

Synthesis of Dendrimers Liquid Crystalline Materials based on 1,3,5-triphenylbenzene

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Received: 6th Feb, 19; Revised: 17th Mar, 19, Accepted: 10th Apr, 19; Available Online: 25th Jun, 2019

ABSTRACT

In this study, new compounds of discotic liquid crystalline dendrimers are prepared which is derived from 1,3,5-triphenylbenzene. The synthesis of these compounds shows the effect of dendrimer unit on the mesogenic properties. The structures of prepared compounds characterized by using spectroscopic method e.g. FT-IR and ¹H-NMR. The liquid crystalline phases of prepared compounds was identified by using the hot-stage polarizing optical microscope (POM) and differential scanning calorimeter (DSC).

Keywords: dendrimer, crystalline, liquid crystalline dendrimer.

INTRODUCTION

Dendrimers are hyper-branched, monodispersity, three dimensional structure which is show a unique group of artificial macromolecules consisting of regular branching points in each monomer unit, which are ordered so that their number growth in a geometric growth bypassing from center to the perimeter¹. Because of their special structure, these have developed physical and chemical properties like high solubility, miscibility and reactivity². These properties made the dendrimers a suitable for many different applications³. Dendrimers are classified with respect to the generation (1st, 2nd, 3rd, ..., nth) be based on the number of the steps branching (the configuration of which usually has the spherical symmetry form), as shown below:

In the late 70's the scientist Vögtle and Tomalia developed the first synthesis of a dendrimers separately. The word "dendrimer" in original comes from two Greek words, (dendri: which means tree branch and mer: which means part). Lately, Dendrimer materials have become of great interest in supramolecular chemistry, mostly due to the possibility of gaining well-defined macromolecules⁴. Basically, dendrimers can be regarded as a class of "intermediate compounds" between low-molecular-mass material and polymers, also dendrimers are acquired by careful the stepwise evolution of sequent layers of generations⁵. Liquid-crystalline dendrimer (LCD) compounds are the molecules of which own a dendritic (i.e., hyper-branched regularly) construction, containing structural units (called mesogenic groups or mesogens) that can be given a form of mesophases⁶. The molecules of such LC dendrimers display two opposite tendency. On the one hand, dendrimers are synthetic compounds with regular branches originating from the center of a macromolecule. As a result, dendrimers have a spherical regularity, by which all branches in a macromolecule tend

to get anisotropic spatial localization under the effect of entropy forces. On the other hand, mesogens molecules show strong orientational interactions, which drives to the formation of anisotropic mesophases producing a large benefit in the enthalpy³.

EXPERIMENTAL PART

Materials and Techniques

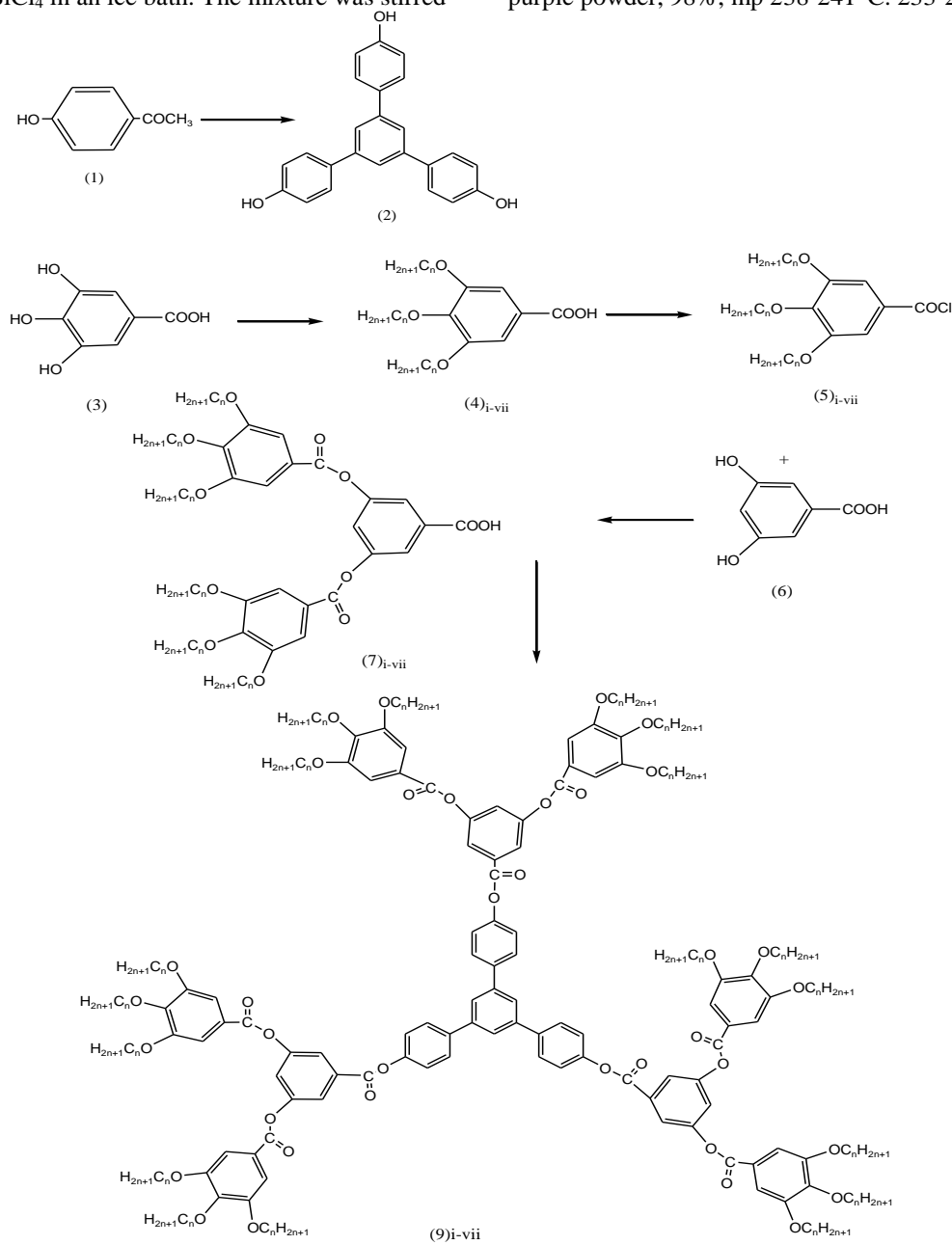
All the chemicals (reagents and solvents) were supplied from Merck, BDH, Fluka and Alfa chemicals Co. and used as received.

The infrared spectra of the prepared compounds were recorded using FT-IR 8300 Fourier transform infrared spectrophotometer of SHIMADZU Company as a potassium bromide (KBr) discs in the wave number range of (4000-400) cm⁻¹, in Al-Nahrain University, Iraq. Uncorrected melting points were recorded on hot stage Gallen kamp melting point apparatus. The ¹H-NMR spectra were recorded on Brüker ACF 300 spectrometer at 300 MHz, using deuterated chloroform or DMSO as solvent with TMS as an internal standard, in the university of Exeter, England. Elemental analysis (CHNS-O) was carried out using EURO EA elemental analyzer instrument. Transition temperatures and enthalpies were scanned in TA instruments LINSEIS DSC PT-1000 differential scanning calorimeter with a heating rate of 10.0°C/min in air and it was calibrated with indium (156.6°C, 28.45 J/g). The temperatures were read as the maximum of the endothermic peaks. The optical behavior observations were made using MEIJI microscope equipped with INSTEC hot stage and central processor controller mK 1000 and connected with Lumenera color video camera, in Al-Nahrain University, Iraq.

Preparation of 1,3,5-tris(4-hydroxyl phenyl)benzene (2)

Dissolved (0.03 mole, 4.08 g) of 4-hydroxy acetophenone (10 ml) of absolute ethanol, then added (6 ml) of silicon tetrachloride SiCl_4 in an ice bath. The mixture was stirred

in room temperature for 48 hours. After that, the mixture was poured onto ice water, filtered and dried. Yield: purple powder, 98%; mp 238-241 °C. 233-240 °C (lit.)⁷



Scheme 1: Synthetic route for dendrimer liquid crystal.

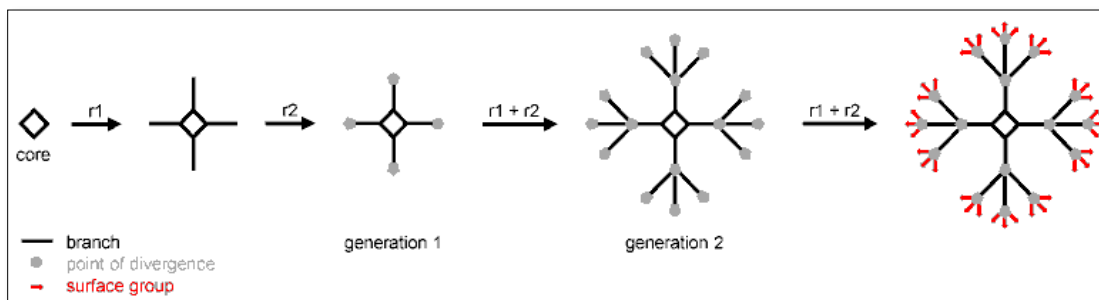


Figure 1: The steps branching of the dendrimers generations.

Preparation of 3,4,5-trialkoxy benzoic acid (4)_{i-vii}

After Dissolve (0.01 mol) of 3,4,5-Trihydroxy benzoic acid (3) in (20 mL) ethanol, (0.03mol) potassium carbonate was added with continues stirring, the mixture

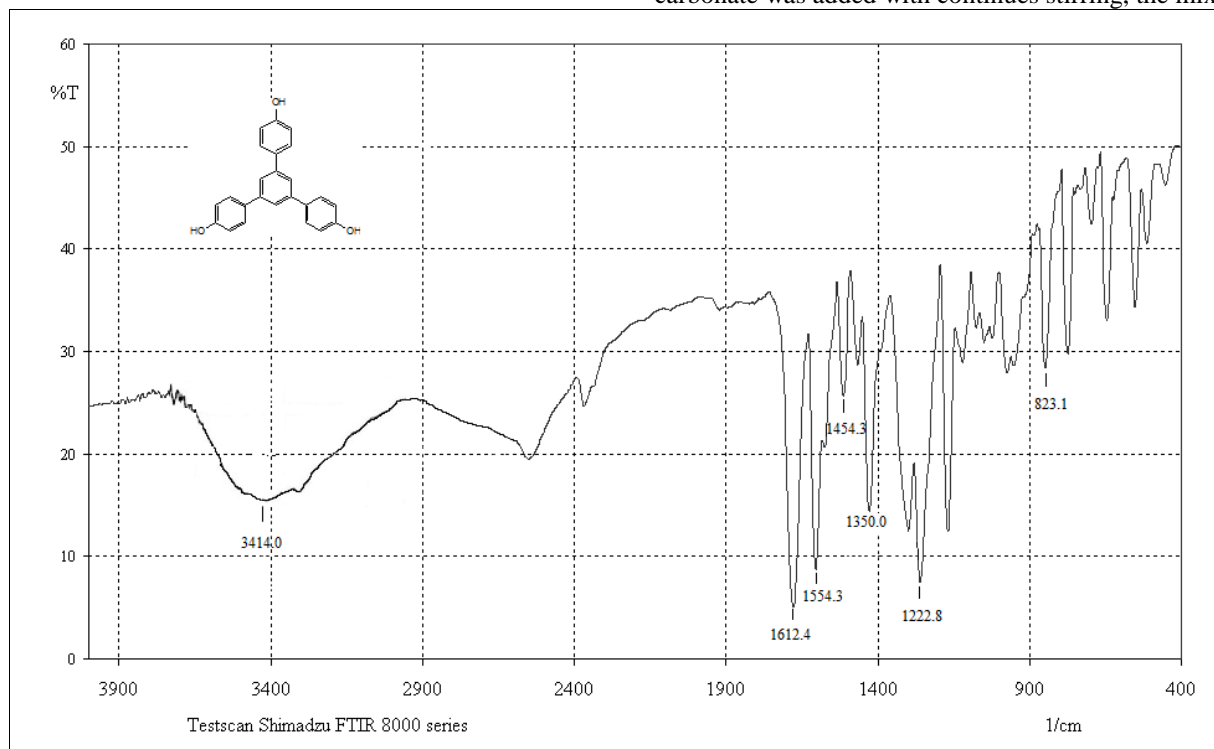


Figure 2: FT-IR spectrum of 1,3,5-tris(4-hydroxyl phenyl)benzene (2).

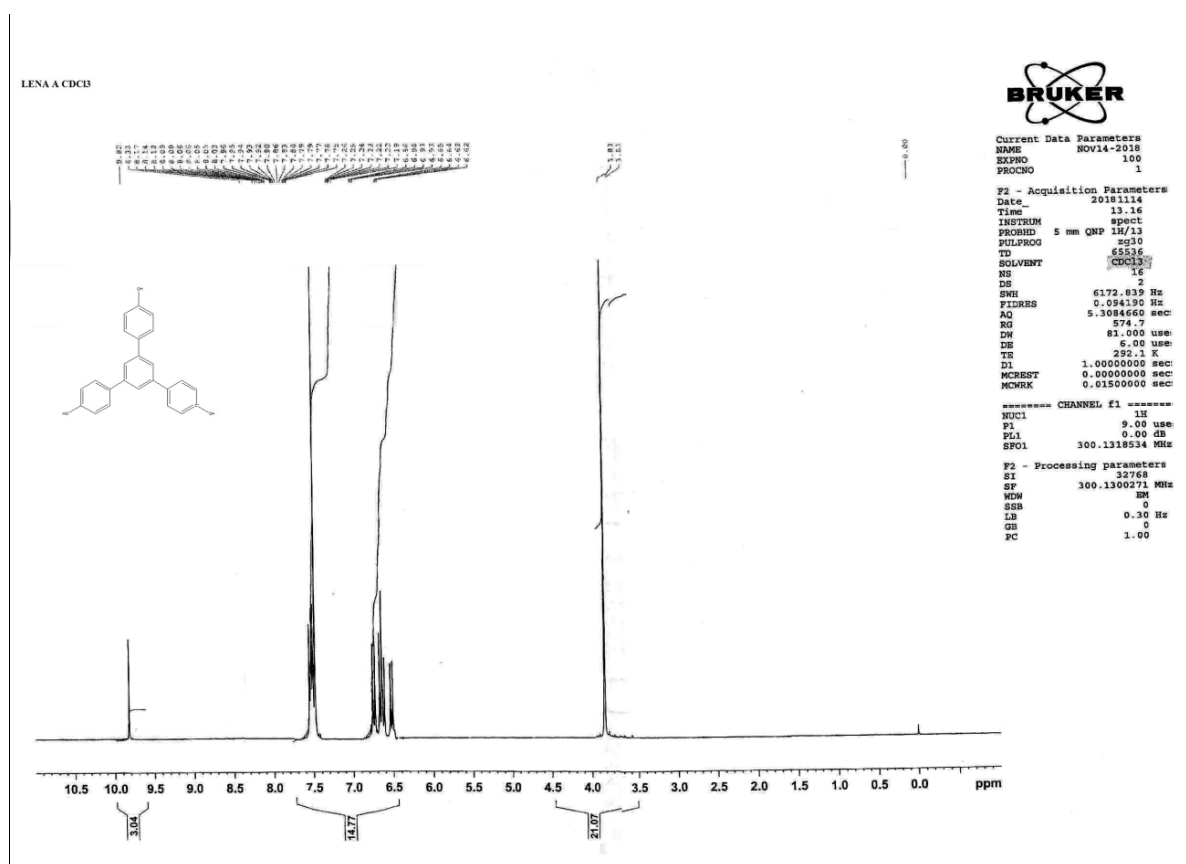


Figure 3: ¹H NMR spectrum of 1,3,5-tris(4-hydroxyl phenyl)benzene (2)

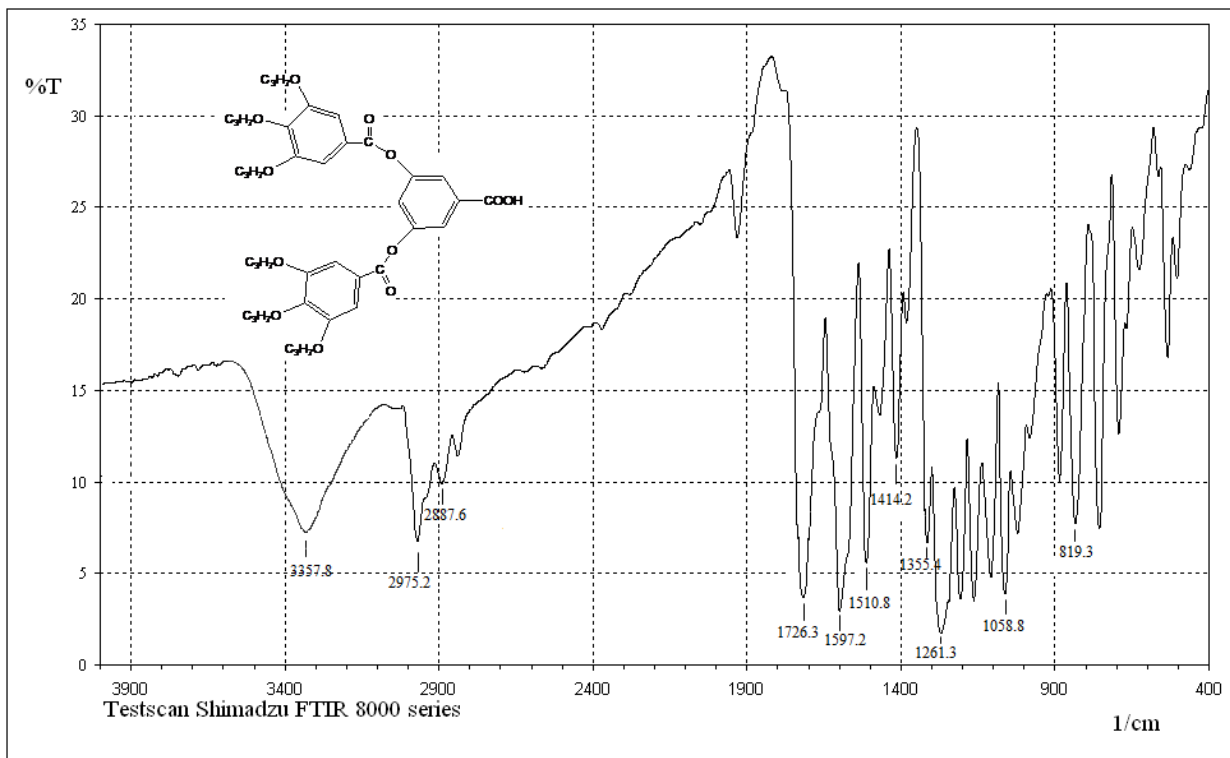


Figure 4: FT-IR spectrum of 3,5-di-(3',4',5'-tripropoxybenzoyloxy)benzoic acid (7)_{iii}

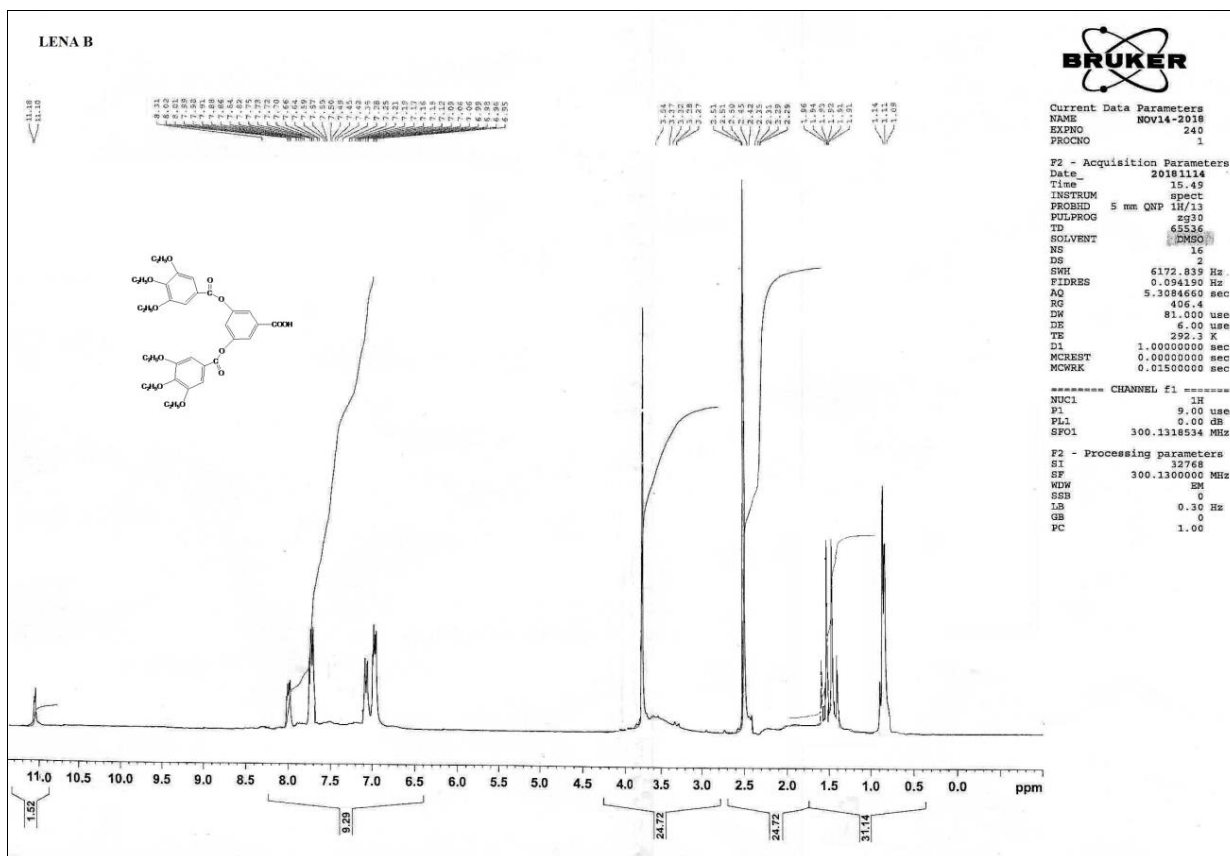


Figure 5: ¹H NMR spectrum of 3,5-di-(3',4',5'-triethoxybenzoyloxy)benzoic acid (7)_i.

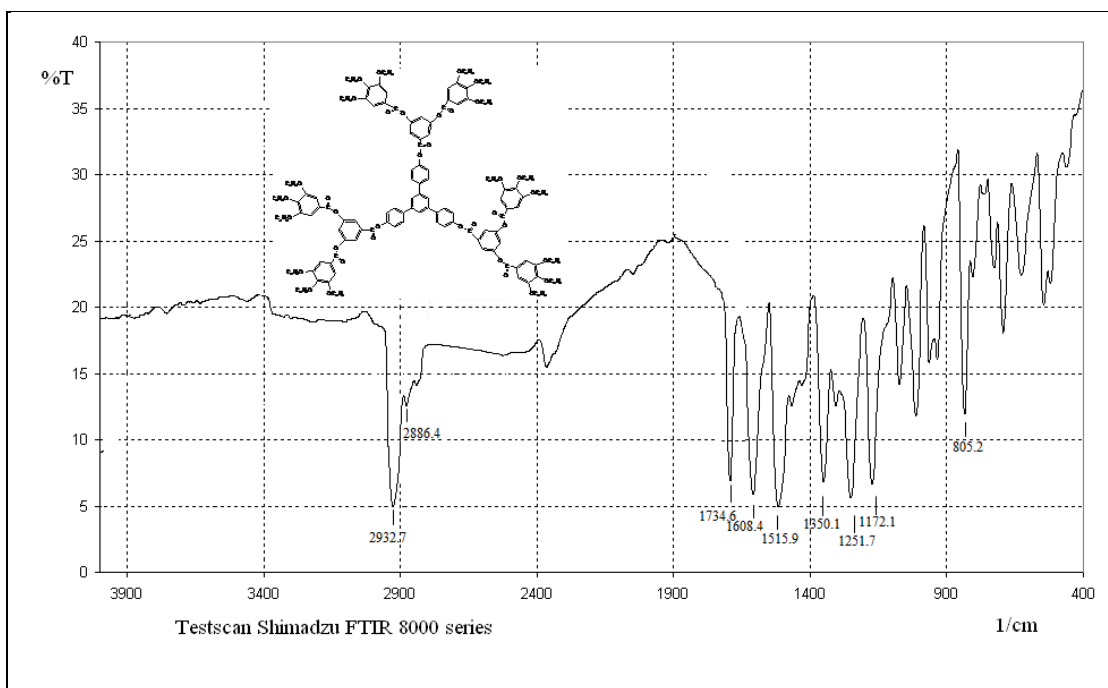


Figure 6: FT-IR spectrum of 1,3,5-tris[3,5-di-(3',4',5'-tri-butoxybenzoyloxyphenyl)benzene (9)_{iii}

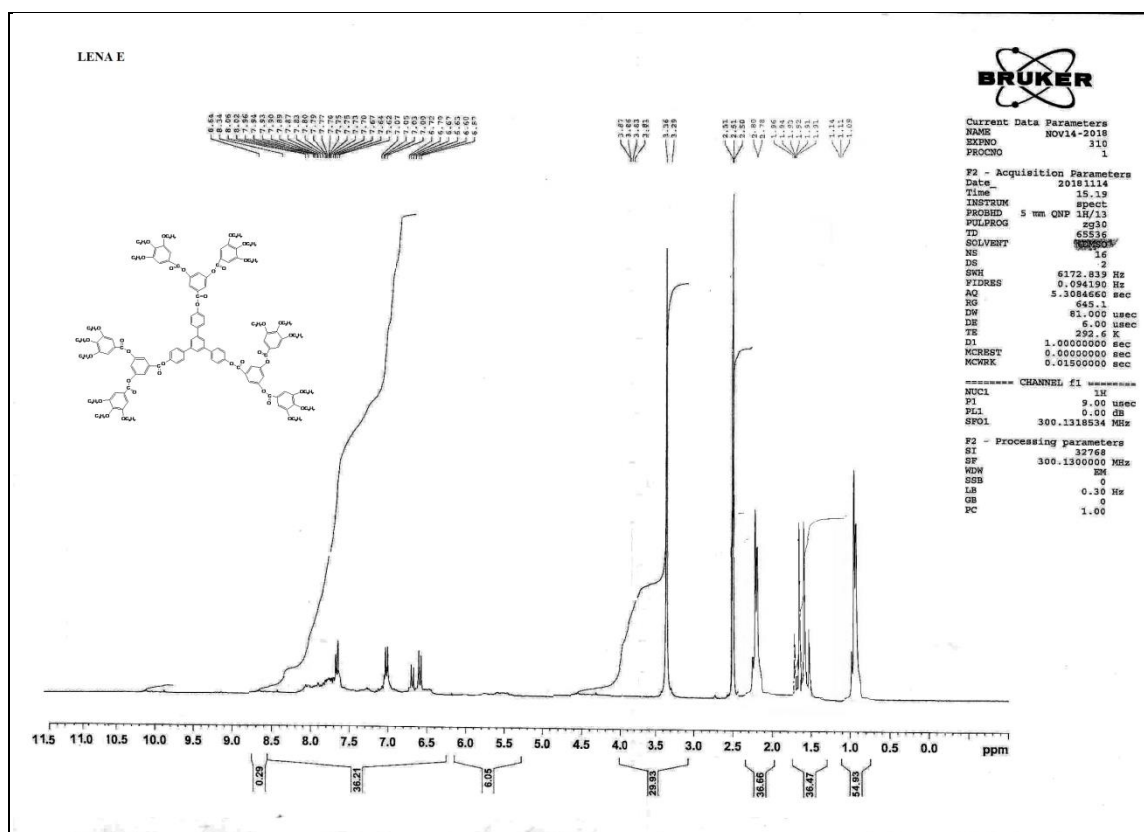


Figure 7: ¹H NMR spectrum of 1,3,5-tris[3,5-di-(3',4',5'-tri-butoxybenzoyloxyphenyl)benzene (9)_{iii}

was cooled to room temperature, then (0.03 mol) of alkyl bromide was added gradually. The solution was refluxed overnight. Then (0.03 mol) potassium carbonate K₂CO₃ dissolved in a little amount of water about (5mL) was added to the reaction mixture and heated for (1-3) hours. The solvent evaporated and an equal amount of water was added, then the solution was heated until became clear.

Acidification with concentrated hydrochloric acid HCl yielded solid precipitate⁸.

Preparation of 3,4,5-trialkoxy benzoyl chloride (5)_{i-vii}

3,4,5-trihydroxy benzoic acid (0.01 mole, 2 g) was refluxed with 15 ml thionyl chloride SOCl₂ and 4 drops of DMF for (3-4) hours. The excess of thionyl chloride was evaporate and the product is dark brown precipitate

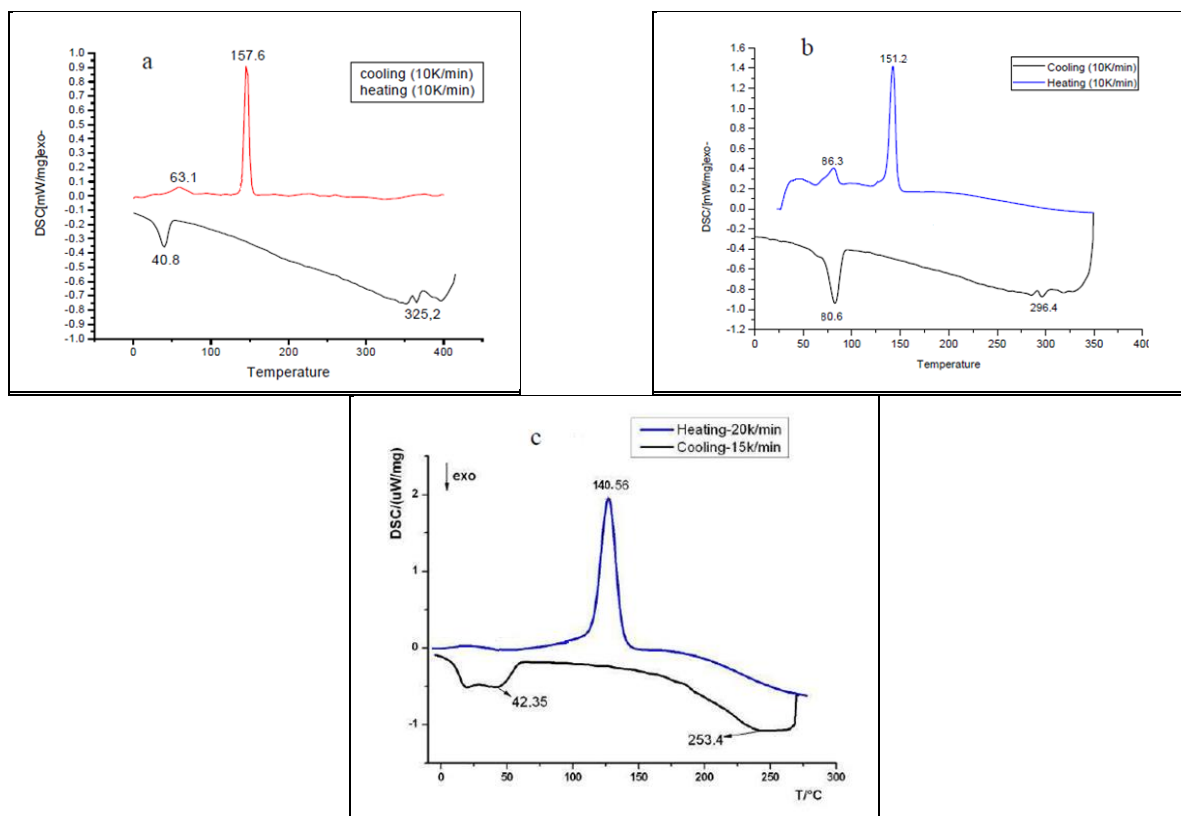


Figure 8: DSC thermograms for compounds (a) (7)_{ii}, (b) (7)_{iv}, c (7)_{vii}.

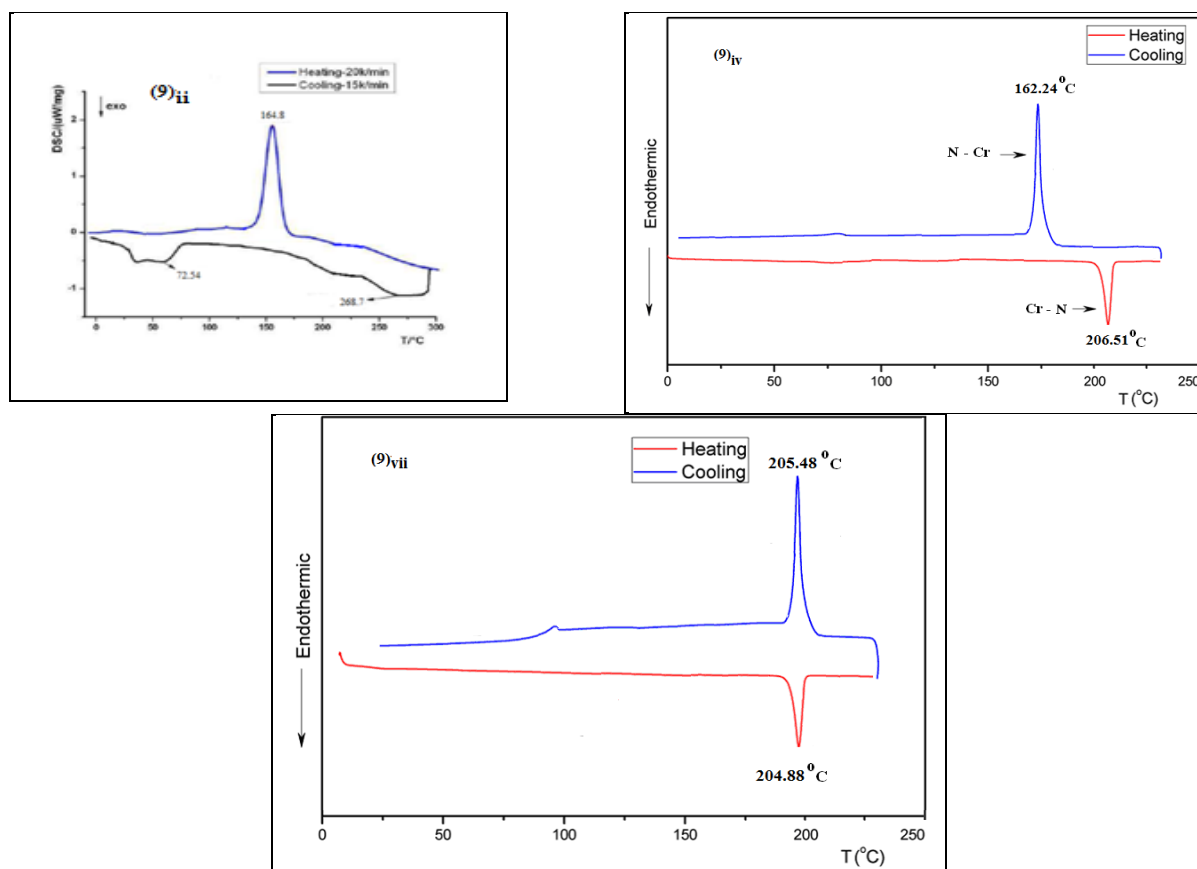


Figure 9: DSC thermograms for compounds (a) (9)_{ii}, (b) (9)_{iv}, c (9)_{vii}.

of 3,4,5-trihydroxy benzoyl chloride. The acid chloride left behind was directly used for further reaction without purification⁸.

Synthesis of 3,5-di-(3',4',5'-trialkoxybenzoyloxy)benzoic acid (7)_{i-vii}

A mixture of 3,5-dihydroxybenzoic acid (0.001 mol) and 3,4,5-trialkoxy benzoyl chloride (0.002 mol) with (15 ml) pyridine were stirred for 24 hours. The mixture were poured in ice water and filtered to give product which have pale brown precipitate⁹. The physical properties of compound (7)_{i-vii} are listed in table (1).

Synthesis of 3,5-di-(3',4',5'-trialkoxybenzoyloxy)benzoylchloride(8)_{i-vii}

3,5-di-(3',4',5'-trialkoxybenzoyloxy)benzoic acid (7)_{i-vii} (0.01 mole) was refluxed with 10 ml thionyl chloride SOCl₂ and 4 drops of DMF for (3-4) hours. The excess of thionyl chloride was evaporate and the product is dark brown precipitate¹⁰. The acid chloride left behind was directly used for further reaction without purification.

Synthesis of 1,3,5-tris[3,5-di-(3',4',5'-trialkoxybenzoyloxy)phenyl]benzene (9)_{i-vii}

A mixture of 1,3,5-tris(4-hydroxyl phenyl)benzene (2) (0.001 mole, 0.35 g) and 3,5-di-(3',4',5'-trialkoxybenzoyloxy)benzoylchloride(8)_{i-vii} (0.003 mole) with (15 ml) pyridine were stirred for 24 hours. The mixture were poured onto ice water, the produced precipitate was filtered and washed with distilled water. The physical properties of compound (9)_{i-vii} are listed in table (1).

RESULT AND DISCUSSION

The general synthetic procedure for the 1,3,5-triphenylbenzene dendrimers is shown in Scheme (1): The dendrimer compounds was synthesized from the reaction of dendrone 3,5-di-(3',4',5'-trialkoxybenzoyloxy)benzoylchloride(8)_{i-vii} with 1,3,5-tris(4-hydroxyl phenyl)benzene (2) which represent the core of dendrimer molecule that contained an activated hydroxy functionality located at the focal point of the growing dendritic.

Structures of the synthesized compounds were confirmed by FT-IR and ¹H NMR.

FTIR spectroscopy provided complementary evidence for the structures.

FTIR spectrum of the core compound (2) shows characteristic hydroxyl absorption stretching at 3414 cm⁻¹ which is the distinguishing feature of the phenol group, stretching band at (1612, 1512, 1454, 1222 and 825) cm⁻¹ which attributed to ν C = C, δ O – H, ν C – O and γ tri substituted benzene ring.

¹H NMR (CDCl₃): δ = 9.92 (s, 3H), 6.52 – 7.26 (m, 12H), 7.72-8.33 (s, 3H).

Spectroscopic identification of the dendrone compounds were carried out using FT-IR and ¹H NMR techniques.

FT-IR of compounds (7)_{i-vii} show characteristic aliphatic C – H band in the range 2932-2975 cm⁻¹ for asymmetrical stretching bands and 2842-2884 cm⁻¹ for symmetrical stretching. The spectra also show bands around 3145-3320 cm⁻¹ of hydroxyl group stretching of carboxylic group, bands at 1734-1742 cm⁻¹ for C = O stretching of

Table 1: Melting point and % yield of prepared compounds.

NO.	Yield%	M.P.°C	NO.	Yield%	M.P.°C
7 _i	64	161-163	9 _i	72	110-115
7 _{ii}	71	178-189	9 _{ii}	65	118-120
7 _{iii}	65	191-194	9 _{iii}	67	125-128
7 _{iv}	68	198-202	9 _{iv}	58	170-175
7 _v	54	185-188	9 _v	52	155-158
7 _{vi}	58	200-203	9 _{vi}	51	160-163
7 _{vii}	62	221-223	9 _{vii}	54	181-184

ester group, bands at 1124-1255 cm⁻¹ for C – O – C stretching band. Compound (7)_{iii}, show the following infrared data (cm⁻¹): 3357, 2975, 2887, 1726, 1597, 1261 and 819.

¹H NMR (7)_i, (CDCl₃): δ = 11.1 (s, 1H, COOH), 7.55-8.31 (s, 3H), 6.95 – 7.50 (d, 4H), 1.91-1.96 (q, 12H, OCH₂), 1.09-1.14 (t, 18H, CH₃)

The synthesized dendrimer compounds structure characterized using spectroscopic techniques FT-IR and ¹H NMR.

FT-IR of compounds (9)_{i-vii} show characteristic aliphatic C – H band in the range 2942-2982 cm⁻¹ for asymmetrical stretching bands and 2831-2879 cm⁻¹ for symmetrical stretching. The spectra also show bands at 1732-1743 cm⁻¹ for C = O stretching of ester group, bands at 1131-1254 cm⁻¹ for C – O – C stretching band. Compound (9)_{iii} show the following infrared data (cm⁻¹): 2932, 2886, 1734, 1608, 1251 and 805.

¹H NMR (9)_i, (CDCl₃): δ = 6.57-8.64 (m, 36H, Ar.), 2.78-2.80 (t, 36 H, OCH₂), 1.91-1.96 (m, 36H, CH₂), 1.09-1.14 (t, 54H, CH₃).

The mesomorphic behavior investigated via means of thermally controlled POM. Dendrone molecules (7)_{ii-vii} show typical nematic texture under microscopic observation (Fig. 7). For the mesomorphism of the synthesized compounds (7)_{i-vii} all the compounds display different phase-transition temperatures related to the length of the chain.

The first compound (7)_i do not reveal any liquid crystalline behavior, but simply changes from the solid crystalline state to the isotropic liquid at 162°C. Compounds (7)_{ii-vii} display enantiotropic mesomorphism. The texture observed by POM on heating the solid crystal are consistent with the presence of columnar mesomorphism, with fan-shaped typical to columnar phases for compounds (7)_{iv,v,vi} and droplet typical to a columnar nematic for compound (7)_{vii} as shown in (Fig. 7a,b,c).

While the mesomorphic behavior of dendrimer molecules compounds (9)_{i-vii} a typical discotic columnar texture-fan shapes (Fig. 8a,b,c) were observed.

All dendritic precursors as well as the final dendrimers displayed liquid-crystalline properties in agreement with their chemical nature and structure.

The thermal behaviors of (7)_{i-vii} and (9)_{i-vii} were shown by DSC (Fig. 9a,b) and Fig. (10a,b)

There is close relationship between mesomorphism and molecular constitution of organic compounds. Hence thermal stability, a measure of mesomorphism, can be

correlated with the molecular constitution of the compounds. The different mesomorphic properties arises due to the presence of different right terminal groups which differ in their sizes and polarities¹¹.

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