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Phthalate Plasticizers Covalently Bound to PVC: Plasticization with Suppressed Migration

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ABSTRACT: The internal plasticization of PVC by displacement of chlorine with phthalate-based thiol additives, that is, the covalent attachment of the plasticizer to the PVC chain, is described for the first time. Using this methodology, a good plasticization efficiency is achieved although flexibility is reduced compared with that of commercial PVC−phthalate systems. However, the migration is completely suppressed. This approach may open new ways to the preparation of flexible PVC with permanent plasticizer effect and zero migration.

Introduction

Poly(vinyl chloride) (PVC) places in the second position in the market share of polymeric materials,[1] which is principally due to its high versatility and excellent balance between low production costs and general properties. Flexible PVC formulations are extensively used for the production of many different articles in the medical field, such as blood or urine bags, transfusion tubing, etc., and are further used for packaging purposes, toys, bathroom curtains, or kitchen floors. In order to obtain the desired flexibility and durability, PVC is sometimes mixed with large amounts of plasticizers. Most of them are based on esters of phthalic acid or adipic acid with linear or branched aliphatic alcohols of long chain length. Di(2-ethylhexyl) phthalate (DOP) is by far the most commonly used plasticizer for PVC.[2] Other important phthalate-based additives are di(isodecyl) phthalate (DIDP) or di(2-ethylhexyl) adipate (DEHA).

The amount of additives in PVC formulation changes according to the required properties. As a function of the final application, the quantities vary between 15 and 60 wt %, being the most common quantity for most of the devices around 35−40% of plasticizer.

Because of thermodynamic reasons, plasticizers tend to migrate to the surface of an article. On one hand, this leads to a progressive loss of its initial properties and, on the other hand, implies serious health hazards when PVC articles for biomedical applications or children toys are dealt with because additives migrated to the article's surface can contaminate physiological fluids like blood, serum, or plasma. In many studies it is described that DOP is liable of producing toxic and adverse effects, especially in animal or human tissues such as the pituitary gland, liver, or testicles.[3−7] For this reason DOP is one of several phthalate plasticizers that has been recently (February 10, 2009) banned by the U.S. Consumer Product Savety Commision (CPSC) for the manufacture of child care articles and toys containing phthalates.

Furthermore, it has been described that the metabolic products of DOP are able to act as potential carcinogenic agents.[8,9] Because of this high risk that implies the exposure of DOP to the human organism, several approaches have been developed to reduce plasticizer migration from flexible PVC to the environments. Some strategies imply the surface modification of flexible PVC articles with peroxides, azides,[10−12] sulfides,[13] or acrylates. Others describe physical treatments of the surface with γ-radiation or plasma exposure.[14−17] In all these cases the intention is to cross-link the article surface leaving the additive behind "bars".

Another approach is to replace the classical plasticizers by materials that are (a) biocompatible and/or (b) have an oligomeric character.[18] The most extensively studied polymeric materials for this approach are based on functionalized poly(ethylene oxide) (PEO) or poly(ε-caprolactone) or their combinations. According to the nature of these systems, the devices should be nontoxic. However, the migration of the plasticizers is still not completely avoided. Furthermore, crystallization or phase separations are possible, and the plasticizing efficacy is limited.

The most challenging strategy to solve any migration problems is the covalent linkage of the additive to the polymer chains. PVC can be chemically modified by nucleophilic substitution of its chlorine atoms. Many studies in this respect have been carried out in the past showing that aromatic para-substituted thiol compounds are the most appropriate nucleophiles to achieve high degrees of modification (up to 80 mol %) without any type of undesired side reactions.[19−21] Another interesting property of thiol groups in a modifier is their ability to efficiently deactivate radicals. In fact, Starnes et al. have proposed the use of aliphatic and aromatic thiol compounds as heat/color stabilizers, replacing in this way the use of heavy metal salts in these formulations.[22] In this context it should be mentioned that the same authors have also shown that radical scavenging is not the only stabilizing function of the thiols but that the major function of these stabilizers actually is to destroy thermally labile structural defects.[23]

In 1985, Michel et al. made use of the high reactivity of thiols toward nucleophilic substitution reactions and described the use of thiol compounds as internal plasticizers for PVC.[24] However, the compounds chosen by these authors were unfortunate as they synthesized esters of mercaptoacetic and thiosalicylic acid. On the one hand, although aliphatic thiols may lower the glass temperature of PVC more efficiently than the stiffer aromatic analogues,[25,26] it is nowadays known that aliphatic thiols do not show the appropriate balance between nucleophilicity and basicity necessary to achieve high degrees of modification and avoid degradation by elimination side reactions. On the other hand, the strong steric hindrance of the thiol moiety in ortho position to the ester

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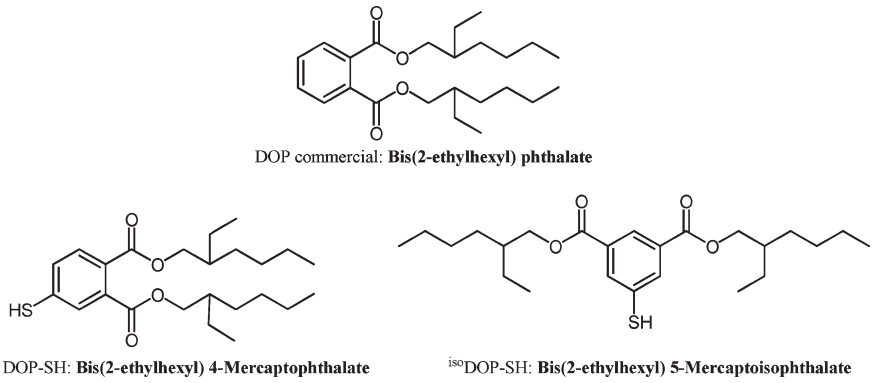
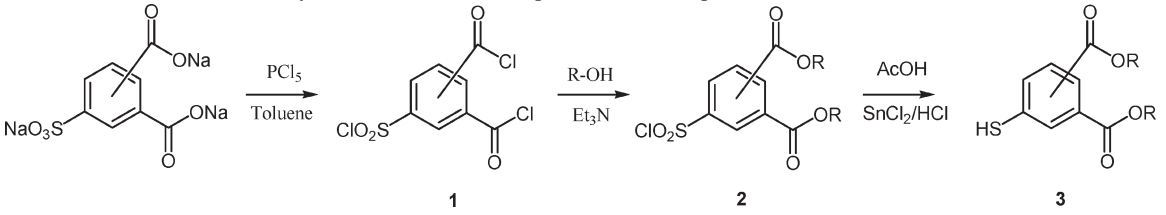


Figure 1. Chemical structures of the plasticizers described in the present contribution.

Scheme 1. Synthetic Route for the Preparation of Mercapto-Functionalized Plasticizers



group in thiosalicylic esters prevented an efficient attachment of the aromatic mercapto derivative onto the polymeric backbone.

Results and Discussion

Synthesis of Functionalized Plasticizers. In order to avoid migration of plasticizers, we have developed a synthetic route to functionalized plasticizers with physicochemical properties similar to those of commercial DOP, but with an additional functional group able to establish a covalent bond to the polymeric backbone. For these reasons, we have synthesized the di(2-ethylhexyl) 4-mercaptophthalate (DOP-SH) and the di(2-ethylhexyl) 5-mercaptoisophthalate (^{iso}DOP-SH). The latter one has been synthesized before by Starnes;[22] DOP-SH is a new compound. The structures of both functionalized additives are schematically shown in Figure 1.

In Scheme 1, the synthetic route to the desired compounds which is different than that described in the literature[22] is depicted. As starting materials, we have used 4-sulfophthalic acid and 5-sulfophthalic acid sodium salt. In the first step, the activation of the functional acid groups has been carried out using PCl_5 as halogenating agent. Then, using 2 equiv of the desired alcohol (2-ethylhexanol), the selective esterification of acyl groups (COCl) was carried out using triethylamine as an acid scavenger. The formation of the sulfonate ester can be completely avoided working at low temperatures and adding first the alcohol and then the amine catalyst. Finally, the selective reduction of the chlorosulfonyl group to a thiol moiety was performed by $SnCl_2$ as the reducing agent. Using this Lewis acid, the ester groups remain unaffected during the reduction. The final overall yield of this synthetic route was 84%. The ^{1}H NMR spectrum of DOP-SH is shown in Figure 2.

Modification of PVC with Plasticizers. The modification reaction of PVC with the novel functionalized additives was carried out in cyclohexanone solution at 60 °C. In Figure 3 ^{1}H NMR spectra of PVC modified with DOP-SH to different degrees of modification are shown. With increasing reaction time, new aromatic (7.0−8.0 ppm) and aliphatic (1.8−0.5 ppm) proton peaks arise increasing their intensities

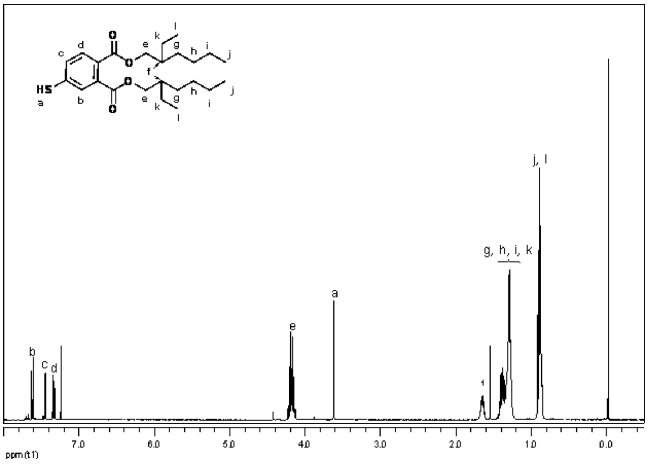


Figure 2. ^{1}H NMR spectrum of DOP-SH.

progressively with the reaction time. These protons arise from the modified units of the copolymers. The signal of the C*H*−Cl protons at 4.5 ppm decreases with conversion while two new signals appear in the same region at 4.8 and 4.2 ppm, which are formed due to C*H*−S and COOC*H*$_2$ protons, respectively. In the case of higher modification degrees, further peaks are observed. These peaks are due to the effect of the chemical composition distribution, which becomes broader when the number of modifier groups in the polymer backbone increases.

The NMR analysis reveals some important features of this modification reaction: DOP-SH and ^{iso}DOP-SH are suitable agents to form flexible PVC with grafted plasticizers; under the experimental conditions used these modification reactions are free of undesired side reactions like cross-linking or elimination of HCl what can be deduced from the absence of corresponding olefinic protons at 5.8 and 6.2 ppm and the white color of the products.

The modification degree MG (%) can be easily calculated from the ^{1}H NMR data using formula 1, where *I*(aromatic) and *I*(5−3 ppm) are the integrals of the respective proton

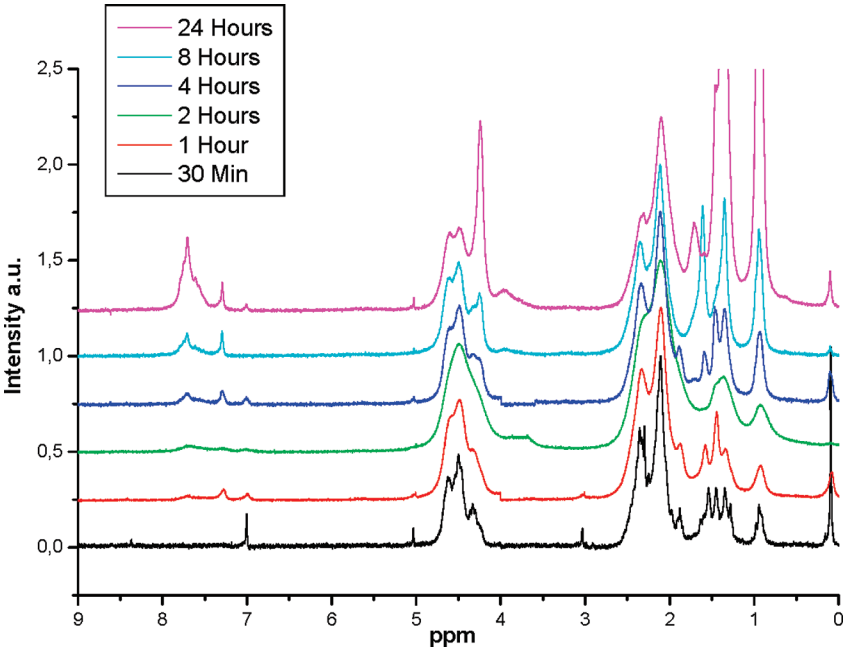


Figure 3. ^{1}H NMR spectra of PVC modified with DOP-SH at different reaction times.

signals. This formula is applicable to both kinds of plasticizers.

$$\mathrm{MG}\ (\%) = 100 \times (I(\mathrm{aromatic})/3)/(I(5-3\ \mathrm{ppm}) - 4/3I(\mathrm{aromatic})) \quad (1)$$

Under the reaction conditions used, the molar percentage of plasticizer that can be linked to the PVC chains was 31 and 23 mol % for ^{iso}DOP-SH and DOP-SH isomer, respectively. It has to be pointed out that these molar conversions correspond to much higher weight percentages. A 30% molar percentage for example corresponds to 75 wt %. That means that it is possible to incorporate similar amounts of thiol plasticizer via a covalent bond into the polymer backbone than is usually employed in commercial plastisol formulations.

The composition of the obtained copolymers was also determined by elemental analysis using the ratio of sulfur and chloride contents and by FT-IR spectroscopy. The results obtained from the three techniques agree very well and thus confirm the proposed structure of the new materials.

Glass Transition Temperature. We have studied the plasticizer efficiency of the novel additives. Therefore, we have measured the evolution of the glass temperatures (T_gs) of the novel copolymers as a function of the degree of modification. The measured T_gs for commercial PVC/DOP mixtures and PVC-S-DOP copolymers with different degrees of modifications are plotted in Figure 4 with respect to the molar percentage of DOP.

For both functionalized additives, the glass temperature is progressively reduced with the grafted amount of plasticizers. Although the plasticizing efficiency in these systems is worse than that of conventional PVC-DOP mixtures, which is a consequence of the higher structural stiffness of the modified monomeric units, it can be seen that the copolymers with high amounts of plasticizer present T_gs around 0 °C. This means that these materials are completely flexible at room temperature.

Another interesting aspect is the difference in the plasticizer efficiency between both isomers. In both cases, the lowest

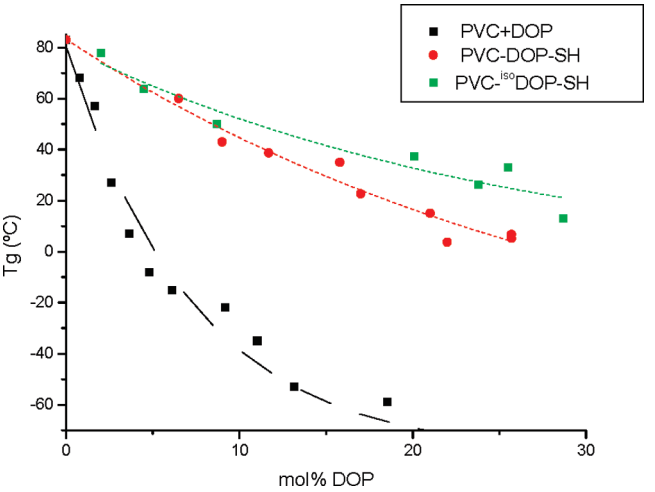


Figure 4. Variation of glass temperature with the content of conventional DOP, DOP-SH, and ^{iso}DOP-SH.

glass temperature was lower than room temperature. However, the PVC/DOP-SH series has lower T_gs than that of PVC/^{iso}DOP-SH. This is probably due to the relative position of the ester groups in the aromatic ring. However, it should also be possible to explain this fact with the increase of generated free volume of DOP-SH with respect to ^{iso}DOP-SH.

Migration of Plasticizers. In order to study the migration tendency of the plasticizer, the migration behavior of the new materials was tested by extraction experiments using heptane at room temperature. In order to quantify the amount of migrated plasticizer, strips of the plasticized films were placed in a flask containing heptane and a small amount of 1,6-hexamethylene diisocyanate as internal reference. From time to time aliquots of the solution were extracted and the amount of plasticizer determined by IR spectroscopy. Absolute values of DOP were obtained using a calibration curve obtained from mixtures of known compositions of diisocyanate and DOP. In Figure 5 the result of these extraction measurements are compared for a conventional PVC/DOP

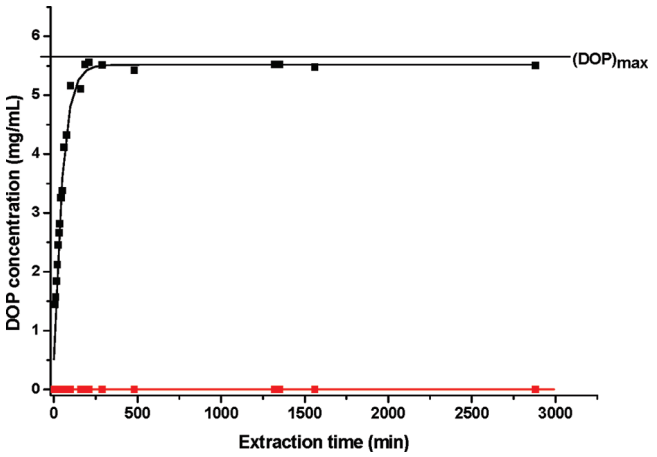


Figure 5. Extraction of plasticized PVC sheets with heptane at room temperature: conventional PVC-DOP (black) and PVC-DOP-SH (red).

mixture and PVC modified with DOP-SNa. As shown by the black symbol, PVC/DOP loses nearly the complete amount of additive after less than 3 h. In contrast, the loss of plasticizer in PVC modified chemically with thiol-functionalized DOP is zero. This demonstrates that the plasticizer in these systems is covalently linked to the polymer chain.

Conclusions

In the present contribution we have developed alternative and promising additives, derivatives of phthalic and isophthalic acid that guarantee plasticization of PVC avoiding any migration of the additive. The structure of the modified polymers and the evolution of the modification degrees with reaction time were studied by NMR, ATR-FTIR spectroscopies, and elemental analysis. Under the selected experimental conditions, the substitution in solution takes place without secondary reactions (elimination or cross-linking).

The efficiency of the novel plasticizers has been demonstrated. The glass transition temperature of modified PVC is largely reduced and is around 0 °C for the highest modified samples.

Experimental Part

Materials. Commercial bulk polymerized PVC with a weight-average molecular weight of $M_w = 112\,000$ g/mol was obtained from ATOCHEM, Spain. The tacticity measured by ^{13}C NMR spectroscopy was syndio = 30.6%, hetero = 49.8%, and iso = 19.6%.

4-Sulfophthalic acid solution 50 wt % in water was purchased from Aldrich. The corresponding sodium salt was obtained by reaction with stoichiometric amounts of sodium hydroxide in methanol. After 3 h at room temperature, the white salt was filtered, washed with methanol, and dried.

5-Sulfoisophthalic acid sodium salt was purchased from Aldrich and used as received (purity 95%). Cyclohexanone was bidistilled prior to use. The rest of the materials were used as received: THF and methanol from Scharlau, sodium hydride (60% dispersion in mineral oil), phosphorus pentachloride (PCl_5), tin(II) chloride hydrate ($SnCl_2$), acetic acid (CH_3CO_2H) from Aldrich, and potassium carbonate from Panreac.

Preparation of Plasticizers. *a. 4-Chlorosulfonylphthaloyl Chloride* (***1a***) *and 5-Chlorosulfonylphthaloyl Chloride* (***1b***). To a 2 L three-necked round-bottom flask 200 g of the corresponding carboxylic acid or its sodium salt and 440 g of PCl_5 were added under stirring. The reaction temperature was 110 °C for 3 h. After this period of time, 500 mL of toluene was added, and the reaction mixture was refluxed overnight. Then, the white solid (NaCl) was eliminated by filtration, and the halogenated product was purified by distillation under reduced pressure (**1a**: $bp^{0.2\,Torr}$: 127 °C; yield: 95%; **1b**: $bp^{0.3\,Torr}$: 132 °C, yield: 95%).

b. Synthesis of Di(2-ethylhexyl) 4-Chlorosulfonylphthalate (***2a***) *or Di(2-ethylhexyl) 5-Chlorosulfonylisophthalate* (***2b***). The chlorosulfonyl derivative ester (**2**) was prepared according to a standard esterification method from **1** (10.0 g, 33.2 mmol, 1 equiv), using chloroform (500 mL) with 2 equiv amounts of 2-ethylhexanol (10.4 mL, 66.4 mmol) and triethylamine (9.2 mL, 66.4 mmol) as an acid scavenger. The reaction mixture was heated to 60 °C for 2 h. Then, the organic phase was washed with HCl (1 M), saturated NH_4Cl aqueous solution, and Milli-Q water. The organic phase was dried over anhydrous $MgSO_4$ and filtered, and the halogenated solvent was evaporated. The yields were 94% (**2a**) and 97% (**2b**).

2a: ^1H NMR ($CDCl_3$, 300 MHz) δ: 8.85 (d, 1H, $J = 1.3$ Hz, Ar−*H*), 8.40 (d, 1H, $J = 6.1$ Hz, Ar−*H*), 8.22 (dd, 1H, $J = 1.3$ and 6.1 Hz, Ar−*H*), 4.31 (d, $J = 5.7$ Hz, 4H, 2 × $COOCH_2$), 1.86−1.71 (m, 2H, 2 × $(CH_2)_2CH-CH_2$), 1.52−1.33 (m, 16H, CH_2), 0.99−0.89 (m, 12H, 4 × CH_3).

2b: ^1H NMR ($CDCl_3$, 300 MHz) δ: 8.96 (s, 1H, Ar−*H*), 8.82 (s, 2H, Ar−*H*), 4.31 (d, $J = 5.7$ Hz, 4H, 2 × $COOCH_2$), 1.86−1.71 (m, 2H, 2 × $(CH_2)_2CH-CH_2$), 1.52−1.33 (m, 16H, CH_2), 0.99−0.89 (m, 12H, 4 × CH_3).

c. Synthesis of Di(2-ethylhexyl) 4-Mercaptophthalate (*DOP-SH,* ***3a***) *or Di(2-ethylhexyl) 5-Mercaptoisophthalate* (*^{iso}DOP-SH,* ***3b***). The diester compound **2** (5.0 g, 10.2 mmol) was dissolved in glacial acetic acid (5.0 mL), and then 2 equiv (4.6 g, 20.4 mmol) of the reductive solution of $SnCl_2$/HCl (100 mL HCl concentrated) was added under stirring. The reaction temperature was 60 °C for 12 h. The mercapto derivative **3** was obtained by extracting the water phase several times with dichloromethane (250 mL). The combined portions were washed once with $NaHCO_3$ (1 M) and twice with Milli-Q water. The organic phases were dried over anhydrous $MgSO_4$, filtered, and concentrated under vacuum. The resulting residue was purified via column chromatography on silica gel and CH_2Cl_2 as the eluent to afford the pure functionalized plasticizers (yields: **3a**: 91%; **3b**: 85%).

3a: ^1H NMR ($CDCl_3$, 300 MHz) δ: 7.62 (d, 1H, $J = 6.3$ Hz, Ar−*H*), 7.45 (d, 1H, $J = 1.2$ Hz, Ar−*H*), 7.34 (dd, 1H, $J = 6.3$ and 1.2 Hz, Ar−H), 4.23−4.12 (m, 4H, 2 × $COOCH_2$), 3.62 (s, 1H, −SH), 1.70−1.60 (m, 2H, 2 × $(CH_2)_2CH-CH_2$), 1.44−1.23 (m, 16H, CH_2), 0.91−0.85 (m, 12H, 4 × CH_3).

3b: ^1H NMR ($CDCl_3$, 300 MHz) δ: 8.35 (s, 1H, Ar−*H*), 8.02 (s, 2H, Ar−*H*), 4.19 (m, 4H, 2 × $COOCH_2$), 3.59 (s, 1H, −SH), 1.71−1.58 (m, 2H, 2 × $(CH_2)_2CH-CH_2$), 1.44−1.12 (m, 16H, CH_2), 0.90−0.78 (m, 12H, 4 × CH_3).

Modification of PVC with Thiol Compounds. PVC (0.5 g, 8 mmol) and 8 mmol of mercapto compound were dissolved in 50 mL of cyclohexanone. Potassium carbonate (1.6 g) was added, and the reaction started under a N_2 atmosphere at 60 °C (route I). PVC modification according to route II was performed using the corresponding thiolate salt prepared in a previous step. The procedure of the reaction between sodium hydride and thiol compound is described elsewhere.[20]

The reactions were stopped by precipitating the mixture in cold methanol/water (2:1). The modified flexible PVC was purified using THF/hexane as a solvent−precipitant system and yielded a slightly yellow material able to form opaque films similar to those of conventional PVC/DOP blends.

Characterization. NMR spectra of the compounds or modified polymers were recorded at 25 °C on a 300 MHz Varian spectrometer operating at 300 MHz using deuterated chloroform or deuterated dimethyl sulfoxide as the solvent.

The IR measurements were performed on thin solvent cast films of the modified polymers using a Nicolet 520 FTIR spectrometer.

Calorimetric measurements of the modified PVC samples were carried out using a Perkin-Elmer differential scanning calorimeter DSC-7. Samples (10 mg) were heated up to 150 °C

under nitrogen atmosphere at 10 °C/min and quenched at a cooling rate of 200 °C/min. The T_g values reported were taken from the second runs and correspond to the midpoint of the DSC curves measured from the extension of the pre- and posttransition baseline.

Elemental analysis was carried out on a CHNS-932 of Leco.

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