



Epoxide and cyclic carbonate with diisononyl succinate backbone as phthalate-free plasticizers



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ABSTRACT

Candidates for new phthalate-free plasticizers are synthesized based on epoxidized diisononyl maleate and carbonylated diisononyl tartrate. Although the carbonation of epoxidized diisononyl maleate with CO₂ failed, the cyclic carbonate was synthesized successfully using triphosgene as carbonylation agent of the respective tartrate. The performance of the synthesized materials as plasticizer was analyzed under standard conditions as plastisols. Results showed potential for the epoxidized maleate and carbonylated derivative to be developed into phthalate free-plasticizers.

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Introduction

Plasticizers are mainly monomeric compounds that are widely used in polymer industry to modify the physical and mechanical performance of the final polymer. About 90% of all plasticizers produced are needed for the synthesis of soft polyvinyl chloride (PVC).¹ Using these additives, workability, distensibility, flexibility, and tear strength of a plastic or elastomer material increase and a lower processing temperature can be achieved in polymer manufacture. According to the definition of the International Union of Pure and Applied Chemistry (IUPAC), a plasticizer may reduce the melt viscosity, lower the temperature of a second-order transition, or lower the elastic modulus of the product.^{2,3} Phthalate esters are the most common plasticizers used with a production volume of about 6 million tons (2010).⁴ However, some low molecular weight phthalate esters, especially diethylhexyl phthalate (DEHP), were suspected to be toxic for reproduction. Therefore the European Union and other countries have passed laws to regulate the use of such low molecular weight plasticizers in medical devices, toys, and childcare articles which can be placed in the mouth.^{5–8} In January 2014, diisononyl phthalate (DINP) or diisode-

cyl phthalate (DIDP) was classified as non-CMR (CMR: carcinogenic, mutagenic, or toxic for reproduction) phthalates.^{9,10} Nevertheless, a variety of efforts was made to expand the portfolio of plasticizers for specific applications. For example, epoxidized and carbonated fatty acid methyl esters (FAME) were tested as phthalate-free plasticizers.^{3,11} Compared to DINP as benchmark, carbonated FAME based on soy bean oil (CFAME) and carbonated methyl oleate (CMO) showed better gelation properties in mixtures with transparent liquid paste compositions of PVC. The softening effect of CMO was better than that of DINP.¹¹ Furthermore, the volatility of CFAME in PVC is significantly reduced compared to the corresponding epoxide. Finally, the synthesis of cyclic carbonates from epoxides with abundant CO₂ as the reagent may improve the carbon footprint of such plasticizers in comparison with phthalate-based materials and may lead to more sustainable products. Thus, the carbonation of epoxidized dialkyl maleates with CO₂ to the cyclic carbonate could be an industrially interesting reaction.

In this study, epoxidized diisononyl maleate (EDINM) and carbonylated diisononyl tartrate (CDINT) were synthesized for the first time. Different routes were investigated for the preparation of the cyclic carbonate, among others the carbonation of EDINM with CO₂ and the carbonylation of diisononyl tartrate (DINT) with triphosgene. Both compounds were tested as plasticizers in liquid paste compositions (plastisol) for PVC. The major physical and mechanical properties were measured and compared with diisononyl

Abbreviations: DINM, diisononyl maleate; EDINM, epoxidized diisononyl maleate; DINT, diisononyl tartrate; CDINT, carbonated diisononyl tartrate; MA, maleic anhydride.

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phthalate (DINP) being an established plasticizer for a large variety of applications.

Results and discussion

Synthesis of phthalate-free plasticizers

The reaction sequence started from maleic anhydride which was esterified with *i*-nonanol to DINM (Scheme 1) in a similar procedure as described by Matsumoto et al. for didodecyl maleate.¹²

Epoxy succinates of shorter chain alcohols are already known, but not isononyl derivatives. Such epoxy succinates were prepared according to different methods using stoichiometric procedures starting from diethyl tartrate,¹³ epoxidation of maleates using the known tungstate/H₂O₂ system¹⁴ or a Bayer–Villiger oxidation of the respective keto epoxide.¹⁵

The enzymatic conversion of glucose to epoxy succinic acid followed by an acid-catalyzed etherification utilized the observation that the epoxy moiety in epoxy succinic acid is less reactive to acidic reagents.¹⁶ A method most suitable for our purposes was an epoxidation in analogy to a procedure, reported by Švenda and Myers for di-*tert*-butyl maleate.¹⁷ A similar conversion was described by Meth–Cohn et al. using lithium *tert*-butyl hydroperoxide prepared as oxidant in situ.^{18,19} The epoxidation of DINM succeeded using potassium *tert*-butyl hydroperoxide prepared in situ. The reaction was already completed after 7.5 h (Scheme 1).

The carbonation of epoxides with CO₂, as known from epoxidized fatty esters^{11,20} and epoxidized diethyl maleate,²¹ failed in the case of EDINM as the starting material. The reaction conditions applied were 100 bar CO₂ at 100 °C using tetrabutylammonium bromide as the catalyst. No reaction was observed after 4 h. Probably, the necessary access of the bromide ion to the epoxide ring was sterically hindered by the neighboring bulky ester groups. Furthermore, the epoxide is very electron poor compared to other epoxides such as fatty ester epoxides or epoxidized olefins. This could also prevent the formation of a carbonate in the reaction. Therefore other efforts were made starting from DINT to get the cyclic carbonate CDINT (2-oxo[1,3]dioxolane-4,5-dicarboxylic acid diisononyl ester). For the first time, DINT could be received easily by acid-catalyzed esterification of tartaric acid with an isolated yield of 90%. The synthesis procedure for DINT was carried out according to a similar method as described by Novotný et al. for didodecyl tartrate.²² Urea was reported as the carbonating agent in the reaction of simple diols like ethylene glycol to cyclic carbonates.²³ The carbonation of dibutyl tartrate (1.5 mmol) with urea (1.5 mmol, synthesized in a similar way as described for DINT) at 150 °C and under reduced pressure (100 mbar) to remove created ammonia and to shift the equilibrium toward the products resulted only in an insufficient conversion of 10% to the cyclic carbonate after 1 h. The preparation of CDINT also failed via reaction of DINT with dimethyl carbonate and sodium as catalyst at 90 °C according to a procedure described in Ref. 22. Only deesterification of DINT was observed.

Finally, the synthesis of CDINT succeeded using a triphosgene carbonylation method of DINT (Scheme 2). A complete conversion of DINT was achieved resulting in an isolated yield of CDINT of about 85%. The carbonation of vicinal diols with phosgene²⁴ or triphosgene^{25–29} was reported by several authors. Triphosgene as a stable crystalline solid (mp 80 °C, only slight decomposition to phosgene at the boiling point of 206 °C) is more safe to handle than phosgene itself.³⁰ Concerning the extremely exothermic reaction of triphosgene with tartrate, an efficient temperature control was crucial to avoid side reactions (e.g., chlorination²⁸) in the successful scale-up of the procedure. Although the use of triphosgene is not applicable on large scale due to a very low atom economy, it was a feasible way to synthesize the samples for application tests.

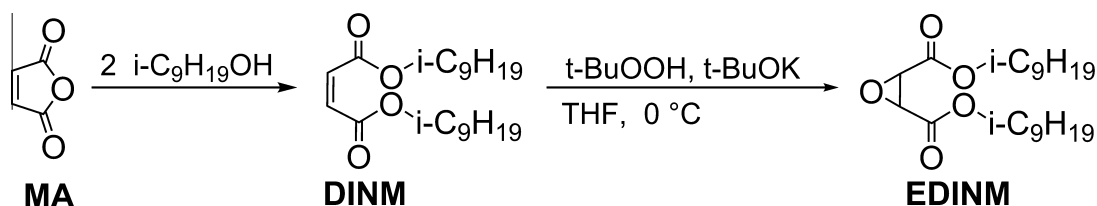
Application tests

To characterize the new compounds as plasticizers the EDINM and CDINT were compared in plastisol applications with DINP and its fully hydrogenated derivative ELATUR CH. For these tests 50 parts of the plasticizer were mixed with 100 parts PVC and 5 parts of stabilizers. As first characterization methods, the gelation and Shore A hardness were determined for the four soft PVC materials. Furthermore, the volatility of the pure plasticizer samples was determined. Gelation describes the physical incorporation of the plasticizer into the PVC matrix. It can be determined by the viscosity in dependency of the temperature. A low starting viscosity and a step-wise increase viscosity at a low temperature are desirable parameters for PVC formulators. Finally, a good plasticizer reaches a high viscosity plateau quickly where the sample has been fully incorporated into the PVC matrix. The performance of EDINM and CDINT is shown in Figure 1.

A benchmark for all plasticizers is DINP which shows an overall superior performance. ELATUR CH exhibits similar starting and end values like DINP but the increase in viscosity is slower than for DINP. In comparison to these values the epoxidized maleate EDINM shows very good gelation properties.

The viscosity at the beginning is comparable to DINP but it shows a fast viscosity increase above 65 °C and reaches its plateau already at about 85 °C. In contrast to these values the carbonylated tartrate CDINT shows poor gelation properties. Compared to the other materials the starting viscosity is increased and the material shows only a moderate increase in viscosity. Furthermore, the material undergoes significant changes above 145 °C where the viscosity is lowered before it is restored at about 180 °C. This might be caused by an irreversible decomposition of the carbonate at temperatures above 140–145 °C. Then CO₂ gas formed may distort further measuring points due to the growing inhomogeneity of the investigated sample.

Secondly, the efficiency of each plasticizer is determined by the Shore A hardness test (Fig. 2). The test gives first indications about the efficiency of the material as plasticizer for PVC. Lower value indicates a higher softening efficiency. With the epoxidized EDINM, a higher plasticizing efficiency was observed compared



Scheme 1. Synthesis of EDINM. Reaction conditions: (i) MA (0.60 mol), *i*-nonanol (1.32 mol), H₂SO₄ (5 mL), toluene (1000 mL), reflux, 3 h; (ii) DINM (17.31 mmol), *tert*-BuOOH (40.15 mmol, 7.3 ml of 5.5 M solution in decane), *tert*-BuOK (5.5 mmol, 1 M solution in THF), THF (170 mL), 0 °C, 7.5 h.

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