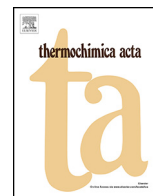




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# A comparative study of the thermal properties of homologous series of crystallisable n-alkyl maleate and itaconate monoesters

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## ABSTRACT

Homologous series of crystallisable C<sub>8</sub>–C<sub>22</sub> even-numbered alkane oligomers with either maleate or itaconate monoesters end-groups were synthesized. Their total phase change enthalpy ( $\Delta H_{tpce}$ ) and entropy ( $\Delta S_{tpce}$ ) on melting, determined by DSC, show a linear dependence with the number of carbons of the alkyl chain. A comparison was performed with corresponding succinate derivatives. The influence of the end functions on  $\Delta S_{tpce}$  was examined in view of  $\Delta S_{tpce}$  values estimated by the group additivity approach. A fair agreement between the experimental and the estimated entropy values could be demonstrated. Thermogravimetric analysis (TGA) has shown that the maleate oligomers are less stable than the corresponding succinate and itaconate derivatives. This behaviour could be confirmed by the activation energies of the degradation process.

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## 1. Introduction

Alkane monomers are molecules with a carbon chain, terminally substituted with a polymerizable group, such as for instance vinyl, acrylic or methacrylic functions. These functional monomers, generally in the molar mass range of a few hundred to tens of thousands, are of major interest for the synthesis of graft copolymers or brush structured block copolymers.

Maleate, fumarate and itaconate end functionalized n-alkanes, from C<sub>1</sub> to around C<sub>22</sub>, are a special class of monomers, as by free radical homo- or co-polymerization, they open, in particular for the higher n-alkanes, a straight way to the synthesis of crystallisable brush type polymers.

Over the last few decades, this approach to the synthesis of such type of alkane monomers and their polymerization has been examined quite extensively for a wide range of n-alkane diesters [1,2]. The corresponding monoesters of maleic-, succinic- and itaconic acids were studied to a relative minor extent as these types of compounds and corresponding maleate and itaconate polymers may have, under certain conditions, a limited hydrolytic and thermal stability [3].

In addition to the alkyl and aryl-alkyl itaconate esters studied extensively by the research group of Katime [4–6], the interest of n-alkyl itaconate monoesters resides mainly in the fact that the remaining free carboxylic end-group leads to amphiphilic products, so-called surface active macromers also designated as surfmers [7].

These monomers, with a hydrophobic n-alkyl chain, a hydrophilic carboxylic function and a polymerizable end-group, have found a large range of application possibilities such as polymerizable surfactants, micellar systems or emulsion polymerization stabilizers [8].

Moreover, alkyl maleate and itaconate monoesters are of common practice for grafting modifications of polyolefines that are carried out at high temperatures by reactive extrusion techniques [9,10]. As under these conditions the thermal characteristics of C<sub>8</sub>–C<sub>22</sub> n-alkyl maleates and itaconates have not yet been studied, it was therefore of interest to examine their stability by thermogravimetric analysis (TGA).

In this context, the aim of the present investigation was to synthesize and to implement the characterization of homologous series of crystallisable maleate, succinate and itaconate monoesters with even-numbered C<sub>8</sub> to C<sub>22</sub> n-alkyl moieties.

For these well-defined products, a comparative study of melting characteristics will be reported. Except some melting points, data such as total phase change melting enthalpy ( $\Delta H_{tpce}$ ) and entropy ( $\Delta S_{tpce}$ ), are, to the best of our knowledge, not available in the literature. The maleic, itaconic and succinic end-group effect

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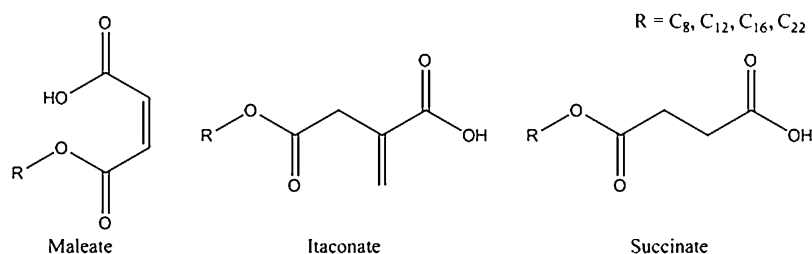


Fig. 1. Chemical structures of synthesized monoesters.

on  $\Delta H_{\text{tpce}}$  and  $\Delta S_{\text{tpce}}$  will be investigated by a group additivity approach, which is classical for pure alkanes as demonstrated by different authors [11,12]. Furthermore, these melting characteristics of the maleate, itaconate and succinic n-alkyl monoesters will be completed by the determination of their thermal stability by TGA.

## 2. Experimental part

### 2.1. Materials

1-octanol (Alfa Aesar, 99%), 1-dodecanol (Alfa Aesar, 98%), 1-hexadecanol (Sigma-Aldrich, 99%), 1-docosanol (Sigma-Aldrich, 98%), maleic anhydride (Sigma-Aldrich, 99%), itaconic anhydride (Alfa Aesar, 97%), succinic anhydride (Sigma-Aldrich, 99%), n-heptane (Carlo Erba, 99%), methanol (Carlo Erba, 99%), dibutyltin dilaurate (Sigma-Aldrich, 95%) have been used as received.

### 2.2. Measurements

Proton NMR analyses were performed in chloroform ( $\text{CDCl}_3$ ) at 20 °C on a Bruker 300 MHz spectrometer.

Differential scanning calorimetry (DSC) was performed by using a thermal analysis system model DSC Q200 from TA Instruments calibrated with indium. The purge gas was a nitrogen flow of 50 mL min<sup>-1</sup>. Aluminium crucibles were filled with about 8–12 mg of sample and sealed hermetically. A heating rate of 10 °C min<sup>-1</sup> was adopted for analyses between –50 °C and 130 °C. Two heating ramps were performed between which a cooling step was carried out at 10 °C min<sup>-1</sup>. The second heating ramp was analysed to determine the melting properties and thanks to the cooling ramp crystallisation was observed.

All thermogravimetric analyses were carried out on a TA Instruments analyser TGA Q500 at a heating rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere (100 mL min<sup>-1</sup>) from 25 °C to 400 °C.

The software TA Universal Analysis 2000 was used to determine the temperature of all thermal events.

### 2.3. Synthesis

The synthesis procedures of maleate, succinate and itaconate monoesters were extensively described in the literature [2,13,14]. These compounds were prepared by heating molar equivalents of the requisite anhydride with different n-alkanols. The corresponding chemical structures obtained by this straightforward technique are presented in Fig. 1.

A typical synthesis example is given herewith for dodecyl maleate. 1-dodecanol (38.16 g, 0.20 mole) was introduced in a one-neck flask and heated at 110 °C. After melting the alcohol, maleic anhydride (20.08 g, 0.20 mole) was added. The reaction mixture temperature was maintained at 110 °C and the medium was stirred for 90 min. The reaction product was poured in heptane (100 mL) under magnetic stirring and left at room temperature for 4 h. The formed precipitate was collected by filtration. White crystals of

dodecyl maleate (53.74 g, 92%) were obtained. <sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ , 20 °C)  $\delta$ (ppm): 0.88 (3H, t, CH<sub>3</sub>), 1.27 (18H, m, CH<sub>2</sub>), 1.72 (2H, q, CH<sub>2</sub>), 4.29 (2H, t, CH<sub>2</sub>), 6.38 (1H, d, =CH), 6.48 (1H, d, =CH).

Octyl maleate (1a), hexadecyl maleate (1b) and docosyl maleate (1c) were obtained using the same procedure with yields about 90–95%. Their NMR characteristics are as follows:

(1a) <sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ , 20 °C)  $\delta$ (ppm): 0.89 (3H, t, CH<sub>3</sub>), 1.28 (10H, m, CH<sub>2</sub>), 1.72 (2H, q, CH<sub>2</sub>), 4.28 (2H, t, CH<sub>2</sub>), 6.38 (1H, d, =CH), 6.48 (1H, d, =CH).

(1b) <sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ , 20 °C)  $\delta$ (ppm): 0.88 (3H, t, CH<sub>3</sub>), 1.26 (26H, m, CH<sub>2</sub>), 1.73 (2H, q, CH<sub>2</sub>), 4.29 (2H, t, CH<sub>2</sub>), 6.38 (1H, d, =CH), 6.48 (1H, d, =CH).

(1c) <sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ , 20 °C)  $\delta$ (ppm): 0.89 (3H, t, CH<sub>3</sub>), 1.26 (38H, m, CH<sub>2</sub>), 1.73 (2H, q, CH<sub>2</sub>), 4.29 (2H, t, CH<sub>2</sub>), 6.38 (1H, d, =CH), 6.49 (1H, d, =CH).

Succinate and itaconate monoesters were obtained with the same reaction conditions by substituting maleic anhydride by succinic and itaconic anhydride respectively. The NMR characteristics of all these compounds are provided in Supporting Information (S1).

Dodecyl maleate diester, as a reference product for thermogravimetric analysis was synthesized in bulk. 1-dodecanol (26.67 g, 0.14 mole) was introduced in three-necked flask fitted with a condenser and heated at 110 °C. After melting the alcohol, maleic anhydride (7.02 g, 0.07 mole) was added. Dibutyltin dilaurate (100 mg, 0.158 mmol) as a catalyst was added. The reaction mixture temperature was maintained at 110 °C and stirred for 60 min. Low pressure (0.5 bars) was applied for 30 min in order to remove residual water. Product was recrystallised from methanol. White crystals of di-dodecyl maleate (30.92 g, 95%) were obtained. <sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ , 20 °C)  $\delta$ (ppm): 0.88 (6H, t, CH<sub>3</sub>), 1.26 (36H, m, CH<sub>2</sub>), 1.67 (4H, m, CH<sub>2</sub>), 4.17 (4H, t, CH<sub>2</sub>), 6.26 (2H, s, =CH).

## 3. Results and discussion

### 3.1. Compounds purity

Maleate, succinate and itaconate monoesters purity was determined by <sup>1</sup>H NMR. Indeed, the chemical shift of CH<sub>2</sub> next to the hydroxyl function in alcohol at 3.30 ppm moves to 4.10–4.29 ppm after the esterification. Taking into account the residual amount of alcohol, the purity of each compound has been determined and the corresponding results are presented in Table 1.

From Table 1 it appears that all the n-alkyl monoesters have a purity of at least 96%. Impurities are generally residual alcohol

Table 1  
Purity of monoester compounds as determined by <sup>1</sup>H NMR.

Compound	Succinates (%)	Maleates (%)	Itaconates (%)
C <sub>8</sub>	99	97	99
C <sub>12</sub>	98	96	98
C <sub>16</sub>	99	97	99
C <sub>22</sub>	99	96	98

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