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# Synthesis, spectral characterisation and thermal behaviours of some new *p*-*tert*-butylcalix[4]arene and calix[4]arene-esters containing acryloyl groups

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### HIGHLIGHTS

▶ In this work, some interesting data on newly synthesised novel/calixarene-esters have been presented.

▶ These compounds may have of significance in synthesising new, novel organic materials.

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### 1. Introduction

Calixarene are macrocyclic molecules made up of *p*-substituted phenolic units linked by methylene bridges *ortho* to the OH groups [1-5]. They are known to be useful building blocks for hollow molecular scaffolds with easily functionalisable hydrophilic and hydrophobic lower and upper rims, respectively [6–8]. Also when appropriately designed, they perform a large variety of functions, e.g., as inclusion compounds, selective complexing agents for metal ions and catalysts [7-10]. Calixarene molecules represent themselves as macrocycles with cavities of sufficient size and hydroxyl groups capable of forming intramolecular- and intermolecularhydrogen bonds. These properties of the calixarene structure and their capabilities of self-organisation and molecular recognition have made them subjects of supramolecular studies. Calixarenes are studied not only for the purely scientific interest evoked in the unusual complex structure and rich conformational possibilities of their molecules, but also for the wide practical applications of this class of compounds [8-12].

The cavity-shaped macrocycles of calixarene have attracted much attention mainly in supramolecular and analytical chemis-

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#### ABSTRACT

The mono-, di-, tri-, and tetra-acryloyl esters of *p-tert*-butylcalix [4]arene and calix[4]arene were synthesised by reacting acryloyl chloride with sodium salts of *p-tert*-butylcalix[4]arene and calix[4]arene in THF. The structures of these compounds were characterised by IR, UV–VIS, <sup>1</sup>H NMR, and <sup>13</sup>C NMR. Thermal behaviour of the compounds were also examined by means of differential thermal analysis (DTA), thermogravimetry (TG), and derivative thermogravimetry (DTG).

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try, because they can form typical host-guest complexes with many neutral molecules and ions, such as cyclodextrins and crown ethers [13]. Owing to their non-planar structure, calix[4]arenes can exist in one of four conformations designated as cone, partial cone, 1,2-alternate and 1,3-alternate [14-18]. Conformations can be locked by placing substituents of hydroxyl hydrogen with groups larger than the methyl group. Very often cone and partial cone conformers were synthesised by alkylation [19] and acylation [20] reactions at the lower rim of calix[4]arene. The ester compounds obtained from calixarenes have been investigated by a variety of spectroscopic techniques to identify their structures and spectral properties, but the literature so far report that calixarene-ester compounds containing unsaturated groups like acryloyloxy moiety are scarce [19,20,21]. The thermal behaviour of calix[4]areneesters having acryloyl groups have not been reported previously. We have previously reported the synthesis, characterisation and dyeing properties of the acryloyloxy derivatives of o,o'-dihydroxyazo [22] and hydroxazo [23] dyes that have polymerisable, and later of the crystal structures of the diacryloyloxy derivatives of *p*-tertbutylcalix[4]arene and calix[4]arene [24,25]. The mono-, di-, tri-, and tetra-acryloyl esters of *p-tert*-butylcalix[4]arene and calix[4]arene compounds can be important in preparing calixarenes containing unsaturated groups in their molecules and undergo





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10  $R_1 R_2 R_3 R_4$ = COCH=CH<sub>2</sub> R' =H

Fig. 1. Synthesis and structures of *p*-tert-calix[4]arene and calix[4]arene having acryloyl groups.

copolymerisation with different vinyl monomers (Fig. 1) [23–26], their antioxidant properties and in other experiments.

As a part of an on going research project, we are interested in exploring the antioxidant properties of acryloyloxy calix[4]arene derivatives with the other our research group. In this study, we report the synthesis and spectroscopic properties of new mixed calix[4]arene-esters with acryloyloxy groups that have polymerisable and probably antioxidant properties. The characterisation of the compounds were determined by IR, UV–VIS, <sup>1</sup>H, and <sup>13</sup>C NMR techniques and also thermal analysis (DTA TG and DTG) techniques.

### 2. Experimental

### 2.1. Materials and methods

Melting points were taken with a digital melting apparatus and were uncorrected. The IR spectra were recorded on a MATTSON 1000 FTIR spectrophotometer using the KBr disc. Absorption spectra in ethanol, chloroform, and DMF were determined on a UNICAM UV2 UV–VIS spectrophotometer. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were observed and recorded on a Bruker AC 200 Fourier Transform Spectrometer operated at 200 MHz in CDCl<sub>3</sub>. Thermal analysis was carried out with a Shimadzu DTG-GOH simultaneous thermal analyser combined with a TAS 100 thermogravimetric analyser using ca. 3.5 mg samples, which were heated at the rate of 10°/min from ambient temperature to 1000 °C. The measurement was obtained using a flowing nitrogen atmosphere.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was used as the reference material. Elemental analyses were performed at the Instrumental Analysis Laboratory of ODTÜ Research Center. Purities of the *p*-*tert*-butylcalix[4]arene derivatives were examined in a mixture of chloroform/methanol (1:3) and those of the other compounds in a mixture of acetone/toluene (1:1) by TLC with Kieselgel 60 HF<sub>254</sub>.

### 2.2. General procedure for synthesis of acryloyl derivatives of p-tertbutylcalix[4]arene and calix[4]arene **3–10**

In first step, *p-tert*-butylcalix[4]arene **1** and calix[4]arene **2** were prepared as described in the literature [27,28]. Acryloyl derivatives of *p-tert*-butylcalix[4]arene and calix[4]arene were synthesised by reacting *p-tert*-butylcalix[4]arene and calix[4]arene with metallic sodium and later with acryloyl chloride in N<sub>2</sub> atmosphere in the order of molar ratios 1:1, 1:2, 1:3, and 1:4. The route of synthesis of the compounds is presented in Fig. 1. A typical procedure used for preparation of the compounds **3–10** is described below.

*p-tert*-Butylcalix[4]arene (0.77 mmol) and fresh metallic sodium (0.77 mmol) in dry THF (40 mL) were stirred together in  $N_2$ atmosphere for 24 h. Acryloyl chloride (molar ratios 1:1, 1:2, 1:3, and 1:4 according to *p-tert*-butylcalix[4]arene and calix[4]arene) was then directly added drop wise to this stirred solution in an atmosphere of dry nitrogen. After stirring the resulting mixture for 4 h, it was filtered and the desired product precipitated out by adding water. The product was filtered and washed several times with water and dried. After, the acrylate derivatives of *p*-*tert*-butylcalix[4]arene **3**–**6** were recrystallised from THF–water mixture, ethyl alchol–water from the other compounds **7–10**.

All acryloyloxy derivatives **3–10** were synthesised in a manner similar to that described above.

### 2.2.1. Monoacryloyloxy derivative of p-tert-butylcalix[4]arene [5,11,17,23-Tetra-tert-butyl-25-acryloyloxy-26,27,28-trihydroxycalix [4]arene] **3**

Yield: 33%, Mp: 275–278 °C, TLC (Chloroform/Methanol (1:3)): $R_{f}$ :0.51, IR (KBr pellet, cm<sup>-1</sup>): 3550 (OH), 3600–3200 (OH), 2967, 2880, 2840 (CH<sub>3</sub>–, –CH<sub>2</sub>–), 1732 (C=O), 1624 (–C=C–), 1278, 1205, 1178 (C–C(=O) –O), and (Ar–O). Analysis by calculation for C<sub>47</sub>H<sub>58</sub>O<sub>5</sub>. H<sub>2</sub>O: C, 78.33; H, 8.26%. Found: C, 78.69; H, 8.03%. Crystal Colour: S<sub>02</sub>O<sub>00</sub>Y<sub>07</sub>.

### 2.2.2. Diacryloyloxy derivative of p-tert-butylcalix[4]arene [5,11,17,23-Tetra-tert-butyl-25,27-diacryloyloxy-26,28-dihydroxy calix[4]arene] **4**

Yield: 27%, Mp: 289–291 °C, TLC (Chloroform/Methanol (1:3)): R<sub>f</sub>:0.83, IR (KBr pellet, cm<sup>-1</sup>): 3540 (OH), 3140<sup>s</sup> (OH), 2967, 2901, 2835 (CH<sub>3</sub>–, –CH<sub>2</sub>–), 1733 (C=O), 1624 (–C=C–), 1290, 1208, 1178 (C–C(=O) –O), and (Ar–O). Analysis by calculation for  $C_{50}H_{60}O_6$ . C, 79.36; H, 7.93%. Found: C, 79.28; H, 8.05%. Crystal Colour:  $S_{02}O_{00}Y_{20}$ .

### 2.2.3. Triacryloyloxy derivative of p-tert-butylcalix[4]arene

[5,11,17,23-Tetra-tert-butyl-25,26,27-triacryloyloxy-28-hydroxycalix [4]arene] **5** 

Yield: 34%, Mp: 293–297 °C, TLC (Chloroform/Methanol (1:3)): R<sub>f</sub>:0.48, IR (KBr pellet, cm<sup>-1</sup>): 3575 (OH), 2967, 2901, 2835 (CH<sub>3</sub>--, -CH<sub>2</sub>--), 1733 (C=O), 1600 (-C=C--), 1301, 1208, 1172 (C-C(=O) -O), and (Ar–O). Analysis by calculation for  $C_{53}H_{62}O_7.C$ , 78.51; H, 7.65%. Found: C, 78.30; H, 7.68%. Crystal Colour:  $S_{02}O_{00}Y_{20}$ .

## 2.2.4. Tetraacryloyloxy derivative of p-tert-butylcalix[4]arene [5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetraacryloyloxycalix [4]arene] **6**

Yield: 54%, Mp:>300 °C, TLC (Chloroform/Methanol (1:3)): R<sub>f</sub>:0.61, IR (KBr pellet, cm<sup>-1</sup>): 3540 (OH), 2978, 2952, 2876 (CH<sub>3</sub>-, -CH<sub>2</sub>-), 1749 (C=O), 1635 (-C=C-), 1306, 1172 (C-C(=O) -O), and (Ar–O). Analysis by calculation for C<sub>56</sub>H<sub>64</sub>O<sub>8</sub>.0.5 THF. 0.5·H<sub>2</sub>O C, 76.78; H, 7.74%. Found: C, 76.56; H, 7.59%. Crystal Colour: S<sub>02</sub>O<sub>00</sub>Y<sub>04</sub>.

### 2.2.5. Monoacryloyloxy derivative of calix[4]arene [25-acryloyloxy-26,27,28-trihydroxycalix[4]arene] **7**

Yield: 30%, Mp: 214–218 °C, TLC (Acetone/Toluene (1:1)): R<sub>j</sub>:0.40, IR (KBr pellet, cm<sup>-1</sup>): 3537 (OH), 3343–3104 (OH), 2939, 2863 (CH<sub>3</sub>–, –CH<sub>2</sub>–), 1747 (C=O), 1626 (–C=C–), 1244, 1251<sup>s</sup>, 1145 (C–C(=O) –O), and (Ar–O). Analysis by calculation for  $C_{31}H_{26}O_5$ . 0.5H<sub>2</sub>O: C, 76.38; H, 5.54%. Found: C, 76.20; H, 5.35%. Crystal Colour:  $S_{02}O_{00}Y_{07}$ .

## 2.2.6. Diacryloyloxy derivative of calix[4]arene [25,27-diacryloyloxy-26,28-dihydroxycalix[4]arene] **8**

Yield: 33%, Mp: 208–212 °C, TLC (Acetone/Toluene (1:1)):  $R_{f}$ :0.67, IR (KBr pellet, cm<sup>-1</sup>): 3537 (OH), 2942, 2863 (CH<sub>3</sub>-, -CH<sub>2</sub>--), 1733 (C=O), 1626 (-C=C--), 1259, 1251<sup>s</sup>, 1152–1132 (C-C(=O) -O), and (Ar-O). Analysis by calculation for  $C_{34}H_{28}O_6$ .C, 76.69; H, 5.26%. Found: C, 75.92; H, 5.26%. Crystal Colour:  $S_{00}O_{00}Y_{07}$ .

### 2.2.7. Triacryloyloxy derivative of calix[4]arene [25,26,27-triacryloyloxy-28-hydroxycalix[4]arene] **9**

Yield: 30%, Mp: 180–183 °C, TLC (Acetone/Toluene (1:1)): R<sub>f</sub>:0.68, IR (KBr pellet, cm<sup>-1</sup>): 3537 (OH), 2967, 2942, 2863 (CH<sub>3</sub>-, -CH<sub>2</sub>--), 1733 (C=O), 1629 (-C=C--), 1259, 1251°, 1152–1132 (C-C(=O)--O), and (Ar--O). Analysis by calculation for  $C_{37}H_{30}O_7.C$ , 75.76; H, 5.11%. Found: C, 75.08; H, 5.08%. Crystal Colour:  $S_{02}O_{02}Y_{20}$ .

### 2.2.8. Tetraacryloyloxy derivative of calix[4]arene [25,26,27,28-tetraacryloyloxycalix[4]arene] **10**

Yield: 63%, Mp: 240–245 °C, TLC (Acetone/Toluene (1:1)): R<sub>f</sub>:0.79, IR (KBr pellet, cm<sup>-1</sup>): 2942, 2874 (CH<sub>3</sub>–, –CH<sub>2</sub>–), 1738 (C=O), 1634 (–C=C–), 1253, 1164 (C–C(=O)–O), and (Ar–O). Analysis by calculation for  $C_{40}H_{32}O_8.0.5$  Toluene.C, 76.09; H, 5.24%. Found: C, 76.41; H, 5.44%. Crystal Colour:  $S_{02}O_{00}Y_{15}$ .

### 3. Results and discussion

#### 3.1. Synthesis

*p*-tert-Butylcalix[4]arene [27] and calix[4]arene [20] were prepared as described by a previously reported method. The acryloyl-ester derivatives of *p*-tert-butylcalix[4]arene and calix[4]arene **3–10** were synthesised by the reactions of *p*-tert-butylcalix[4]arene and calix[4]arene with metallic sodium and then with acryloyl chloride in N<sub>2</sub> atmosphere in molar ratios in the order 1:1, 1:2, 1:3, and 1:4. Fig. 1 shows the synthesis and structures of the *p*tert-calix[4]arene and calix[4]arene having acryloyl groups **1–10** and the experimental conditions employed.

The characterisation of the synthesised compounds **3–10** were based on the IR, UV–VIS, <sup>1</sup>H NMR, and <sup>13</sup>C NMR data. Spectroscopic and analytical data of these compounds are given in Tables 1–4.

### 3.2. IR spectral analysis of the compounds

The FT-IR data of the *p-tert*-butylcalix[4]arene and calix[4]arene-ester derivatives 3-10 (the structures of these compounds are illustrated in Fig. 1) were given in Section 2. The characteristic stretches of the carbonyl groups of acryloyl moiety of the synthesised compounds were identified as a very strong singlet absorption at 1749–1732 cm<sup>-1</sup> [24–26]. The OH group stretching vibration of *p-tert*-butylcalix[4]arene and calix[4]arene **1**, **2** was observed at ca. 3170 cm<sup>-1</sup> due to very strong intramolecular hydrogen bonds as reported in the literatures [11,28]. After esterification in molar ratios in the order 1:1, 1:2, and 1:3, two kinds of hydroxyl peaks appeared; the first, at  $3600-3104 \text{ cm}^{-1}$  for the compounds containing intramolecular hydrogen bond and the second, as narrow peak at 3575–3537 cm<sup>-1</sup> for these with non-intramolecular hydrogen bonds. The intramolecular hydrogen bonds among the OH groups and free forms of O-H bonds showed conformational changes in the molecules. The hydroxyl group in the tetraacryloyloxy derivative of calix[4]arene 10 was not observed because of the esterification between the hydroxyl groups and the acryloyl chlorides, but in tetraacryloyloxy derivative of p-tert-butylcalix[4]arene 6, the hydroxyl group appeared due to the presence of 0.5 mol H<sub>2</sub>O. The esterification in all the synthesised compounds was confirmed by the appearance of the intensive absorption bands between 1732 and 1749 cm<sup>-1</sup> which are attributed to the carbonyl groups of the acryloyl moiety. When in the acryloyl derivatives of *p-tert*-butylcalix[4]arene **3–6**, three aliphatic C–H stretching bands were observed in the range 2980–2835 cm<sup>-1</sup>, in the acryloyl derivatives of calix[4]arene **7–10**, two C–H stretching appeared at ca. 2940 and 2863 cm<sup>-1</sup> as given in Section 2. The other characteristic features coming at  $1635-1593\,\mathrm{cm}^{-1}$  and

Table 1UV-VIS data of the related compounds.

Compounds	Wavelength $[\lambda_{max} (nm)][\log \varepsilon (L/mol cm)]$									
	CHCl <sub>3</sub>	EtOH	DMF	pH 1–2 (DMF)	pH 12 (DMF)					
1	280 (4.47)	279 (3.08)	290 (4.16)	282 (3.66)	290 (4.19)					
			311 <sup>a</sup> (3.68)		311 <sup>a</sup> (3.95)					
2	275 (4.81)	275 (3.99)	286 (4.12)	278 (3.83)	287 (4.17)					
			308 <sup>a</sup> (3.66)		302 <sup>a</sup> (4.07)					
3	281 (4.69)	282 (3.72)	291 (4.04)	283 (3.42)	290 (4.14)					
			311 <sup>a</sup> (3.59)		311 <sup>a</sup> (3.88)					
4	281 (3.76)	281 (3.88)	290 (4.07)	283 (3.79)	290 (4.15)					
			311 <sup>a</sup> (3.61)		311 <sup>a</sup> (3.89)					
5	278 (3.71)	274 (3.63)	287 (3.95)	279 (3.56)	288 (3.93)					
			311 <sup>a</sup> (3.33)		311 <sup>a</sup> (3.38)					
6	277 (4.38)	275 (3.62)	288 (4.12)	278 (3.81)	288 (4.13)					
			314 <sup>a</sup> (3.48)		314 <sup>a</sup> (3.55)					
7	276 (4.73)	275 (3.83)	286 (4.18)	279 (3.58)	288 (4.24)					
			$308^{a}(3.78)$		305 <sup>a</sup> (4.09)					
8	277 (3.75)	275 (3.73)	285 (4.20)	280 (3.21)	285 (4.17)					
			305 <sup>a</sup> (3.80)		305 <sup>a</sup> (3.80)					
9	276 (3.75)	275 (4.48)	285 (3.87)	280 (3.55)	286 (4.16)					
			308 <sup>a</sup> (3.45)		308 <sup>a</sup> (3.95)					
10	273 (4.44)	271 (3.74)	285 (3.85)	279 (3.20)	285 (3.82)					
			308 <sup>a</sup> (3.41)		308 <sup>a</sup> (3.40)					

<sup>a</sup> Shoulder.

1306–1132 cm<sup>-1</sup> are attributed to the ethenyl (CH<sub>2</sub>=CH–) and the aromatics -C=C-, -C(O) -O- and Ar–O, respectively. These findings indicates that the synthesised compounds exist in calixareneesters forms as proved by studies in the literature [24,25–32].

### 3.3. UV-VIS spectral analysis of the compounds

The UV–VIS absorption bands of the related compounds 1–10 were given in Table 1. The absorption behaviours of the *p*-tertbutylcalix[4]arene and calix[4]arene-ester derivatives 3-10 were investigated in a different solvents such as absolute ethyl alcohol, chloroform, and DMF depending on their solubility and also in DMF of pH = 2 and 12. As can be seen from Table 1, the absorption maxima ( $\lambda_{max}$ ) for the compounds **1–10** were observed at 271– 282 nm in ethyl alcohol, at 273-281 nm in choloroform, at 285-291 nm with a shoulder at 305-314 nm in DMF, at 278-283 nm in DMF of pH = 2, at 285-290 nm with a shoulder at 302-314 nm of pH = 12. While the synthesised compounds represent one absorption band in ethyl alcohol and chloroform, they show two absorption band in DMF, one of which is a shoulder as pointed out above. The above given bands with high extinction coefficient are attributed to the aromatic  $\pi \rightarrow \pi^*$  transitions of the related compounds. Comparing the UV-VIS spectral data for different values of pH in DMF, the absorption maxima of the compounds showed a hypsochromic shift up to ca. 8 nm at pH = 2 depending on the hydrogenation of probably azo and oxygene of acryloyl groups. However, there were no shift at pH = 12, indicating that aqueous sodium hydroxide at pH = 12 does not hydrolyse the compounds **3–10** containing acryloyl groups. As a result, the acryloyl derivatives of calixarenes 3-10 give similar absorption bands in the UV region resembling that of the *p-tert*-butylcalix[4]arene and calix[4]arene 1-2 because of the electronic effects of the acryloyloxy moiety instead of the hydroxyl groups. The UV-VIS electronic spectra of the compounds 1, 3, 6 and 2, 7, 10, in CHCl<sub>3</sub> (as  $1 \times 10^{-4}$  M) are shown as two parts in Fig. 2a and b. Examining the UV-VIS spectra of the compounds 4, 5, 8 and 9, it was found that their spectra in the same region are similar to each other.

### 3.4. NMR spectral analysis of the compounds

The <sup>1</sup>H NMR chemical shift values of the related compounds recorded in CDCl<sub>3</sub> are given in Table 2. The <sup>1</sup>H NMR spectrum of the calix[4]arene **7** containing one acryloyl group, was shown in Fig. 3 as a typical example. The esterification in the compounds **3–10** was confirmed by the existence of the resonance peaks between 6.50 and 5.00 ppm which are attributed to the ethenyl group of the acryloyl moiety. In addition, the attaching of acryloyl groups was observed by displacement and disappearence of the hydroxyl signals. After esterification in molar ratios in the order 1:1, 1:2, and 1:3, the hydroxyl peaks were generally appeared as two kinds of peaks; the first, at ca. 10.2 ppm for the compounds containing intramolecular hydrogen bonds and the second peaks at 4.44–5.41 ppm for those with non-intramolecular hydrogen bonds (see Table 2 and Fig. 3).

In the *p*-tert-butylcalix[4]arene derivatives **3**, **4** containing one and two acryloyl group, respectively, the hydroxyl protons resonated at 10.20 and 10.30 ppm as weak intramolecular hydrogen bonds as reported in the literature [1] and at 4.53 and 4.58 ppm without hydrogen bonds. The other *p*-tert-butylcalix[4]arene derivative **5** having three acryloyl groups does not represent intramolecular hydrogen bond because of one structural hydroxyl group. In the compound **6** containing four acryloyloxy groups, the hydroxyl resonance peak cannot be observed due to the esterification with acryloyl chlorides of all hydroxyl groups in the structure.

In examining hydroxyl peaks of the calix[4]arene derivatives not containing *p-tert*-butyl groups, the hydroxyl groups of the compound **7** containing one acryloyl group was defined by the 10.19 ppm peak origination from weak intramolecular hydrogen band and the peak at 5.41 ppm without hydrogen bond. The intramolecular hydrogen bonding in compound **8** having two acryloyl group was not observed because of the absence of intramolecular hydrogen bond but two hydroxyl groups gave rise to peaks at 5.41 and 5.07 ppm. In the other calix[4]arene derivative **9** having three acryloyl groups, intramolecular hydrogen bond was not observed as expected because of one hydroxyl group in the structure. In the last compound **10**, the hydroxyl resonance was not there due to the lack of hydroxyl groups (Table 2). The proton signals of hydroxyl groups in all the calix[4]arene derivatives **3–10** were determined by making exchange with D<sub>2</sub>O.

The resonance peaks of ethenyl hydrogen atoms in acryloyl groups of the compounds **3–10** were identified as three different groups (H13, H14, H15) at 6.50–4.50 ppm in agreement with the literature [26,32,33]. When the acryloyl proton peaks of the

**Table 2**<sup>1</sup>H NMR data of the related compounds.



Table 3The <sup>13</sup>C NMR data of the compounds.



1 n=0, 3 n=1, 4 n=2, 5 n=3, 6 n=4

2 n=0, 7 n=1,8 n=2, 9 n=3, 10 n=4

Compounds	>C=0	Phenol group							Acryloyl group		>CH <sub>2</sub>	tert-Butyl		
	C14	C7	C10	C13	C8, C12	C1, C5	C2, C4	C3	C9, C11	C16	C15	C6	C17	C18
1	-	149.8	-	-	-	129.7	125.0	143.6	-	-	-	32.4	41.3	31.4
2	-	148.7	-	-	-	128.9	128.2	122.2	-	-	-	31.6	-	-
3	163.6	149.0	146.6	144.0	132.2	127.0	126.5	141.8	125.8	131.9	127.6	33.9	35.1	31.6
														31.1
4	163.6	150.5	148.9	144.0	132.2	126.9	126.5	141.8	125.8	132.9	127.6	33.8	35.1	31.6
														31.4
														31.0
5	166.0	151.5	148.0	143.5	132.5	127.6	126.0	141.8	125.4	134.3	128.2	34.1	36.6	31.8
	165.0												35.1	30.9
6	164.9-	-	146.6	144.0	133.0	-	-	-	127.1	134.1	129.1	34.0	38.8	31.8
	163.2												35.8	31.0
7	163.6	152.6	126.8	145.2	132.2	129.2	128.9	119.8	127.6	133.4	127.2	32.9	-	-
		148.7										31.6		
8	163.5	152.6	126.7	146.6	132.3	129.2	127.6	119.8	127.2	133.0	130.2	37.3	-	-
	163.1			145.2				119.6				33.7		
-					100.0							32.9		
9	163.5	152.6	127.1	147.8	133.0	130.2	125.8	119.8	127.6	133.4	129.5	37.3	-	-
	163.1		126.9	146.6	132.3	130.1		119.6	127.2		129.2	33.7		
10	162.9		126.7	145.2	100.0				107.1	400.0	129.0	32.9		
10	164.7	-	125.8	148.9	133.0	-	-	-	127.1	132.9	130.2	37.2-	-	-
	163.1			146.6							129.3	29.6		

compounds **3–6** which have the *p-tert*-butyl groups, were seen at 6,50–4.50 ppm, in the other calix[4]arenes **7–10** without *p-tert*-butyl groups, these peaks were observed between 6.39–5.25 ppm depending on the increase in the number of acryloyl group. The resonance intervals above, belong to the protons H13, H14 and H15 (Table 2). For example, the peaks of the H15 in Z configuration according to carbonyl group in an acryloyl moiety were came at 6.50–6.08 ppm as doublet of doublets and multiplets. On the other hand, the peaks of the H14 in E configuration according to carbonyl group were seen at 5.96–5.00 ppm as generally multiplets. For the geminal H13, the related peaks resonate at 6.20–5.10 ppm. As a result, with increasing the number of the acryloylgroups in the compounds **3–10**, the resonance peaks of ethenyl hydrogen atoms were observed as mixed multi-peaks in the above internal.

The aromatic = C—H resonance signals of the compound **1** were observed as singlet at 6.73 ppm and for compound **2**, as doublet and triplet at 7.02 and 6.72 ppm, respectively (Table 2). The aromatic = C—H resonance peaks in the compounds **3–10** resonated between 7.41 and 6.61 ppm as multipletsas a result of attachment of the acryloyl groups to hydroxyl groups in the compounds **1**, **2**. In parallel with the numberof the acryloyl groups in the synthesised compounds **3–10**, the aromatic = C—H resonance signals were determined as mixed multi-peaks. In the tetraacryloyl derivatives of *p-tert*-butylcalix[4]arene **6**, the proton peaks H2 and H4 were not observed as expected because of the absence of the hydroxyl group in the aromatic structure and also the protons H2, H3, and H4 of compound **10** does not have hydroxyl group. The protons of —CH<sub>2</sub>— groups of all calix[4]arenes **3–10** were shifted both

up-field and low field with increasing the number of the acryloyl groups. The related values can be seen in Table 2. These findings indicate that the compounds **3–10** exist in calixarene-ester forms [24–32].

The <sup>13</sup>C NMR chemical shift values of the compounds **1–10** were summarised in Table 3. It is clearly seen from >C=O group signals between 166.0 and 163.1 ppm in the <sup>13</sup>C NMR data of the compounds **3–10** that acryloyl group was attached to the oxygen of hydroxyl group in comparison with *p*-tert-butylcalix[4]arene and calix[4]arene 1, 2 without acryloyl group. The peaks of C15 atom of CH moiety found in acryloyl group resonated at 130.2-127.2 ppm and also at 134.4–131.9 ppm for C16 atom of CH<sub>2</sub> as expected [25,26,33,34]. Close similarities among all these values are clearly seen in Table 3. When the phenyl groups of *p*-tert-calix[4]arene compounds resonated at 151.5-125.4 ppm, the same signals were observed at 152.6–119.6 ppm in the calix[4] arene derivatives without tert-butyl groups. The C8 and C12 atoms of the phenyl groups of the *p-tert*butylcalix[4]arene-esters 3 (Fig. 4), 4 and 5 shifted to low field at 5.2-2.2 ppm according to C1 and C5 atoms, at 3.1-0.3 ppm in the calix[4] arene-esters 7, 8, and 9 under the electronic attraction effect of the acryloyl groups. When the --CH<sub>2</sub>-- groups of the calix[4]arene compounds 7-10 with out tert-butyl groups resonated at 37.3-29,6 ppm, in the calix[4]arene derivatives **3–6** having *tert*-butyl groups, the same signals were observed at 34.1-33.8 ppm as mixed-peaks with the C17 and C18 peaks of tert-butyl groups because of the resonance in the same regious (Table 3).

As given in Section 2, the colour codes of the related compounds **3–10** are from Farbenatlas [35].

### Table 4

Thermoanalytical results of the compounds.

Compounds	Decompositio	on	DTG <sub>max</sub> (°C)	% Mass loss	% Total mass loss	
	Stage	Temperature range (°C)				
C <sub>44</sub> H <sub>56</sub> O <sub>4</sub> (1)	1	111-301	203 (-)	9.78		
	2	301-435	385 (+)	62.98		
	3	435-748	489 (+)	17.37		
	4	748-1392	1157 (+)	7.39		
					97.52	
C <sub>28</sub> H <sub>24</sub> O <sub>4</sub> (2)	1	93–247	203 (-)	4.63		
	2	247-454	378 (+)	49.82		
	3	454-1393	522 (+)	23.16		
					77.61	
C <sub>47</sub> H <sub>58</sub> O <sub>5</sub> (3)	1	109-214	140 (-)	2.22		
	2	214-699	414 (+)	79.38		
	3	699-1345	1145 (-)	12.04		
					93.64	
C <sub>50</sub> H <sub>60</sub> O <sub>6</sub> (4)	1	133-356	333 (-)	8.31		
	2	356-872	413 (+)	77.05		
					85.36	
C <sub>53</sub> H <sub>62</sub> O <sub>7</sub> (5)	1	90-190	144 (+)	3.28		
		250-620	432 (+)	80.45		
					91.18	
C <sub>56</sub> H <sub>64</sub> O <sub>8</sub> (6)	1	90-275	200 (-)	4.37		
	2	275-495	434 (+)	74.65		
	3	495-1382	525 (+)	17.72		
					96.74	
C <sub>31</sub> H <sub>26</sub> O <sub>5</sub> (7)	1	229-358	335 (+)	9.48		
	2	358-511	403 (+)	50.53		
	3	511-1393	526 (+)	24.79		
					86.09	
C <sub>34</sub> H <sub>28</sub> O <sub>6</sub> (8)	1	100-301	276 (-)	2.66		
51 20 0 ( )	2	361-511	422 (+)	53.70		
	3	511-890	542 (+)	10.45		
					66.81	
C <sub>37</sub> H <sub>30</sub> O <sub>7</sub> (9)	1	105-600	425 (+)	58.96		
	-		( )		69.80	
C40H32O8 (10)	1	220-849	631 (+)	66.95		
	2	849-1395	1371 (+)	10.32	77.27	
	-	2.10 1.000		10.02		



Fig. 2. UV–VIS spectra of *p-tert*-butylcalix[4]arene and calix[4]arene derivatives in CHCl<sub>3</sub>.



Fig. 3. <sup>1</sup>H NMR spectrum of the calix[4]arene derivative 7.



Fig. 4. <sup>13</sup>C NMR spectrum of the *p-tert*-butylcalix[4]arene derivative 3.

#### 3.5. Thermal analysis

The thermoanalytical results obtained from TG, DTA and DTG curves of the compounds **1–10**, were summarised in Table 4. All these values were taken from ambient temperature to 1000 °C in flowing nitrogen atmosphere. The TG, DTG and DTA curves of the compound **4** containing two acryloyl groups were illustrated in Fig. 5 as the typical example.

The TG, DTG and DTA curves of all calixarene compounds containing acryloyl groups clearly show that the mass losses of the compounds which contain *tert*-butyl groups and non-*tert*-butyl groups, are similar to each other by exothermic change but the first mass losses of all compounds, during endothermic/exothermic processes as can be seen from Table 4. The first and final mass losses of the investigated compounds takes place slowly, whereas the second stage mass loss of these compounds becomes sharp as shown by the  $DTG_{max}$  at 414–434 °C but the compound **10**, at 631 °C. In the second stage, the thermal mass losses of the synthesised compounds occur between 214 and 361 °C and completed in the interval 422–872 °C together with the mass losses between 49.82% and 79.38%. The second thermal mass loss stage of these compounds is the basic decomposition stage but the first stage in the compound **10** being four acryloyl groups, at 220–849 °C with the mass loss of 66.95%.

Considering the TG curve of the compound IV (Fig. 5) containing two acryloyl groups, it is seen that the mass losses in the first and second stages appear at 133–356 °C and 356–872 °C, respectively, the mass losses of this compound were determined as 8.31% and 77.05%, respectively. As can be seen from DTG and DTA curves in Fig. 5, the DTG values of the given compound were about 333 °C



Fig. 5. TG, DTG and DTA curves of the *p*-tert-butylcalix[4]arene derivative 4.

by endothermic process and 413°Cby exothermic process, respectively.

Although the decomposition mechanism of the *p-tert*-butylcalix[4]arene and calix[4]arene-ester derivatives **3–10** is complex, it probably consists of a splitting of the calixarene bonds similar the most of the calixarenes and the acryloyl groups. In all the compounds, the total mass loss occuring in two or three stages but one stage in the compound 9, during heating changes from 66.81% to 97.52% as depending on the number of the acryloyl groups in the structure as can be seen from Table 4.

### 4. Conclusion

The structural properties of the newly synthesised the mono-, di-, tri-, and tetraacrylate derivatives of *p-tert*-butylcalix [4]arene and calix[4]arene were characterised and discussied by IR, UV-VIS, <sup>1</sup>H NMR, and <sup>13</sup>C NMR. The esterification in these compounds was confirmed by both the appearance of the vibrational bands between 1732 and 1749 cm<sup>-1</sup> due to the carbonyl groups of the acryloyl moiety and <sup>1</sup>H NMR data between 6.5 and 5.00 ppm originating from the resonance peaks of ethenyl hydrogen atoms in acryloyl groups which were also confirmed by the presence of mixed multi-peaks in relation with the increase in the number of acryloyl group. The basic mass loss stage of all calixarene compounds containing acryloyl groups clearly took place between 214 and 361 °C and except the compounds 9,10.

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