently attached DEHP/PVC mixtures, the PEG-PPO TCTA system plasticizes at a similar efficiency when two high EO content jeffamines were used (bis-1000, bis-2070, bis-3085). Interestingly, $T_m = 24\ °C$ was observed for several polymers, which the authors attribute to the fusion of crystallized ethylene glycol segments.

[Scheme 1.9]

In 2019, Zhou et al.[24] reported a method to attach epoxidized biomass-based plasticizers, including cardanol glycidyl ether, epoxidized acetylated castor oil methyl ester, and epoxidized soybean oil to PVC using thiosalicylic acid (**Scheme 1.10**). Three biomass-based plasticizers were attached by carboxylate nucleophilic addition to epoxides with the same molar amount. The lowest T_g value obtained was 38 °C with epoxidized soybean oil. T_g values for the grafted epoxidized acetylated castor oil methyl ester and cardanol glycidyl ether were 44 °C and 42 °C, respectively.

[Scheme 1.10]

In 2019 the Yoshioka group performed nucleophilic substitutions on PVC with three different thiols: thiophenol, octanethiol and isooctyl thioglycolate (**Scheme 1.11**).[25] Reaction with ocatanethiol resulted in nearly as much elimination as substitution, while thiophenol and isooctyl thioglycolate gave significantly more substitution. Thiophenol was slightly plasticizing, giving a T_g value of 75 °C at 36% substitution, while octanethiol and isooctylthioglycolate were more effective, both resulting in a T_g value of 66 °C at only 6% substitution.

[Scheme 1.11]

From these sulfide-linked plasticizer studies, one can conclude: 1) at a constant weight percent of incorporation, high molecular weight plasticizers efficiently decrease the T_g value, as they require the introduction of fewer anchor points to the PVC backbone per weight of plasticizer.

The anchor points, which are considered anti-plasticizing, reduce the free movement of the PVC backbone. 2) Miscibility of the plasticizer with PVC is important. One can use these results to further improve internal plasticizer design. There are several drawbacks to sulfides: a) Sulfides are susceptible to oxidation;[26] b) the resulting oxidation products (sulfoxides, sulfones, etc.) can undergo elimination, leading to degradation of the polymer as it ages; and c) sulfides and thiols can release foul odors upon degradation, as well as potential odors from residual thiols in the material. Sulfides and other sulfur compounds often lead to discoloration of the PVC products.

1.2   *Amine Linkages*

Amines are good nucleophiles, capable of displacing chlorines on PVC. This strategy has been employed by various research groups to attach plasticizing groups to PVC. One downside of the use of amines is that although they are nucleophiles, they are also good bases, leading to significant amounts of competing elimination. Many of the studies in this section do not address elimination, although it is likely a competing process. In addition, the use of bisamines as nucleophiles can cause cross-linking of PVC as a side reaction; this is addressed by some authors but not by others.

In 2005, Jayakrishnan et al. reported attachment of PEG to PVC by a series of reactions.[27] First, PVC was treated with diethylamine, as a nucleophile to displace some of the chlorine atoms. The resulting PVC-amine was then treated with a diisocyanate, which was then allowed to react with hydroxy-terminal PEG (**Scheme 1.12**). Each of these steps has the potential to cause cross-linking: insoluble precipitates were observed when any of the three steps was allowed to run for too long. In an effort to minimize cross-linking, reaction times were kept short so that all products were soluble in THF. The T_g of the final PVC-*g*-PEG was 25-30 °C.

[Scheme 1.12]

8

The Zhou group published two papers, one using tung oil[28] and one using cardanol[29] as sources of internal plasticizers. Cardanol is a waste by-product of the cashew industry: it is found in the oil from the cashew shells, which can cause dermatitis upon contact for sensitive individuals.[30] These plasticizers were covalently bonded to PVC by nucleophilic substitution, using an amine as the nucleophile. To prepare the amine-terminated plasticizing group, tung oil was transesterified with methanol to give the methyl ester (**Scheme 1.13**). Aminolysis with propylenediamine formed an amide with a terminal amine. This aminated tung oil was attached to PVC by substitution of chlorine under heat. There was no mention of competitive HCl elimination by the primary amine. The lowest T_g value achieved was 44 °C. Tensile modulus and tensile strength decreased while elongation at break increased.

[Scheme 1.13]

The cardanol-based plasticizer[29] was synthesized in 2 steps (**Scheme 1.14**). In the first step, Williamson Ether Synthesis with the phenolate of cardanol and *n*-butyl chloride gave cardanol butyl ether. In the second step, a reactive iminium ion generated from diethylamine triamine was allowed to react with cardanol butyl ether by aromatic electrophilic substitution to give the cardanol butyl ether attached to an amine. However, the authors proposed formation of the regioisomer that is least likely to be formed due to steric hindrance. Instead, one would expect a mixture of the other two regioisomers indicated in **Scheme 1.14**. Nonetheless, the cardanol derivative was then attached to PVC as a plasticizer by amine nucleophilic solution. Possible competing base mediated elimination of PVC was not discussed. The lowest T_g value obtained was 49 °C for 38 wt% of cardanol based plasticizer.

[Scheme 1.14]

The Zhou group also used a similar Mannich reaction with diethylenetriamine to attach a fatty acid ester to PVC (**Scheme 1.15**).[31] Methanolysis of waste cooking oil provided the long-chained methyl ester, making it a sustainably sourced plasticizer. The modified PVC had a T_g value of 44 °C, and showed lower tensile strength and higher elongation at break than unmodified PVC.

[Scheme 1.15]

In 2021, Bu *et al.*[32] also employed a Mannich reaction with diethylenetriamine, lauraldehyde and diethyl phosphite in a three component coupling; this material was then attached to PVC via nucleophilic displacement by the remaining primary amine (**Scheme 1.16**). T_g values as low as 31 °C were measured, along with decreased tensile strength and increased elongation at break.

[Scheme 1.16]

In 2019, the Zhou group used dehydroabietic acid, a diterpenoid found in coniferous trees, as an internal plasticizer using two different attachment routes.[33] One route used oxalyl chloride to activate the acid, followed by amidification with diethylenetriamine, which was then used as a nucleophile to attack PVC. The other method used epichlorohydrin to install an epoxide on the dehydroabietic acid, which was then opened by triethylenetetramine, followed by attachment to PVC (**Scheme 1.17**). When compared at the same wt%, the epoxide derived material with the triethylenetetramine linker performed slightly better, giving T_g values 2 to 7 °C lower than with the diethylenetriamine linker. The lowest T_g value observed was 34 °C for PVC using the triethylenetetramine linker.

[Scheme 1.17]

In 2020, Najafi and Abdollahi modified PVC using diethanolamine to provide a bis-alcohol-functionalized PVC, which was used to attach three different plasticizing groups (**Scheme 1.18**).[34] In one case, the alcohol groups reacted with epoxy-terminated silicone to give PVC-*g*-silicone. In the other two cases, the alcohols reacted with a diisocyanate, providing a pendent isocyanate group, which then reacted with either oleic acid or tributyl citrate. The silicone, oleic acid, and citrate plasticizers resulted in materials with T_g values of 63, 53, and 43 °C, respectively. All plasticized polymers showed decreased tensile strength and increased elongation at break compared to unmodified PVC.

[Scheme 1.18]

1.3   *Carboxylate Linkage*

In 2013, Liu and Cheng modified PVC using several fatty acids.[35] The PVC was first treated with sodium iodide, exchanging some chlorides for the more reactive iodides. Displacement by sodium carboxylate nucleophiles derived from C12, C14, or C18 fatty acids provided the modified PVC materials (**Scheme 1.19**). The lowest T_g value observed was 80 °C compared to 90 °C for unmodified PVC. The T_g values did not consistently decrease with increasing substitution.

[Scheme 1.19]

1.4   *Covalent Attachment of Plasticizers to PVC via 3+2 Azide-Alkyne Cycloaddition*

As a non-basic and excellent nucleophile, azide is able to displace chlorine atoms on PVC without significant competing elimination. The resulting PVC-azide can then take part in azide-alkyne cycloaddition reactions to attach alkyne-functionalized plasticizers to PVC. Two major variants exist: the metal-free thermal azide-alkyne cycloaddition, and the copper-catalyzed azide-alkyne cycloaddition (CuAAC) with terminal alkynes. The thermal reaction is an attractive option

as it does not leave any metal residue, which can be difficult to remove from the polymer. However, CuAAC is also commonly used due to the simplicity of the reaction and the ease of appending terminal alkynes onto substrates of interest.

1.4.1 *Copper-Free 3+2 Thermal Azide-Alkyne Cycloaddition*

The thermal azide-alkyne cycloaddition is governed by the HOMO(azide)-LUMO(alkyne) interaction,[36] and is therefore facilitated by the presence of electron withdrawing groups on the alkyne. Studies on the relative rates of this reaction with various alkynes have shown that electron-withdrawing groups, including amides, esters, and sulfones, can significantly enhance reactivity.[37,38] Of these groups, esters and amides are electron-withdrawing groups while also providing a convenient attachment point for plasticizing side chains. In addition, the triazole products formed by reacting with alkyne diesters resemble the benzene ortho diesters of phthalates such as DEHP, and were thus expected to be good plasticizers (**Figure 1.1**).

[Figure 1.1]

In 2014, Earla and Braslau[39] demonstrated covalent attachment of phthalate mimics to PVC via thermal Huisgen cycloaddition (**Scheme 1.20**). In 2018, Higa and Braslau expanded the scope of ester substituents to polyethylene glycol methyl ethers.[13] The lowest T_g value obtained is -29 °C for PEG$_{550}$Me at 15 mol% plasticizer. Interestingly, the T_g value for the dimethyl ester phthalate mimic (R=Me) is 96 °C,[13] which is higher than the T_g of unmodified PVC (81 °C). This indicates that the rigidity of triazole ring is inherently anti-plasticizing.

[Scheme 1.20]

In 2017, Earla and Braslau used an alkyne with a single ester as a linker to attach a DEHP derivative to PVC-azide using thermal addition (**Scheme 1.21**).[40] Spacing the DEHP moiety farther from the PVC backbone (compared to the phthalate mimic in **Scheme 1.20**) was expected

to increase the rotational freedom of the aromatic group, enhancing the plasticization. PVC substituted with 15 mol% of covalently linked DEHP resulted in a material with a T_g of 60 °C.

[Scheme 1.21]

In 2018, Higa and Braslau further explored this class of triazole plasticizers, this time with phthalate mimics attached by a six-carbon linker to a propargyl ester. (**Scheme 1.22**).[13] The T_g values for internal plasticization with this six-carbon linker are lower than the analogous PVC samples where the triazole diester is directly attached to the PVC chain. The lowest T_g obtained in this series is 18 °C, where R = TEGMe at 15 mol% azidation. Larger plasticizers with a triazole bearing two additional triazoles were also explored (**Scheme 1.23**). The lowest T_g value is -17 °C for the sample bearing two TEGMe polyether esters. Unfortunately, this system required multistep synthesis, including protection of the diester alkyne as a dibromofumarate. The much simpler and cost efficient alternative using PEG esters directly attached to propiolic acid (**Scheme 1.24**) provided a better approach. PEG chain propargyl esters proved to be the simplest to synthesize, while also being the most effective plasticizers: a T_g value of -42 °C was obtained with $PEG_{2000}Me$ at 15 mol% azidation.

[Scheme 1.22]

[Scheme 1.23]

[Scheme 1.24]

In 2019, Li and Braslau used thermal Huisgen azide-alkyne cycloadditions to attach branched plasticizers to PVC.[41] Alkynes activated by two electron-withdrawing amides were selected, to enhance reactivity in the dipolar cycloaddition. Each amide contained a branded glutamate linker to provide attachment of four plasticizing chains per azide anchor point on PVC (**Scheme 1.25**). These chains were varied to include alkyl and polyether moieties. Plasticization

efficiency increased with chain length, and polyethers were more effective plasticizers than the corresponding alkyl esters. T_g values as low as -1 °C at 12 mol% were obtained.

[Scheme 1.25]

1.4.2   *Copper-Catalyzed 3+2 Azide-Alkyne Cycloadditions*

Following the publication of the attachment of phthalate mimics to PVC by thermal azide/alkyne cycloaddition in the Braslau lab,[39] in 2015 the Shi group[42] used the propargyl ether of cardanol in copper-catalyzed 3+2 azide-alkyne cycloaddition (CuAAC) to attach 10 mol% cardanol to PVC (**Scheme 1.26**). The lowest T_g value of the modified PVC was 51 °C.

Using that same procedure, the Zhou group grafted cardanol groups onto PVC-azide using a propargyl linker (**Scheme 1.26**).[43] They observed a T_g value of 42 °C, and proposed that the cardanol groups added more movement to the PVC chain, thereby increasing free volume. Both Shi and Zhou used two equivalents of copper (relative to alkyne) for the CuAAC reaction.

[Scheme 1.26]

In 2015, Demirci and Tasdelen[44] utilized photoinduced copper-catalyzed 3+2 azide-alkyne cycloaddition to attach alkyne-terminated poly(epsilon-caprolactone) (PECL) to azide-functionalized PVC. Alkyne-terminated PECL was synthesized from propargyl alcohol by ring opening polymerization catalyzed by $Sn(Oct)_2$. Cycloaddition was conducted under UV light with 1 equivalent of $Cu(II)Br_2$ and PMDETA as the ligand, using 2,2-dimethoxy-2-phenyl acetophenone as photoinitiator in DMF (**Scheme 1.27**).

[Scheme 1.27]

In 2016, the Kwak group[45] developed a hyperbranched polyglycerol (HPG) plasticizer, which was grafted onto PVC utilizing CuAAC. The HPG was synthesized by a one-pot ring opening polymerization (**Scheme 1.28**). Gel permeation chromatography (GPC) data indicated an

M_n of 1606 g/mol. Excellent low T_g values were achieved: T_g of 16 °C, -5 °C, and -29 °C were found for 3.6 mol%, 5.8 mol%, and 9.0 mol% plasticizer, respectively. The storage modulus and loss tangent data indicates that HPG modified PVC was more flexible than PVC/DEHP with the same T_g values. Elongation at break for HPG covalent modified PVC increased with increasing mol% of HPG and reached to 912% (elongation at break of pure PVC = 0%) at 9.0 mol%. This shows great stretchability of HPG modified PVC. On the other hand, the highest elongation at break value for a non-covalently bound PVC/HPG mixture was 153% at 1.7 mol%.

[Scheme 1.28]

In 2017, the Zhou group[46] covalently attached a triethyl citrate based plasticizer to PVC via CuAAC to give a material with a T_g value of 36 °C (**Scheme 1.29**). The TGA data indicate this modified PVC is thermally more stable compared to unmodified PVC.

Using the same procedure as Zhou, Najafi and Abdollahi prepared the propargyl ether of tributyl citrate and attached it to PVC-azide (**Scheme 1.29**).[34] A T_g of 53 °C was observed. Notably, only 2 mol% of copper was needed for the azide-alkyne cycloaddition step in the presence of ascorbate.

[Scheme 1.29]

Also in 2017, the Zhou group[47] covalently attached mono-2-ethylhexyl phthalate derivatives to PVC to achieve a T_g value of 66 °C (**Scheme 1.30**). The TGA data showed that this modified PVC was less stable than unmodified PVC.

[Scheme 1.30]

In 2017, Earla and Braslau prepared a DEHP derivative by Diels-Alder cycloaddition, followed by benzylic bromination and propargylation, and covalently attached it to PVC via CuAAC (**Scheme 1.31**).[40] An ether linker as well as an ester linker were investigated. The T_g

data suggest that the ether linker enhanced the rotational degrees of freedom of the attached plasticizer, resulting in a lower T_g value compared to the ester linker. PVC with 15 mol% of covalently linked DEHP using an ether linker resulted in a T_g of 55 °C, while an ester linker gave a T_g of 60 °C at the same mol%.

[Scheme 1.31]

In 2017 and 2019, the Zhou group used propargyl bromide as a linker to attach two different castor oil derivatives to PVC (**Scheme 1.32**). When castor oil containing a phosphaphenanthrene group was attached to PVC, a T_g value of 46 °C was observed.[48] Similarly, a castor oil derivative containing a cyanurate group and two phosphate groups was grafted to PVC, giving a T_g value of 51 °C.[49] The plasticized PVC showed decreased tensile strength and increased elongation at break, and also showed fire-retardant properties as measured by the limiting oxygen index.

In 2018, Chu and Ma[50] also applied CuAAC to attach a propargylated castor oil based derivative to PVC-azide (**Scheme 1.32**). The T_g value for this modified PVC was 42 °C. TGA indicates that direct attachment of this triazole group decreases the thermal stability of the modified PVC.

[Scheme 1.32]

The Zhou group[51] used biomass-sourced dehydroabietic acid as a plasticizer which was covalently attached to PVC-azide (**Scheme 1.33**). Among three materials, the lowest T_g value achieved was 37 °C. The modified PVC materials were less thermally stable at 150-300 °C than unmodified PVC, this instability was attributed to the triazole group. Similar observations of decreased thermal stability due to the triazole moiety have also been noted by other researchers.[13]

[Scheme 1.33]

The strategy of nucleophilic substitution of chlorine atoms on the PVC chain as an attachment point for plasticizing species has been investigated using sulfur, nitrogen and carboxylate nucleophiles. Thiols are excellent nucleophiles and poor bases, providing good S_N2 substitution, but the long-term oxidation derivatives may pose problems as these hybrid materials age. Amine nucleophiles are also good bases, suffering from competing HCl elimination reactions. In the case of bidentate amines, cross-linking is another competing process. Azides are excellent nucleophiles, but industry is understandably reticent to adopt azidization of PVC on a large scale, due to concerns of the explosive nature of the azide reagent, reaction waste, and possible small molecule azides formed as side products. The use of copper-mediated azide alkyne cycloaddition leaves behind residual copper; this is not acceptable for biomedical and electronic applications. Ultimately, multi-step synthesis to build up or attach plasticizers is not practical for industry that can simply compound PVC with a small molecule plasticizes. Strategies to replace external plasticizers with internal plasticizers need to be inexpensive and ideally one-step in order to be industrially viable.

2 Grafting Plasticizing Polymers from the PVC Backbone

PVC has been used as a macroinitiator to create brush-like copolymers with polymer side chains on the PVC backbone. By designing the appended polymer chains to be both flexible and miscible with PVC, internal plasticization can be achieved.

2.1 *Cationic Polymerization*

In 1981 Marian and Levin[11] used silver perchlorate as a Lewis acid to produce carbocations from the secondary chlorides of PVC. These carbocations were used to initiate a ring-opening polymerization of THF (**Scheme 2.1**). Although the T_g was not measured, the modified

polymer showed a lower tensile strength and higher elongation at break than neat PVC, which indicates plasticization. The authors noted the cost of the silver salts as a potential drawback to this method.

[Scheme 2.1]

2.2   *Free Radical Polymerization*

Alkoxy radicals abstract hydrogen atoms from PVC to produce carbon radicals, which then initiate radical polymerizations with available monomer. In 2004, Maiti and Choudhary[52] performed a free-radical polymerization on PVC at 170 °C using dicumyl peroxide as a radical source and butyl methacrylate as monomer (**Scheme 2.2**). The T_g of the modified polymer was 61 °C. Interestingly, the same reaction in the absence of peroxide generated a polymer with roughly the same degree of grafting, and a similar T_g of 63 °C. It is possible that defect sites in the PVC have weak C-Cl bonds that can homolyze at the high reaction temperature, thus acting as initiators in the absence of an external radical source.

[Scheme 2.2]

In 2017 the Odelius group used free radical chemistry to modify PVC with acrylic acid and crotonic acid.[53] Acrylic acid (AA) undergoes polymerization, giving PVC-*g*-PAA copolymers, while under the same conditions crotonic acid (CA) undergoes radical addition, adding just a single crotonic acid unit per graft site (**Scheme 2.3**). At 10 wt% internal plasticizer, the T_g values of PVC-*g*-PAA and PVC-*g*-CA were 71 °C and 75 °C respectively.

[Scheme 2.3]

2.3   *Atom Transfer Radical Polymerization*

Atom transfer radical polymerization (ATRP) is a technique that has become very popular because it combines the wide functional group tolerance of radical polymerizations with levels of molecular weight control and end group fidelity similar to those seen in ionic polymerizations. Although ATRP was applied to PVC-co-poly(vinyl chloroacetate) by Matyjaszewski[54] (see **section 3:** copolymerizations), the first example of ATRP directly on PVC was in 2001 when Percec studied the inherent reactivity of the different types of chlorines in PVC.[55] Through a series of model reactions, it was determined that the secondary chlorides of PVC do not act as ATRP initiators. However, PVC includes tertiary and allylic chlorides as defect sites along the backbone. The allylic chlorides in particular, and to a lesser extent the tertiary chlorides, are capable of initiating ATRP. After determining this, the authors performed several graft polymerizations on PVC with different monomers (**Scheme 2.4**). Poly methyl methacrylate and poly 4-chlorostyrene side chains were found to be antiplasticizing, but grafting poly n-butyl acrylate from PVC decreased the T_g value to -4 °C.

[Scheme 2.4]

In two studies, Bicak et al. grafted ethylhexyl acrylate (EHA) from the defect sites of PVC (**Scheme 2.5**). The polymerization was done first in dichlorobenzene,[56] then adapted to work in a water suspension for a more cost effective and greener synthesis.[57] A hydrophobic ligand was used to ensure the copper stayed in the organic phase. The T_g value of the modified polymer was 58 °C.

[Scheme 2.5]

Several studies by both the Hong group[58,59] and the Kim group[60,61,62,63] have grafted polyoxyethylene methacrylate (POEM) from PVC defect sites. In all cases the polymerizations were done at 90 °C in N-methylpyrrolidinone (NMP) with catalytic CuCl and

hexamethyltriethylenetetramine (HMTETA) as the ligand (**Scheme 2.6**). In all but one of these cases, two separate T_g values were seen, indicating phase separation. The T_g values are given in **Table 2.1**, with the lower T_g corresponding to the POEM phase and the higher T_g corresponding to the PVC phase. In one example[63] a single T_g value was observed but phase separation was still seen by TEM, so the second T_g may have simply not been visible due to the relatively small amount of PVC in the final material.

[Scheme 2.6]

[Table 2.1]

In another study by the Kim group,[64] ionic liquid polymers were grafted from PVC (**Scheme 2.7**). This also led to phase separation, with two T_g values: 55°C and 88°C. The graft copolymer with 65 % ionic liquid by weight showed higher elongation at break and lower tensile strength and modulus than pure PVC.

[Scheme 2.7]

Poly(*N,N*-dimethylaminoethyl methacrylate) has also been explored as a plasticizing side chain (**Scheme 2.8**).[65] After grafting, the T_g value decreased to 58 °C for polymers with 57% of internal plasticizer by weight. The graft polymerization was carried out at the relatively low temperature of 65 °C, due to the higher reactivity of methacrylate compared to acrylate monomers.[66]

[Scheme 2.8]

In 2014, Liu and Bao[67] used Activators ReGenerated by Electron Transfer (ARGET) ATRP to graft polybutyl acrylate from a specially prepared PVC with an increased number of allylic defect sites (**Scheme 2.9**). Copper chloride and tris(pyridylmethyl)amine (TPMA) ligand were used, along with diethylhexyl tin ($Sn(EH)_2$) which acts as a reducing agent to regenerate the

active Cu^I species. This allows the reaction to be run with only 0.1 mol% copper, although the potential for tin residues becomes a concern with 5 mol% tin being used. The T$_g$ of the resulting PVC-g-PBA was 8 °C.

[Scheme 2.9]

In two studies in 2021, Li and Braslau used ATRP to grow copolymers of butyl acrylate and 2-(2-ethoxyethoxy)ethyl acrylate (2EEA) as grafts from a PVC backbone: PVC-*g*-(PBA-*co*-P2EEA) (**Scheme 2.10**).[68,69] The ratio of BA to 2EEA was varied; all resulting polymers had T$_g$ values below 0 °C, with the lowest being -50 °C, and each had a single T$_g$ value, indicating the lack of phase separation. The process was scaled up from 2g to 14g with similar results observed at both scales. In the second study, they varied the ratio of plasticizer to PVC, allowing them to tune the T$_g$ value anywhere between 54 °C and -54 °C.

[Scheme 2.10]

In contrast to the plasticizing side chains discussed above, many monomers have been found to produce *antiplasticizing* side chains when grafted from PVC. These monomers include ethyl acrylate,[70] methyl methacrylate,[55,71] *tert*-butyl methacrylate,[72] hydroxyethyl methacrylate,[73] 3-sulfopropyl methacrylate,[74] styrene,[75,76] 4-chlorostyrene,[55] and 4-vinyl pyridine.[77] Methods for adding these graft copolymers include traditional free radical polymerization,[70] ATRP,[55,71,72,73,74,75,77] and nitroxide-mediated polymerization.[76]

3 Polymerization of Monomers with Vinyl Chloride to Internally Plasticize PVC

Internal plasticization of PVC by copolymerization of vinyl chloride (VC) with other monomers with has been investigated since the 1930s. These strategies include forming linear copolymers as either random copolymers or block copolymers. In addition, a few approaches have

been developed that entail PVC copolymers as part of more elaborate polymeric architectures. The field of using blends of PVC with macromolecular plasticizers does not constitute internal plasticization, and while important, will only be reviewed in this article when the macromolecular plasticizer contains blocks of PVC. Both uncontrolled traditional radical polymerization in solution or in emulsion as well as reversible deactivation radical polymerization[78] of vinyl chloride has been utilized.

3.1 *Random Copolymerization of Monomers with Vinyl Chloride to Achieve Internal Plasticization*

In 1936, Curme and Douglas[79] wrote in *Industrial and Engineering Chemistry* "unplasticized polyvinyl chloride had such a high softening temperature that it was found difficult to use in standard molding practice." The copolymerization of vinyl chloride and vinyl acetate (VAc) produced what they described as a "conjoint polymer," forming a series of five types of materials that were trademarked as Vinylite.™ The classifications of Vinylites varied from hard, durable, high tensile strength materials to increasingly softer materials, most made with 85 - 88% VC and 15 - 12% VAc, with the softest "Vinyloid" finishes used in lacquers made of 65% VC and 35% VAc. All were differentiated by average molecular weights, ranging from 15,800 to 5,800. Four years later, the Carbide and Carbon Chemicals Corporation[80] had expanded the average molecular weight ranges from 25,000 for the hardest materials, to 6,000 for the softest. An iconic example of Vinyloid™ use in commercial products was in phonographic records replacing those made of shellac in the early to mid-1900s. Extensive investigation into PVC-*co*-PVAc random copolymers by Staudinger and Schneiders[81] in 1939 gave polymers with varying amounts of VC incorporation, which were separated by fractional precipitation, suggesting non-homogeneous

polymer formation. This was an early hint at reactivity ratios:[82] the growing radical chain adds to VC faster than to VAc.

The random copolymerizations of VC with a variety of monomers were investigated; a review by Liepins in 1969[83] entitled "Some Observations on Internal Plasticization of Polyvinyl Chloride" summarized work by various authors on vinyl esters with longer and varied R groups beyond vinyl acetate, as well as acrylates, methacrylates and crotonates. The conclusions in this review for effective internal plasticization of PVC entailed: (1) use of comonomers of solubility parameter around 8.5 or 10.5 $cal^{1/2}cm^{-3/2}$, (2) use of high molecular weight (long chain) comonomers in a low molar ratio, and (3) their non-uniform incorporation in the PVC chain. In particular, Liepins' work with Marvel and Magne from 1967[84] on the random copolymerization of VC with PEG_{750} acrylates (PEG repeat units of 16-17, solubility parameter = 8.4) (**Scheme 3.1**). is notable, preparing copolymers with 70-84% VC and 30-16% PEG acrylate . The flexible 78/22 material demonstrated a milling temperature of 240 °F, far lower than the comparison material made of 95/5 VC/VAc + 25% DEHP external plasticizer with a milling temperature of 340 °F.

[Scheme 3.1]

Our own group has collaborated with Coelho[85] in the random solution radical polymerization of VC with acrylates bearing a flexible hexyl tether connected to a triazole mimic of the phthalate DEHP: "DEHT" (di-2-ethylhexyl triazole). This triazole is conveniently prepared by mild thermal Huisgen cycloaddition of the corresponding azide with the acetylene diester. A variety of materials were prepared with varying ratios of VC/DEHT hexyl acrylate (DEHT-HA), with T_g values ranging from 78 to -27 °C as measured by dynamic mechanical thermal analysis (DMTA).

[Scheme 3.2]

Hanna and Fields[86] utilized micro-dispersed suspension radical polymerization to create random copolymers of VC with 1.0 to 5.5 wt. % of ethylene monomer (**Scheme 3.3**). As the VC monomer was consumed faster than the ethylene monomer, the autoclave reactor was automatically vented during the polymerization to keep the pressure constant and the molar ratio of VC to ethylene unchanged. The copolymer was compounded with a barium stabilizer plus 9 phr (parts per hundred parts PVC) DEHP, giving a blend that was slightly better than PVC + 20 phr DEHP in terms of T_g and tensile properties, leading the authors to conclude that the polyethylene copolymer is more effective than DEHP as a plasticizer. However, even at 5.5% polyethylene, crystallinity was still present in all variations of copolymers examined.

[Scheme 3.3]

3.2 *Block Copolymers of PVC with Polyesters or Polyethers to Achieve Internal Plasticization: AB, ABA and (AB)$_x$ Copolymers*

In recent work, Feng, Moad and Thang[87] prepared PVC-*b*-PCL as a macro-plasticizer by Reversible Addition Fragmentation chain Transfer (RAFT) polymerization of VC, followed by Ring Opening Polymerization (ROP) with ε-caprolactone which provided the second polycaprolactone (PCL) block (**Scheme 3.4**). A xanthate initiator bearing a primary terminal hydroxy group provided **PVC-OH**, which was then subjected to ROP polymerization with ε-caprolactone catalyzed by the mild acid diphenyl phosphate to form **PVC-*b*-PCL**. The length of the PCL block was varied: a PVC_{10K}-*b*-$PCL_{89.5K}$ diblock material (subscripts denote the molecular weight in kilodaltons) when blended with PVC gave better plasticization and no migration, as compared to a similar blend of PVC with conventional DEHP. Small amounts of PVC-*b*-PCL suppressed migration of PCL from PVC/PCL blends.

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[Scheme 3.4]

Coelho[88,89,90] has prepared ABA triblock copolymers of PVC-*b*-PBA-*b*-PVC to instill flexibility into PVC, taking advantage of the elastomeric properties of poly(*n*-butylacrylate) (PBA). The use of a symmetrical bidirectional α,ω-diiodo macroinitiator, easily prepared from iodoform,[91] using Single-Electron Transfer Degenerative Chain Transfer Living Radical Polymerization SET-DTLRP,[92] builds the triblock copolymer from the middle outwards (**Scheme 3.5**). Hydroxypropyl methylcellulose "Methocel F50" and partially hydrolyzed poly(vinyl alcohol) were used as suspension agents, and the synthesis was successfully demonstrated on a 5 L pilot reactor scale. PVC content ranged from 19-80% on scale-up and molecular weights of the PBA + PVC blocks varied from 11K + 38 K for the shortest, to 115K + 94K (K = kiloDaltons), with T_g values ranging from 56 °C to -16 °C, as measured by DMTA. Increasing the relative amount of the elastomeric PBA block compared to the PVC blocks gave the greatest depression in T_g values. However, despite the low T_g values, the mechanical properties were disappointing, with low elongation capacities.

[Scheme 3.5]

Inspired by the use of macro-diazo initiators used to make ABA triblock copolymers of PVC-*b*- (polyether)-*b*-PVC by Furukawa, Takamori and Yamashita[93] in 1967, Laverty and Gardlund[94] in 1977 applied this strategy to the preparation of ABA triblock copolymers of **PVC-*b*-PEG-*b*-PVC** with the specific aim of internal plasticization. Polyethylene glycol (PEG) diols of varying molecular weights were converted into macro-diazo initiators for emulsion or solution polymerization of VC (**Scheme 3.6**). They were able to incorporate up to 15 wt % of PEG in these PVC materials; attempts to include a larger PEG component resulted in extensive graft copolymerization off of the PEG backbone.

[Scheme 3.6]

Four years later, Laverty and Gardlund[95] prepared (AB)$_x$ block copolymers by condensation polymerization using carbamate (urethane) linkages to connect PVC to several different plasticizing polyether blocks: poly(propylene oxide) (PPO), and poly(tetramethylene oxide) (PTMO). This strategy prevents the undesired grafting observed during VC polymerization in their 1977 work. PVC α,ω-diols were prepared by ozonolysis followed by reduction of commercial PVC (containing some alkene due to elimination of HCl). These were then condensed by tin catalyzed isocyanate addition with di-isocyanate capped polyether blocks prepared from the corresponding polyether α,ω-diols and 4,4′-methylenebis(phenyl isocyanate) (**Scheme 3.7**). Polyester blocks (polycaprolactone and poly(4-butylene adipate) were likewise investigated, as was a more flexible diisocyanate linker.

[Scheme 3.7]

3.3 *Macromolecules of Complex Architecture containing PVC blocks as Compatibilizers and Plasticizers*

In 1998, Paik and Matyjaszewski used a commercially-made random copolymer of VC and vinyl chloroacetate to prepare brush-like copolymers of PVC (**Scheme 3.8**).[54] The chloroacetate groups acted as ATRP initiators, allowing the growth of other polymer chains from the PVC backbone. Using this method, styrene, methyl methacrylate, methyl acrylate, and butyl acrylate were polymerized. Methyl acrylate and butyl acrylate acted as plasticizers: a PVC brush with 50 mol% methyl acrylate had a T_g value of 21 °C, and a PVC brush with 65 mol% butyl acrylate had a T_g value of -19 °C.

[Scheme 3.8]

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Very recently, Feng, Moad and Thang[96] prepared mikto-star polymers containing a PVC block as well as PBA blocks as elastomeric plasticizers using RAFT polymerization (**Scheme 3.9**). A mikto star is an asymmetrically substituted star polymer in which at least one arm is non-identical to the other arms. The initial RAFT polymerization utilized a xanthate (dthiocarbonate) initiator, which is effective in reacting with "Less Active Monomers," enabling controlled growth of a PVC block. Esterification with two trithiocarbonate RAFT initiators (which react with "More Active Monomers") allowed simultaneous growth of PBA blocks as two new arms of the star, and chain extension to provide a PVC-*b*-PBA arm. The T_g value of this exotic mikto-star was -36 °C: blends with PVC gave no migration of the plasticizing mikto-star into hexane, however no T_g values were reported for the PVC blends.

[Scheme 3.9]

In the quest for phthalate-free plasticized PVC, the groups of Pan and Zhong[97] have prepared latex composites made of approximately 180 nm diameter cross-linked "seeds" of PBA formed by emulsion polymerization, followed by polymerization of predominately VC in the presence of partially hydrolyzed and condensed hydrophilic 3-(trimethoxysilyl) propyl methacrylate, and allyl methacrylate to provide colloidal particles of a PBA/PVC latex. Addition of BA, expected to swell these particles, followed by emulsion polymerization provided an undefined latex composite material, termed "flower-like latex particles" by the authors. Films made of this complex PBA-PVC composite + 2.5% by weight of the organotin heat stabilizer tin Beijing 8831 were compared to conventional mixes of PVC with DEHP (3:2 by weight) + 1.5% by weight heat stabilizer tin Beijing 8831: the mechanical properties were compared. The flexibility using these composites was evaluated as comparable and the stretchability superior.

Conclusion

Why has DEHP reigned as the most popular plasticizer for PVC, prior to bans due to health concerns? DEHP is miscible with the amorphous regions of PVC; the branched 2-ethylhexyl chain helps break up potential ordered stacking, while maintaining significant contact between the plasticizer and the polymer chain. The stereogenic center at the ethyl-2-hexyl junction adds to the disorder as there are two stereogenic centers, giving a total of three diastereomers of this branched phthalate molecule: (R,R), (S,S) and *meso*.

Chemists have utilized a number of experimental probes to formulate an understanding as to how DEHP (and presumably related phthalates) interacts with PVC. In 1975, Tabb and Koenig[98] used FT-IR spectroscopy, finding that the ester carbonyl stretching frequency changes in relation with the amount of plasticizer added to PVC, and suggested bonding between the ester carbonyl oxygen and the chlorine atom on the polymer. In 1996, Sivaran[99] used solid-state ^{13}C NMR, focusing on spin-lattice relaxation times and spin-spin relaxation times to provide evidence for strong hydrogen bonding between the ester carbonyl oxygen and the methine hydrogen on the carbon bearing chlorine in the PVC chain. More recently, Wang and Xue[100] in 2014 used ^{1}H NMR and FT-IR spectra coupled with calculations to postulate a three-centered hydrogen bond between the two proximal ester carbonyl oxygens and the hydrogen on the methine carbon bearing chlorine. Saunier[101] has suggested both dipolar interactions as well as hydrogen bonding as important factors in the interactions of DEHP with PVC. Overall, these studies indicate that the 1,2-diester motif is useful in bonding DEHP to the PVC backbone, either through dipolar or hydrogen bonds. With an internal plasticizer, this H-bonding is replaced with a covalent bond, making the diester motif unnecessary. Our work on covalent triazole monoester plasticizers and polyacrylate graft copolymers on PVC indicate that internal plasticizers do not require 1,2-diester substitution, but

that the identity of the side chain is the more important factor. Polyether side chains are particularly effective plasticizers, most likely due to their good miscibility with PVC.

Does the aromatic group of phthalates play a significant role in plasticization? In Wang and Xue's study, they compared DEHP plasticizer with the cyclohexane 1,2-dicarboxylate analogue. Both ^{1}H NMR & FT-IR spectroscopies indicated stronger interaction of the cyclohexyl-based plasticizer with PVC compared to the traditional aryl phthalate, indicating that the benzene ring of phthalates is not required, but rather acts only as scaffolding to present the proximal ester groups. In our own work covalently attaching phthalates or triazole-phthalate mimics to the PVC chain, we found that immediate attachment of triazole diesters to PVC was inherently anti-plasticizing, much as the benzene rings instill rigidity into polystyrene. Both non-covalent and covalent plasticization need rotational and translational freedom of the plasticizers in order to permeate the PVC matrix and break up rigid regions between polymer chains. In this regard, internal plasticizers with flexible tethers are preferable to aromatic groups.

Different applications of PVC will demand different plasticizers, but for any internal plasticizer to be adopted, minimizing the overall cost and number of synthetic steps is paramount. The focus on utilizing unwanted industrial by-products as plasticizers (example: cardanol from the cashew nut industry) is attractive, as long as there is the potential supply for huge scale-up, and the number of synthetic steps is very low. Another consideration is the chemical stability of internal plasticizers over time. Covalent attachment of plasticizers using amine linkages may suffer from the amines acting as internal bases, leading to dehydrochlorination when the material is exposed to heat. Sulfide linkages can become oxidized to sulfoxides or higher oxidation states, with new chemical and mechanical profiles emerging as the chemistry of the covalent attachments change.

Embedding functionality that can scavenge HCl, such oxiranes in epoxidized soybean oil, may enhance the durability and longevity of the plasticized material over time.

In terms of minimizing the number of synthetic steps, graft polymerization and copolymerization methods are attractive strategies. The ability to polymerize grafts directly from defect sites in PVC allows for plasticization in a single synthetic step from commercial PVC, as long as the monomers used are readily available. Copolymerization with VC allows plasticized PVC to be prepared in a single step, but separate batches of PVC must be made for different degrees of plasticization. Additionally, these graft and copolymers are linked by carbon-carbon bonds and are thus expected to be stable over time.

It is costly for industry to change production of a huge scale, well-established commodity product where the overall supply chains, mechanical equipment, and waste stream treatments are already in place, and the overall performance of the final materials have been optimized. However, a change of course is already underway. The use of external plasticizers is an environmental insult, and for many small molecule plasticizers, a health danger. In addition, the plethora of "additive packages" to PVC makes recycling presently untenable. Internal plasticization decreases the need for these additives and increases the useful lifetimes of PVC products. Covalent attachment of plasticizers will grow in popularity as the cost drops and the benefits of attached plasticizers are either enforced by legislative decree or demanded by consumers.

Disclosure statement

The authors have no competing interests.

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Table 2.1 T_g values for PVC-*g*-POEM

Source	T_{g1} (ºC)	T_{g2} (ºC)
[58]	-68	32
[59]	-67	34
[60]	-57	30
[61]	-58	70
[62]	-62	96
[63]	-59	–

Scheme 1.1

Michel:

del Val:

Scheme 1.2

Scheme 1.3

R = -OH   -NH₂   -NMe₂

Strongly antiplasticizing

Slightly antiplasticizing

Slightly plasticizing

Scheme 1.4

NaS–Ar

Cyclohexanone
60 °C

Ar=

Increasing plasticization efficiency

Scheme 1.5

C₈H₁₇=2-ethylhexyl

Scheme 1.6

R:

C₈H₁₇=2-ethylhexyl

ortho or para

<div align="center">Scheme 1.7</div>

	Y₁	R₁	Y₂	R₂
1	N(C₈H₁₇)	C₈H₁₇	N(C₈H₁₇)	C₈H₁₇
2	N(C₄H₉)	C₄H₉	N(C₄H₉)	C₄H₉
3	O	C₂H₅	N(C₈H₁₇)	C₈H₁₇
4	O	C₈H₁₇	O	C₈H₁₇
5	S	C₆H₁₃	S	C₆H₁₃

TCTA

<div align="center">Scheme 1.8</div>

R= H, nButyl, 2-ethylhexyl,
and mixtures of isomers of C₁₃H₂₇

Jeff600	x=9, y=1
Jeff1000	x=3, y=19
Jeff2005	x=29, y=6
Jeff2070	x=10, y=31
Jeff3085	x=8, y=58

TCTA

Scheme 1.9

Scheme 1.10

Scheme 1.11
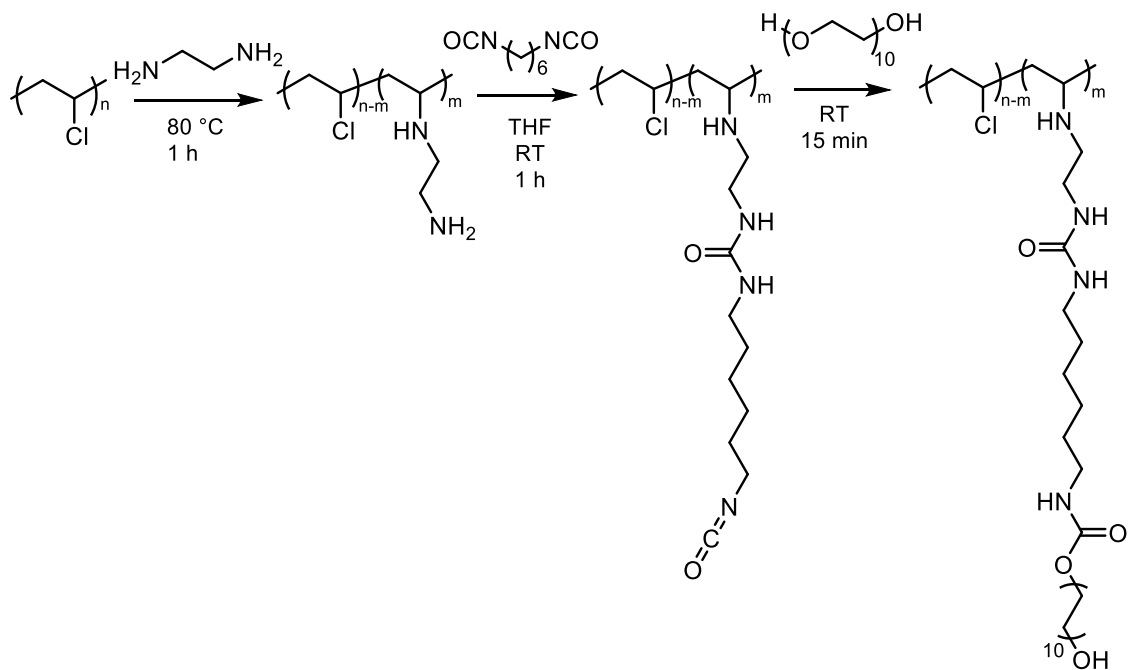
Scheme 1.12
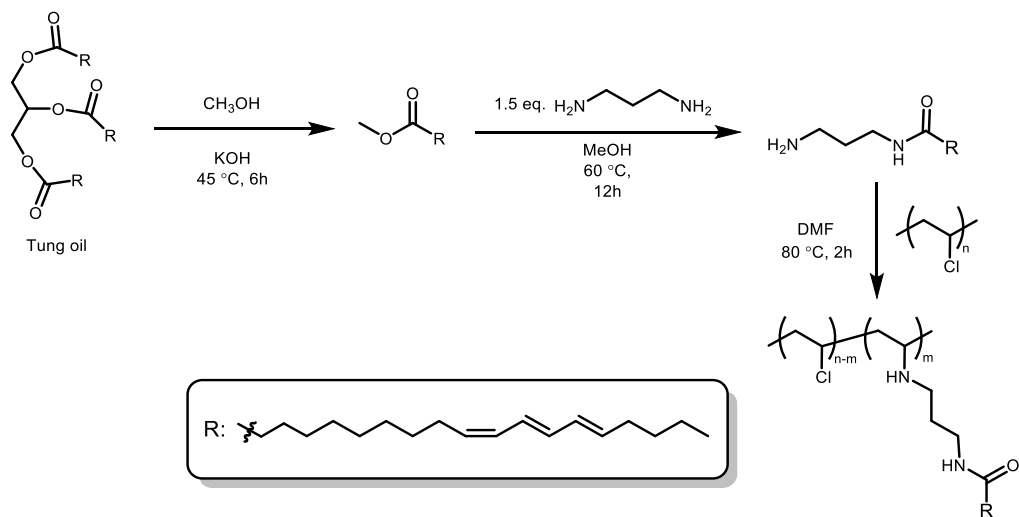
Scheme 1.13
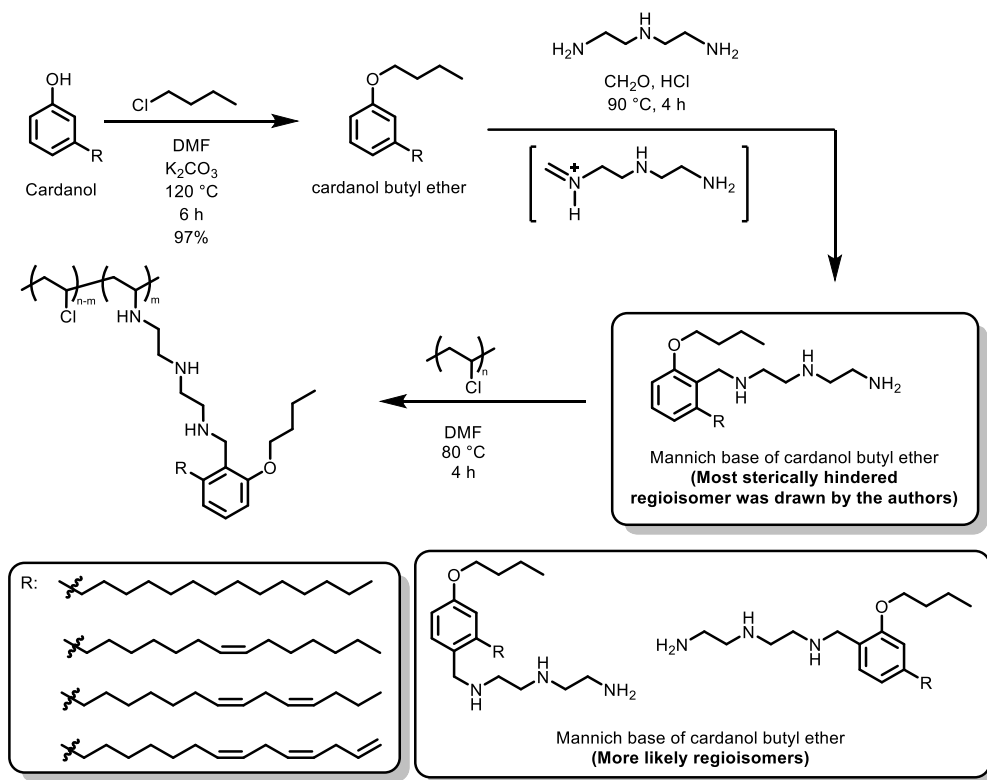
Scheme 1.14
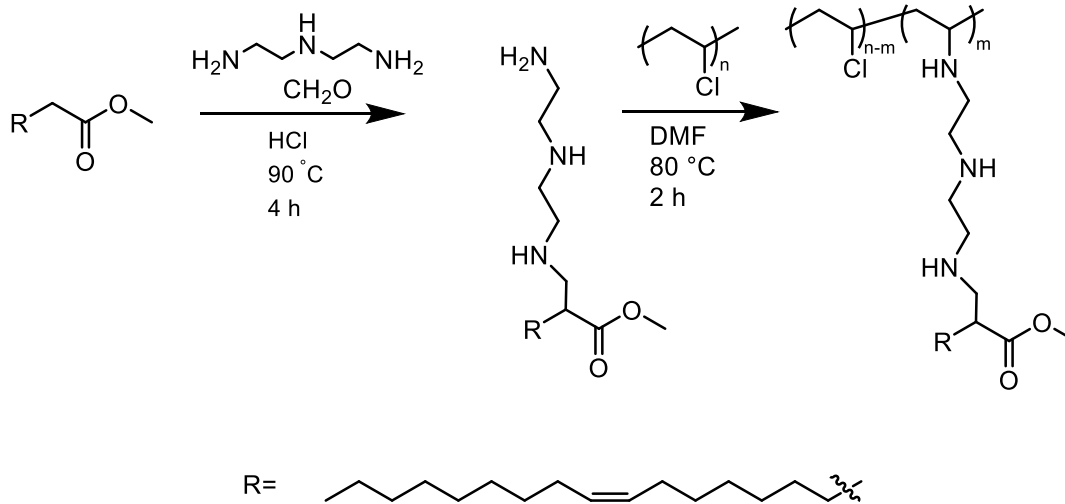
Scheme 1.15
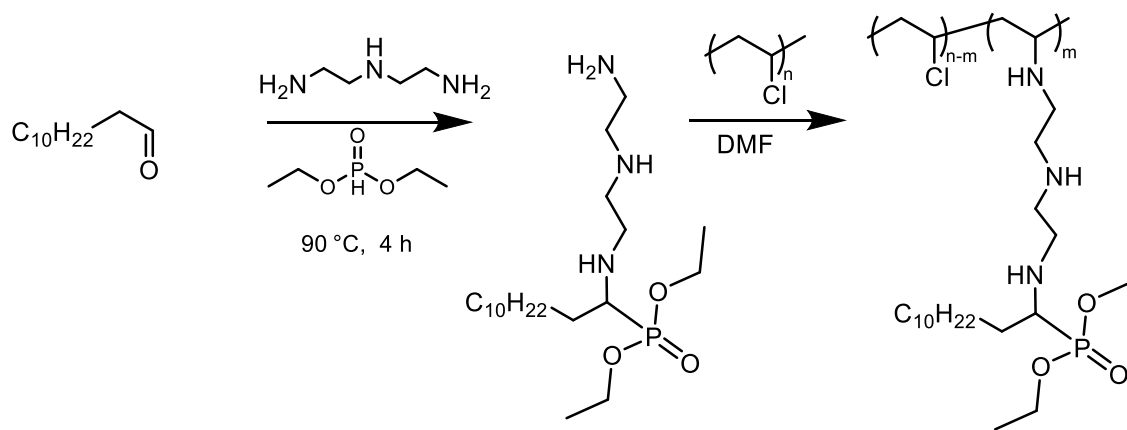
Scheme 1.16
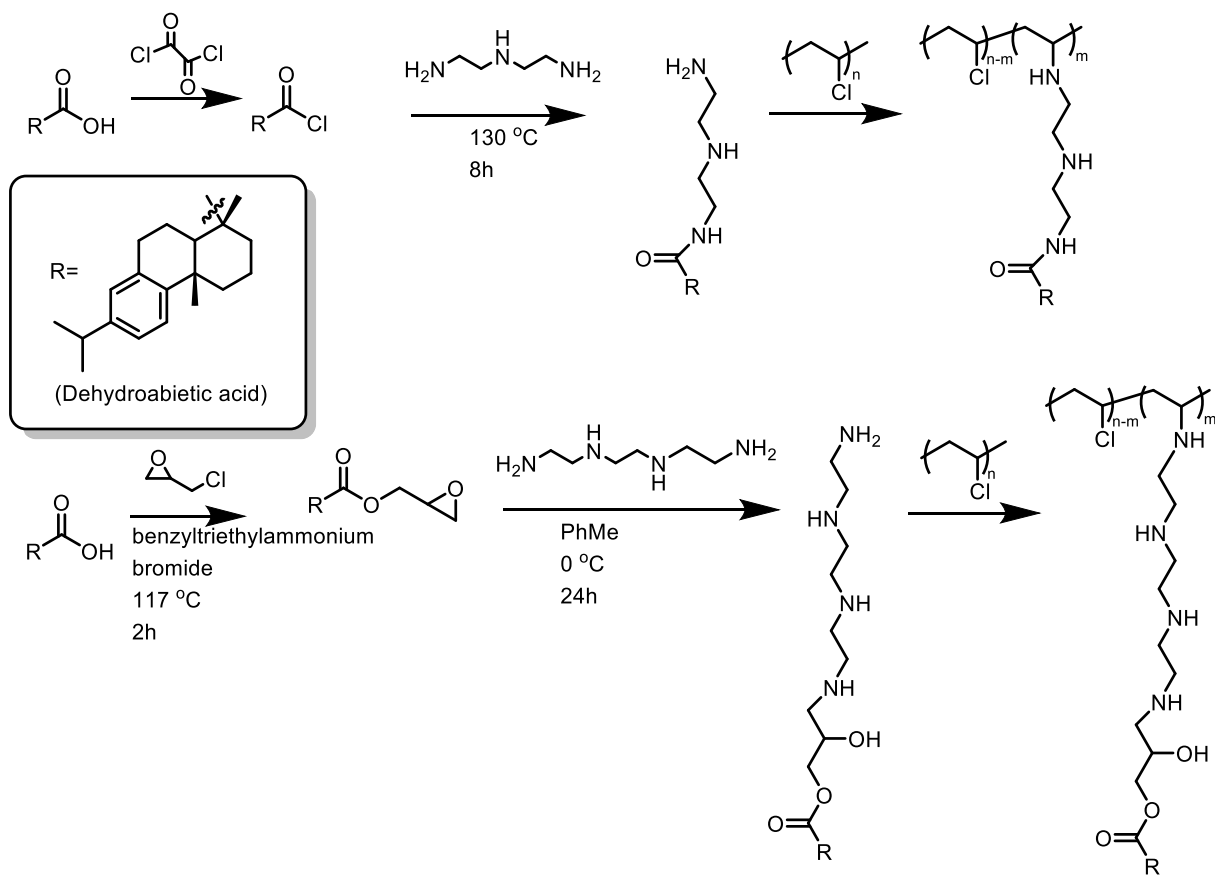
Scheme 1.17
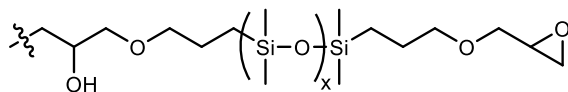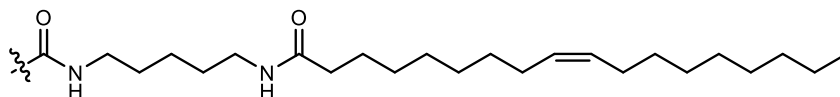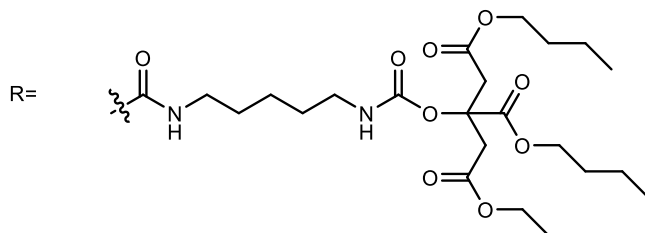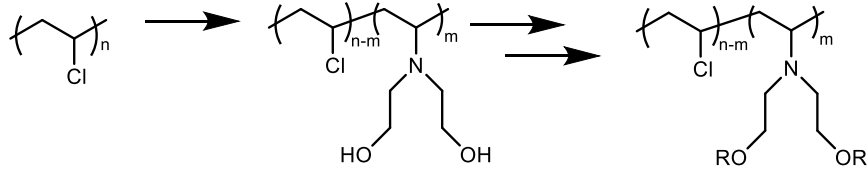
Scheme 1.18

Scheme 1.19

Figure 1.1

Scheme 1.20

Scheme 1.21

Scheme 1.22

48
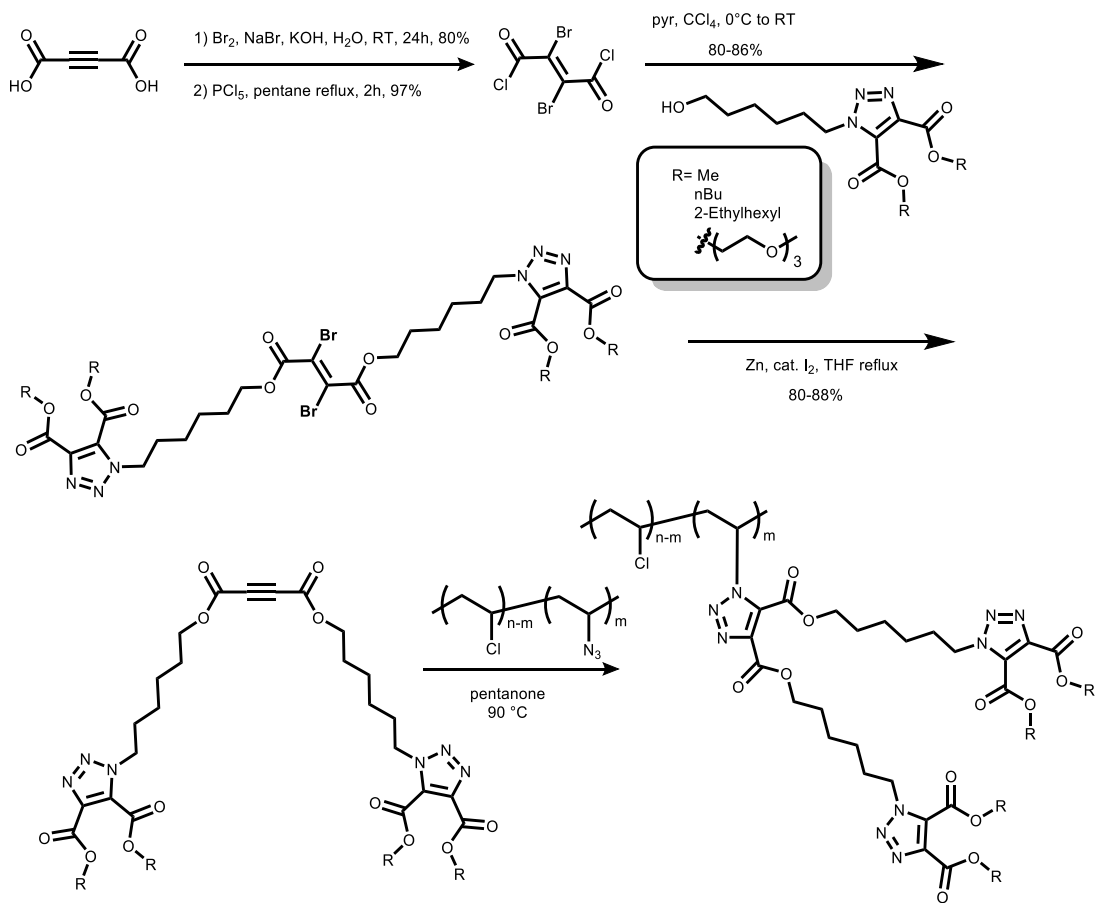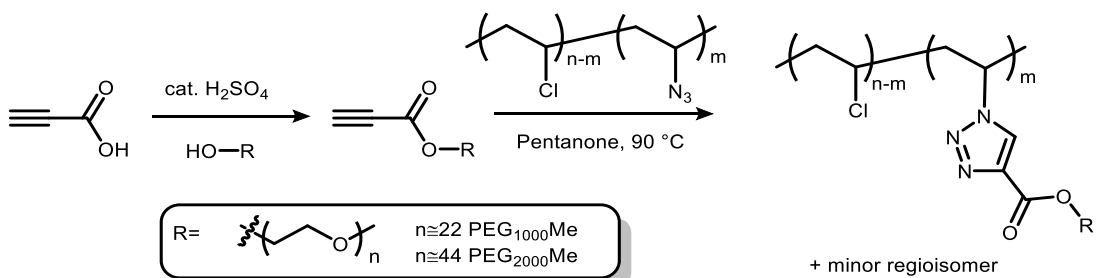
Scheme 1.23

Scheme 1.24

Scheme 1.25
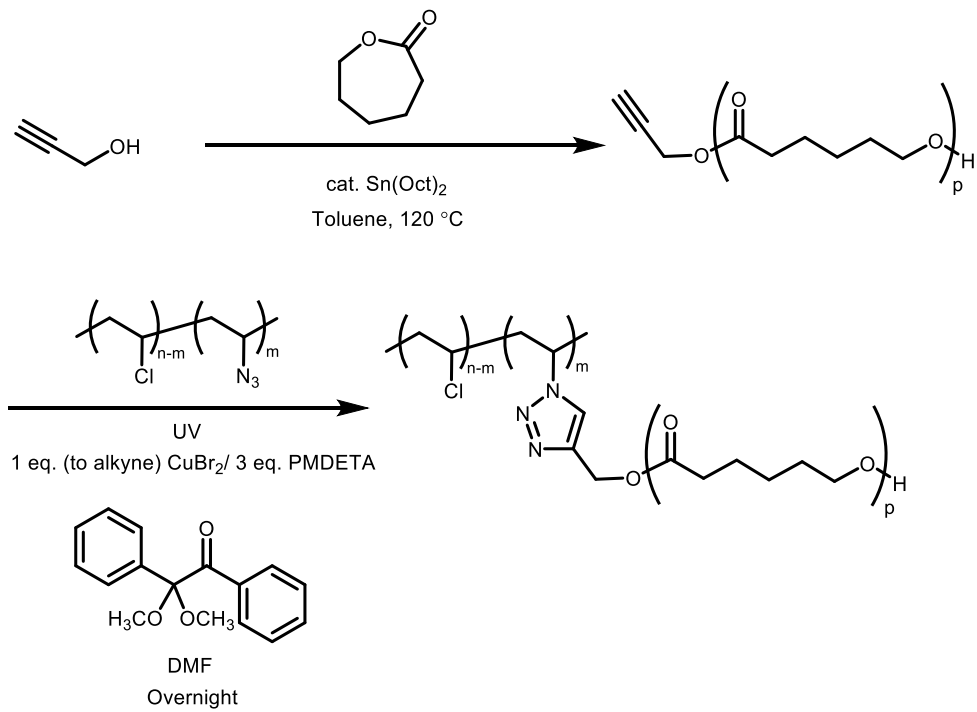
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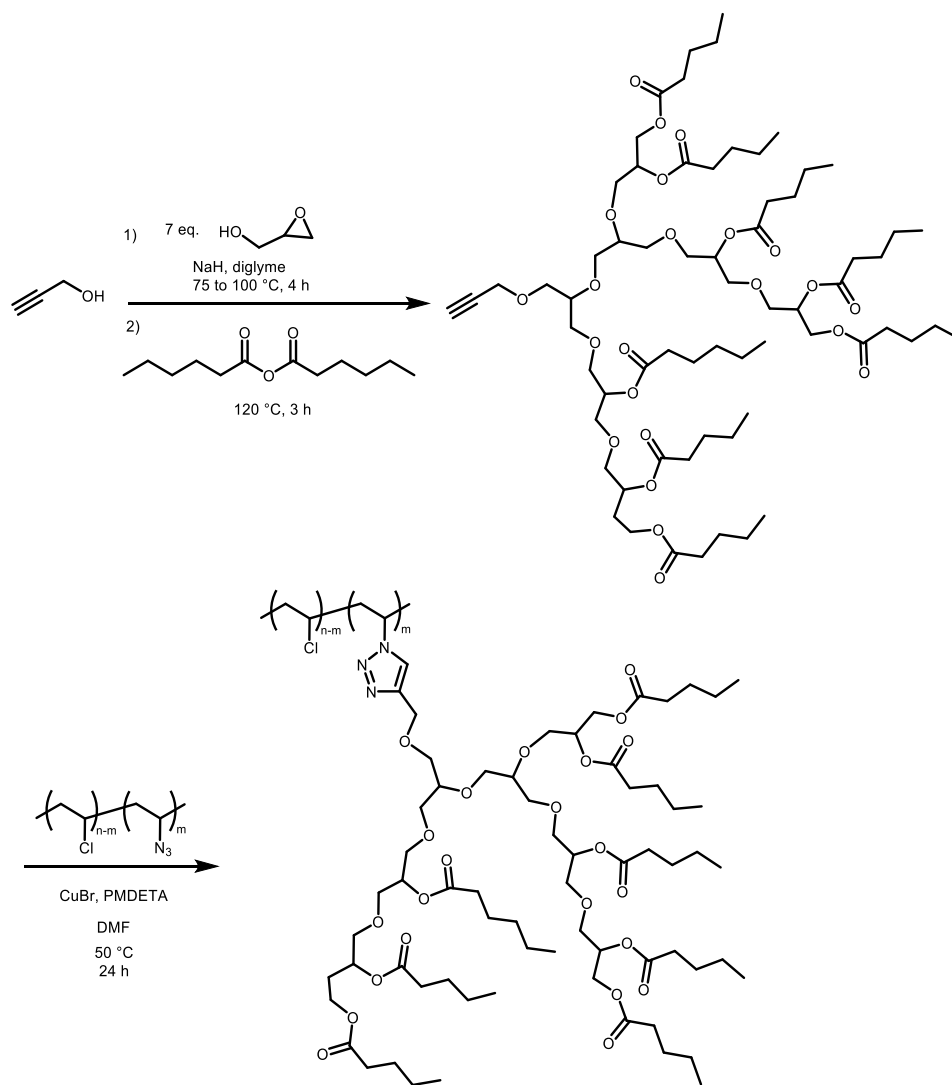
Scheme 1.27

Scheme 1.28
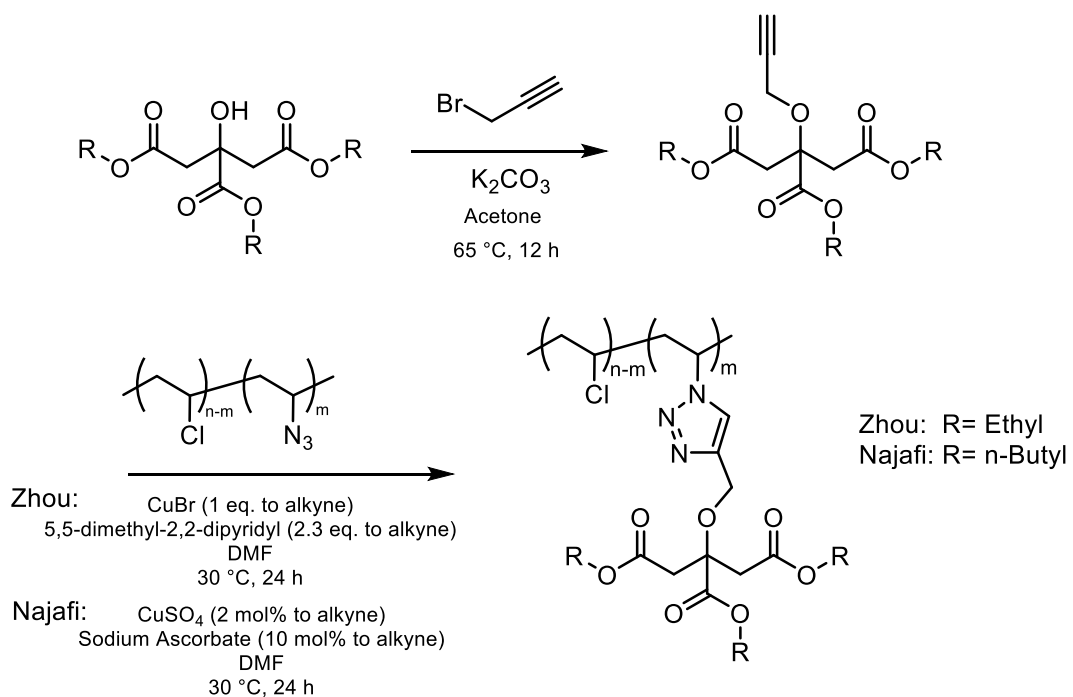
Scheme 1.29
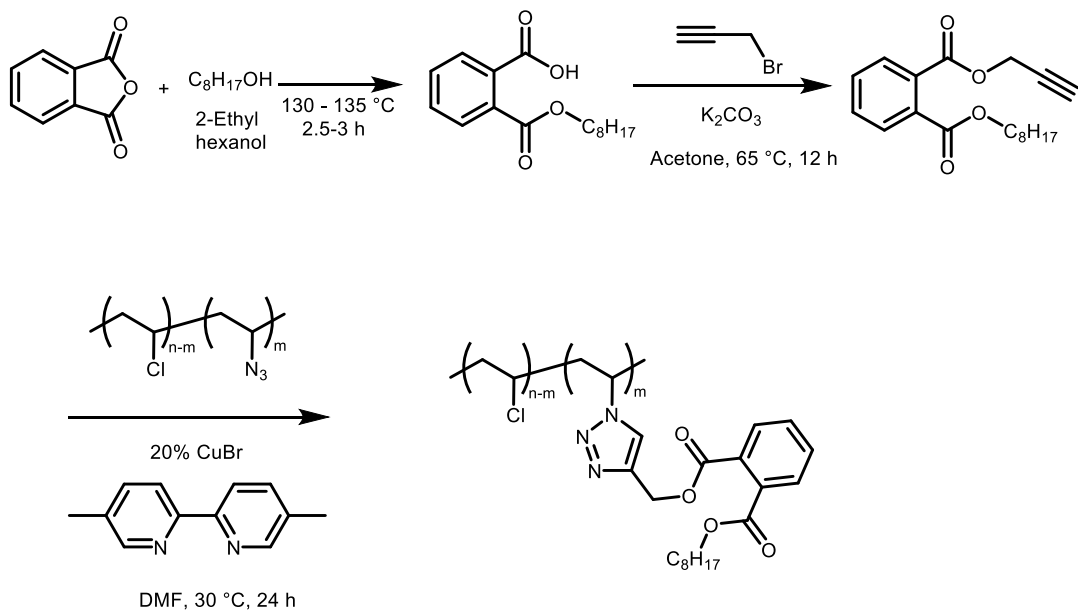
Scheme 1.30
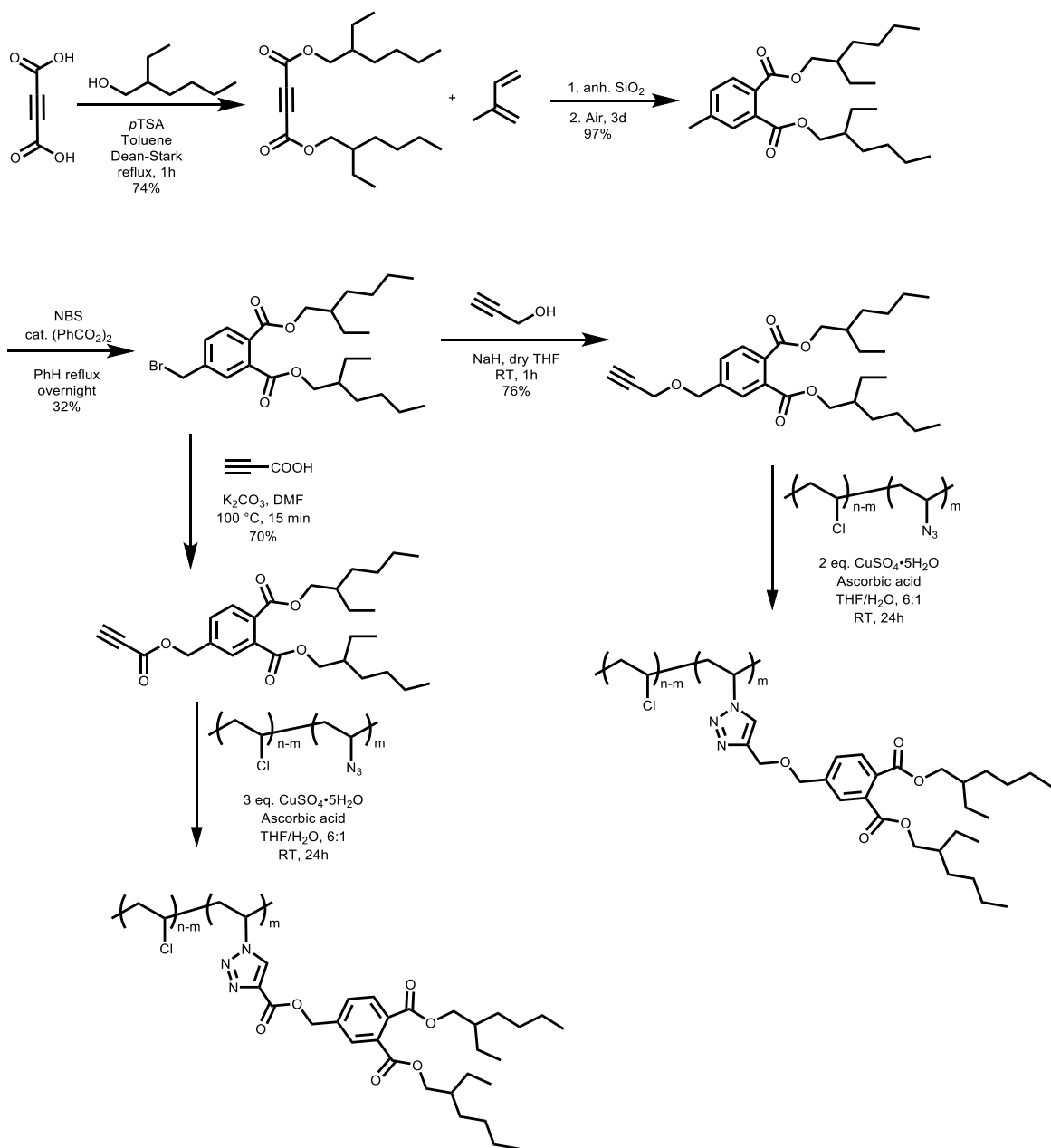
Scheme 1.31
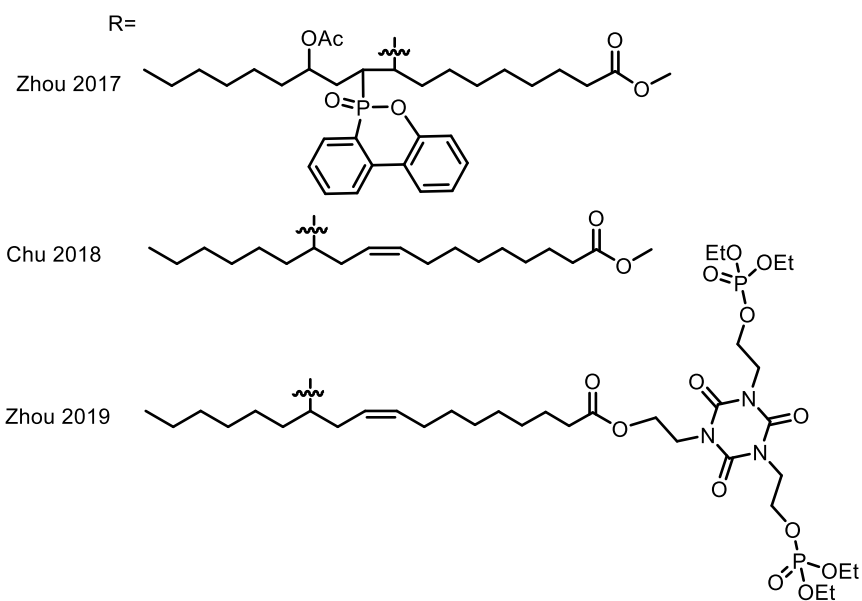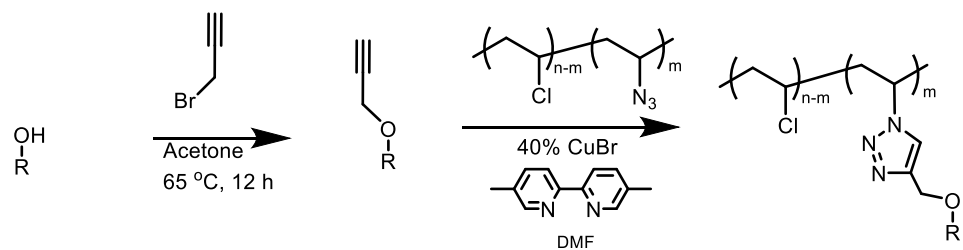
Scheme 1.32

Scheme 1.33

Scheme 2.1

neat 170 °C
5 min

Scheme 2.2

cyclohexanone
50 °C
3.5 h
vacuum

cyclohexanone
50 °C
3.5 h
vacuum

Scheme 2.3

cat. Cu₂O
Ph₂O 120 °C
2 h
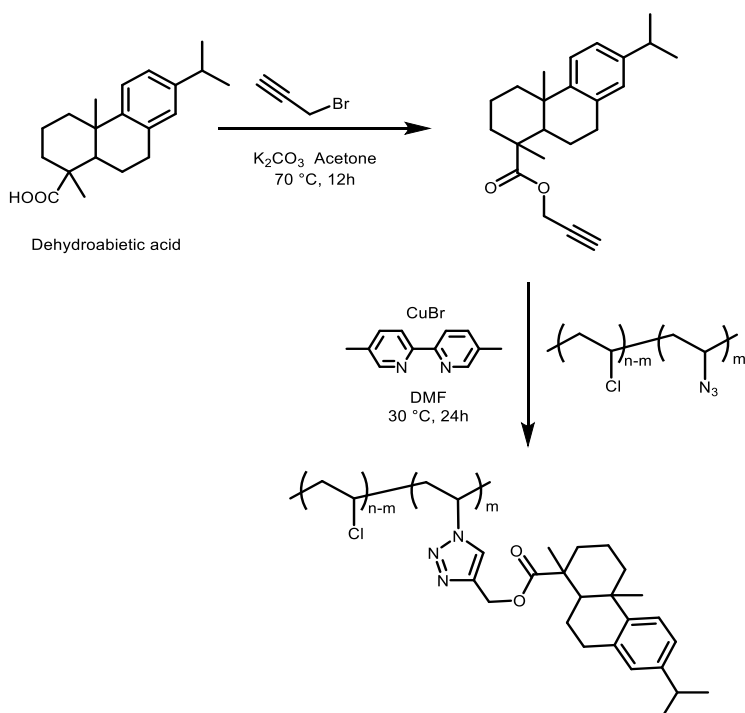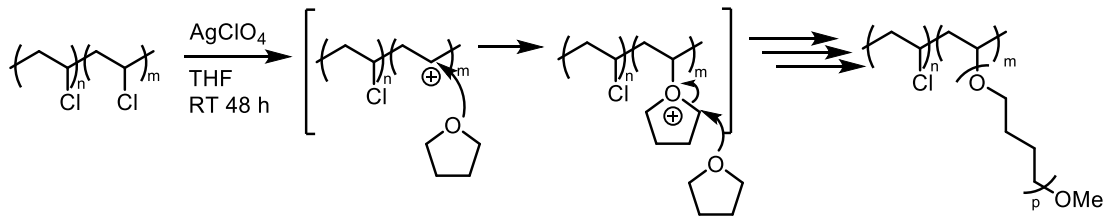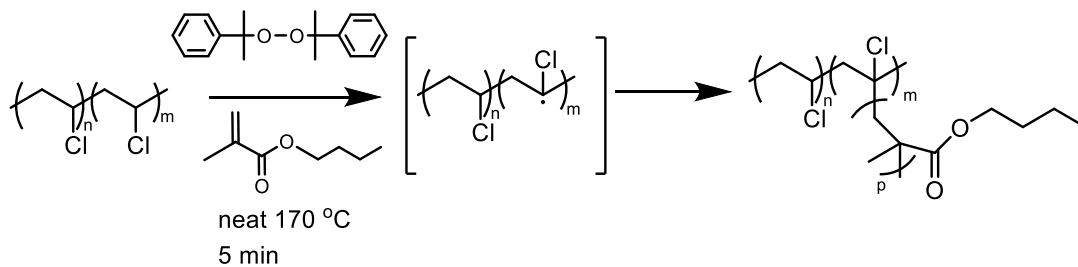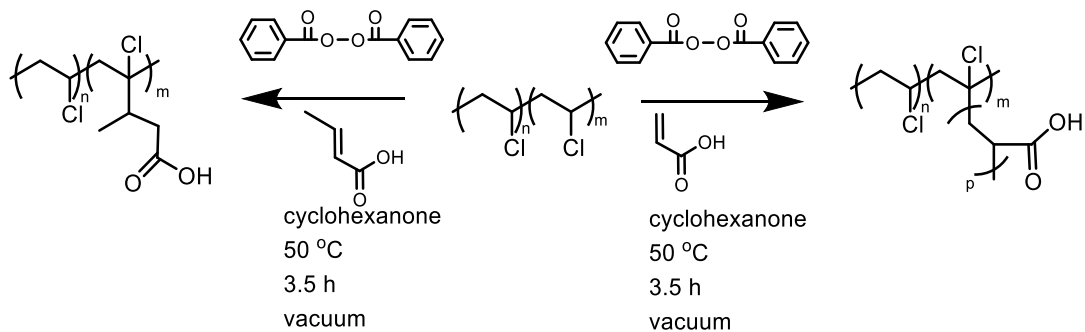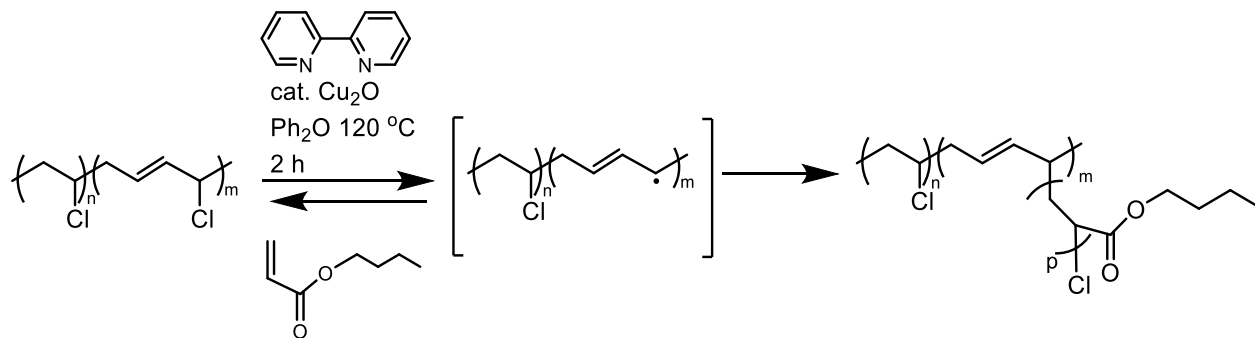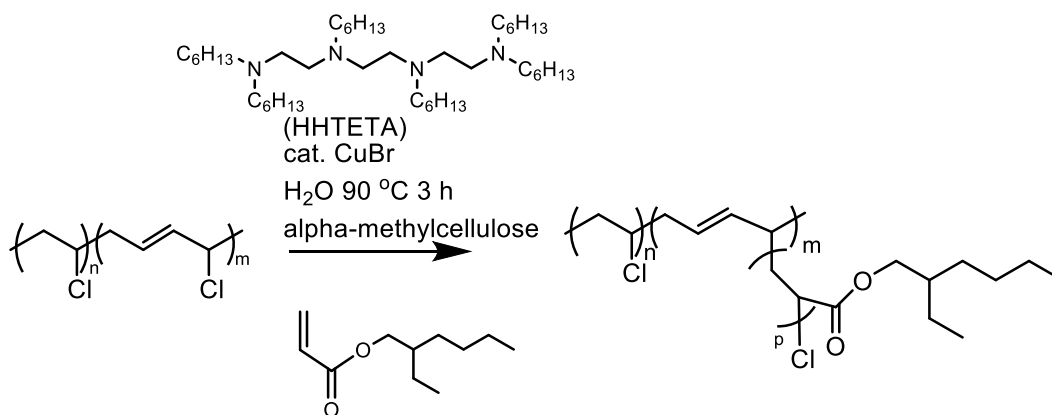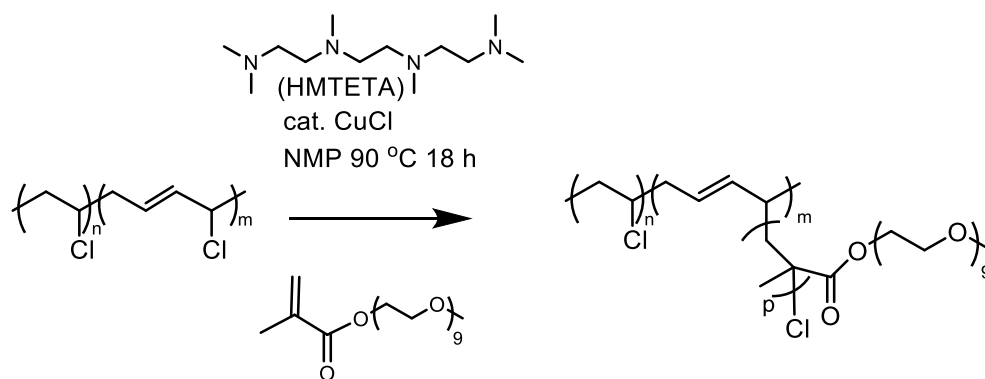
Scheme 2.4

Scheme 2.5

Scheme 2.6
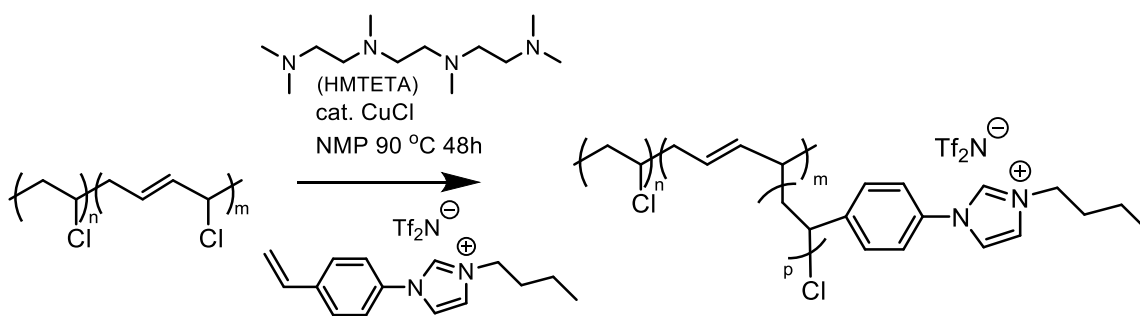
Scheme 2.7
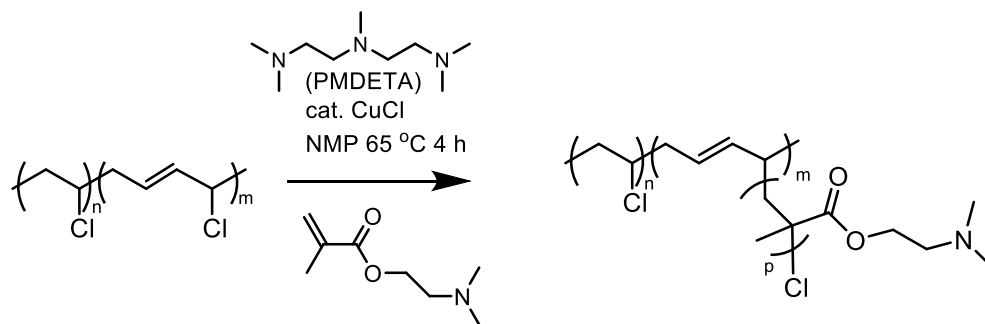
Scheme 2.8

Scheme 2.9

Scheme 2.10

Scheme 3.1

"hexyl acrylate"

DEHT,
a phthalate mimic

PVC-*r*-P(DEHT-HA)

Scheme 3.2

PVC-*r*-PE

Scheme 3.3

Scheme 3.4

Scheme 3.5

Scheme 3.6

polyether diols:

HO—PPO—OH = HO$\left(\right.$CH$_2$—O—CH$_2\left.\right)_n$OH

HO—PTMO—OH = HO$\left(\right.$CH$_2$CH$_2$CH$_2$CH$_2$—O$\left.\right)_n$OH

O=C=N— ... —N=C=O
2.03 equiv.

HO—polyether—OH
80 - 100 °C
neat

O=C=N— ... —NH—C(=O)—O—polyether—O—C(=O)—NH— ... —N=C=O

1. O$_3$
2. O$_2$
3. LiAlH$_4$

PVC → HO—PVC—OH

cat. Bu$_2$Sn(O—C(=O)—C$_{11}$H$_{23}$)$_2$
cat. Et$_3$N
DMF, 80 °C

EtOH capping agent

Et—O—C(=O)—NH— ... —NH—C(=O)—O—polyether—O—C(=O)—NH— ... —NH—C(=O)—O—PVC—O$\left.\right]_n$

(A-B)$_x$ alternating copolymer   **(polyether-*b*-PVC)$_n$**

Scheme 3.7

cat. Cu$_2$O
Ph$_2$O 120 °C
2 h

Scheme 3.8

Scheme 3.9

Scheme 3.6 PEG-containing diazomacroinitiator forms ABA triblock **PVC-*b*-PEG-*b*-PVC** copolymers via free radical polymerization

Scheme 3.7 Condensation polymerization to form alternating copolymer **(PVC-*b*-polyether)$_n$** for internal plasticization

Scheme 3.8 Brush copolymers grown from a PVC-*r*-(vinyl chloroacetate) macroinitiator

Scheme 3.9 Synthesis of **mikto star-[PVC-*b*-PBA;(PBA)$_2$]**: an exotic internal plasticizer, and possible external macroplasticizer