ORIGINAL RESEARCH PAPER

THERMAL DEGRADATION IN NON-ISOTHERMAL CONDITIONS OF SOME FERROCENE DERIVATIVES

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Abstract: The study of the thermal behavior of some symmetrically monosubstituted and disubstituted ferrocene derivatives, with liquid crystal properties, presented in this work, assesses the structure – thermal stability relation, necessary for the knowledge of the field of applicability, of the processing conditions and for the valorization of industrial waste. The influence of the length of the flexible part, of the azoaromatic unit and of the presence of the cholesteryl unit on thermal stability has been proven.

Keywords: *thermal behavior, ferrocene derivatives, influence of molecular structure*

INTRODUCTION

The properties of materials are determined by the combinations of functional units within their structure. The main factor in inducing the special characteristics in the case or organometallic molecules is represented by the presence of the metal, which can contribute with its specific properties as well as with molecular shapes that cannot be found in other organic derivatives [1 – 3]. The thermal stability of synthesized materials is one of the most important requirements in the discovery of new properties. As thermotropic liquid crystals are materials in which the property of arrangement into crystalline liquid crystals occurs within a specific temperature field and involves the growth of the system temperature, one can easily understand the important role that thermal stability plays for these compounds. Although the thermal stability of polymer liquid crystals has been intensely studied [4 – 10], small-molecule liquid crystals were investigated to a much more reduced extent in terms of their thermal stability [11 – 14]. Following molecular simplicity, this type of compounds enable a much clearer understanding of the degradation processes, and, thus, systematic study can contribute with essential additional information.

Given the above mentioned aspects, the main objective of this paper consisted in establishing the influence of the molecular structure on thermal stability for a series of symmetrically monosubstituted and disubstituted ferrocene derivatives. The study of the thermal stability of these compounds is motivated by the presence of high transition temperatures and especially by the isotropy temperatures, which exceed, at times, the thermal stability of the material.

MATERIALS AND METHODS

Symmetrically monosubstituted and disubstituted ferrocene derivatives were obtained via esterification reactions between ferrocene acids and the phenol unit, in the presence of DCC/DMAP, at room temperature. The confirmation of the structure of the synthesized ferrocene derivatives was obtained via the MRI, RI and mass spectroscopy techniques [15]. The structures of the compounds, the stability of which was analyzed in this paper, are presented in Table 1.

The mesomorphic properties of the compounds **P1**, **P2**, **P3** and **P4** were analyzed via optic microscopy at polarized light and differential calorimetry. The liquid crystal properties for the compounds **P1**, **P2** and **P4** (Figures 1 – 3) were emphasized. The monosubstituted derivative which does not contain the azo-mesogenic unit does not generate liquid crystalline properties, probably because of the increased flexibility of molecules.

By analyzing the structures of the compounds presented in Table 1, one may notice that one can establish the influence of various factors: the length of the flexible part, of the azoaromatic unit and of the presence of the cholesteryl unit on thermal stability.

Table 1. *Structures of the symmetrically monosubstituted and disubstituted ferrocene derivatives*
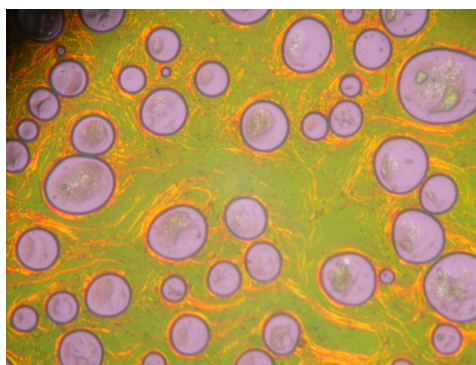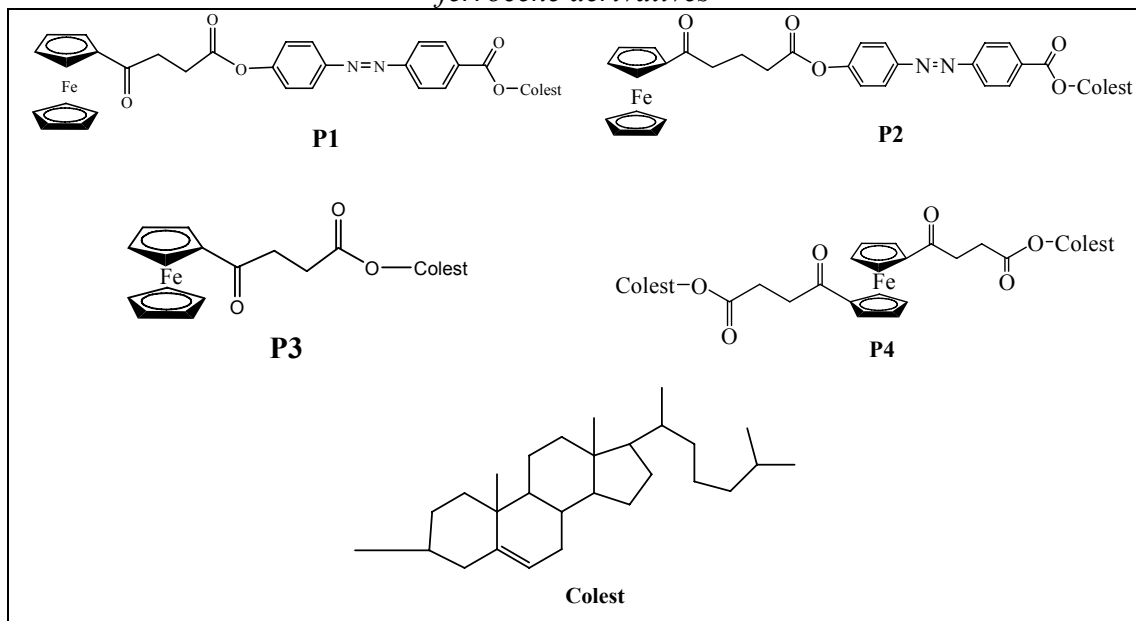
Figure 1. *Textures of the compound P1 at the second heating at a 183°C temperature*
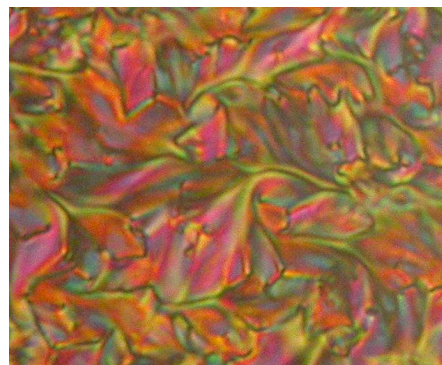
Figure 2. *Textures of the compound P2 at the first cooling at a 154°C temperature*
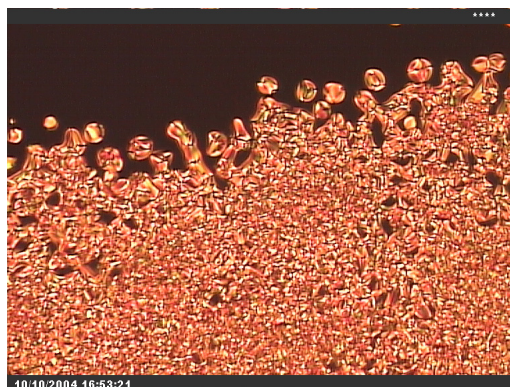
Figure 3. *Textures of the compound **P4** at the first cooling at a 135°C temperature*

The thermal analysis was performed with the help of a derivatograph of the Mettler Toledo TGA-SDTA851^e type, in an atmosphere of N_2 with a flow of 20 mL/min, at the heating speed of 10 ºC/min, in the temperature interval 25 – 900 ºC and at a sample weight of 3 ÷ 5 mg. The operational parameters were kept constant for all the samples, for the purposes of obtaining some comparable data.

RESULTS AND DISCUSSIONS

The thermogravimetric curves (TG) and the derivative thermogravimetric curves (DTG) registered with the Mettler Toledo derivatograph in inert atmosphere (N_2) are presented in Figures 4 and 5 for the symmetrically monosubstituted and disubstituted ferrocene derivatives.

From the thermograms one may notice that the onset temperature of the weight loss of the studied samples is situated at values higher than 240 °C. The thermal decomposition of the monosubstituted ferrocene derivatives (**P1**, **P2** and **P3**) and of the symmetrically disubstituted compound (**P4**) occurs in three or four degradation stages, with different weight losses, depending on the chemical structure (Table 2).

As concerns the samples **P1** and **P2**, the most important weight loss was registered in the second degradation stage, at temperatures between 300 and 400 °C. The samples **P3** and **P4** have a different behavior, and the most important weight losses (approximately 55%) occur during the first stage, within the same temperature interval. One may notice that the thermal degradation of all the samples is not complete and that a certain quantity of residue with values between 17 and 24% remains.

If one considers thermal stability as a criterion for the onset temperature of thermal degradation (T_{onset}) starts, one may notice that the thermal stability of the analyzed compounds increases according to the series:

$$\textbf{P1} < \textbf{P2} < \textbf{P3} < \textbf{P4}$$
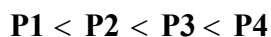
One obtains the same thermal stability series if one considers as a criterion for thermal stability the temperature at which the degradation speed is maximum (T_{peak}).

The study analyzed the influence of thermal stability on certain factors, respectively the influence of the length of the flexible part, of the azoaromatic unit and of the presence of the cholesteryl unit. For the purposes of obtaining additional information on the influence of the structure on thermal stability, one resorted to conformational studies by using the HyperChem 7.5 modeling software. The geometry of the investigated compounds, obtained with an energy minimum, is rendered in Figure 6, and Table 3 presents the molecular descriptors obtained via modeling with the help of the HyperChem 7.5 software.
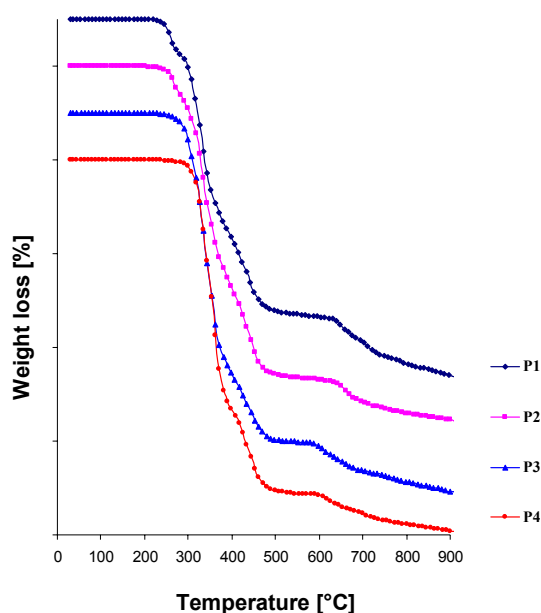
Figure 4. TG curves

The following steps were performed during the HyperChem 7.5 modeling process:
- ➤ Drawing of the molecules;
- ➤ The transformation of the molecules from 2D into 3D;
- ➤ The minimization of the system energy via the application of various optimization methods: Polak-Ribière, Steepest Descendent or Fletcher-Reeves;
- ➤ Geometric measurements – length, diameter, volume and surface of the molecule (geometric descriptors);
- ➤ Topological measurements – molecular mass (topological descriptors);
- ➤ Electronic measurements – polarizability (electronic descriptors).

Molecules are easily drawn in HyperChem; moreover, this software contains a graphic interface which enables the monitoring of the construction of the molecules. By using the drawing instrument, one can obtain a bi-dimensional (2D) representation of a molecule and, subsequently, a tri-dimensional (3D) structure will be obtained with the help of the "Model Builder". The Model Builder implicitly adds the hydrogen atoms to the drawn molecules. The software measures the lengths of the bonds, the angles, the torsion angles and the atomic charges as soon as the model is built or after its construction. HyperChem also has a database with various subunits (amino acids, nucleic acids, etc.), so as to allow the fast construction of the compounds which contain these subunits.
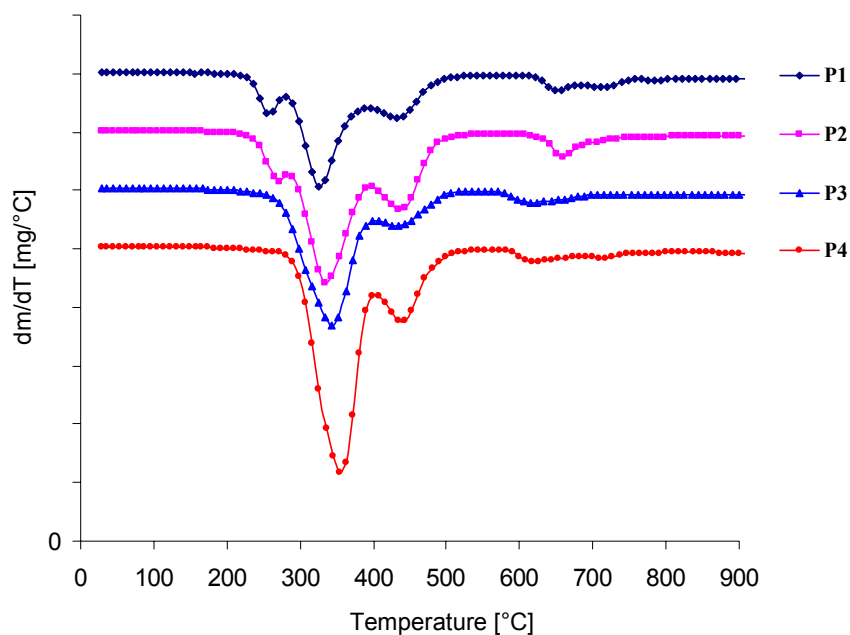
Figure 5. *DTG curves*

Table 2. *Thermogravimetric data*

| Sample	Degradation stage	T_{onset} [°C]	T_{peak} [°C]	T_{endest} [°C]	Weight loss [%]
P1	I	246	258	264	7.54
	II	296	327	356	35.00
	III	401	435	468	20.61
	IV	640	650	845	13.19
	residue				*23.66*
P2	I	255	270	275	7.20
	II	310	337	373	37.91
	III	408	439	457	21.56
	IV	644	661	850	9.30
	residue				*24.03*
P3	I	282	345	372	55.34
	II	372	436	476	16.76
	III	586	612	856	11.12
	residue				*16.78*
P4	I	311	356	382	54.53
	II	421	441	467	17.64
	III	593	614	853	7.14
	residue				*20.69*
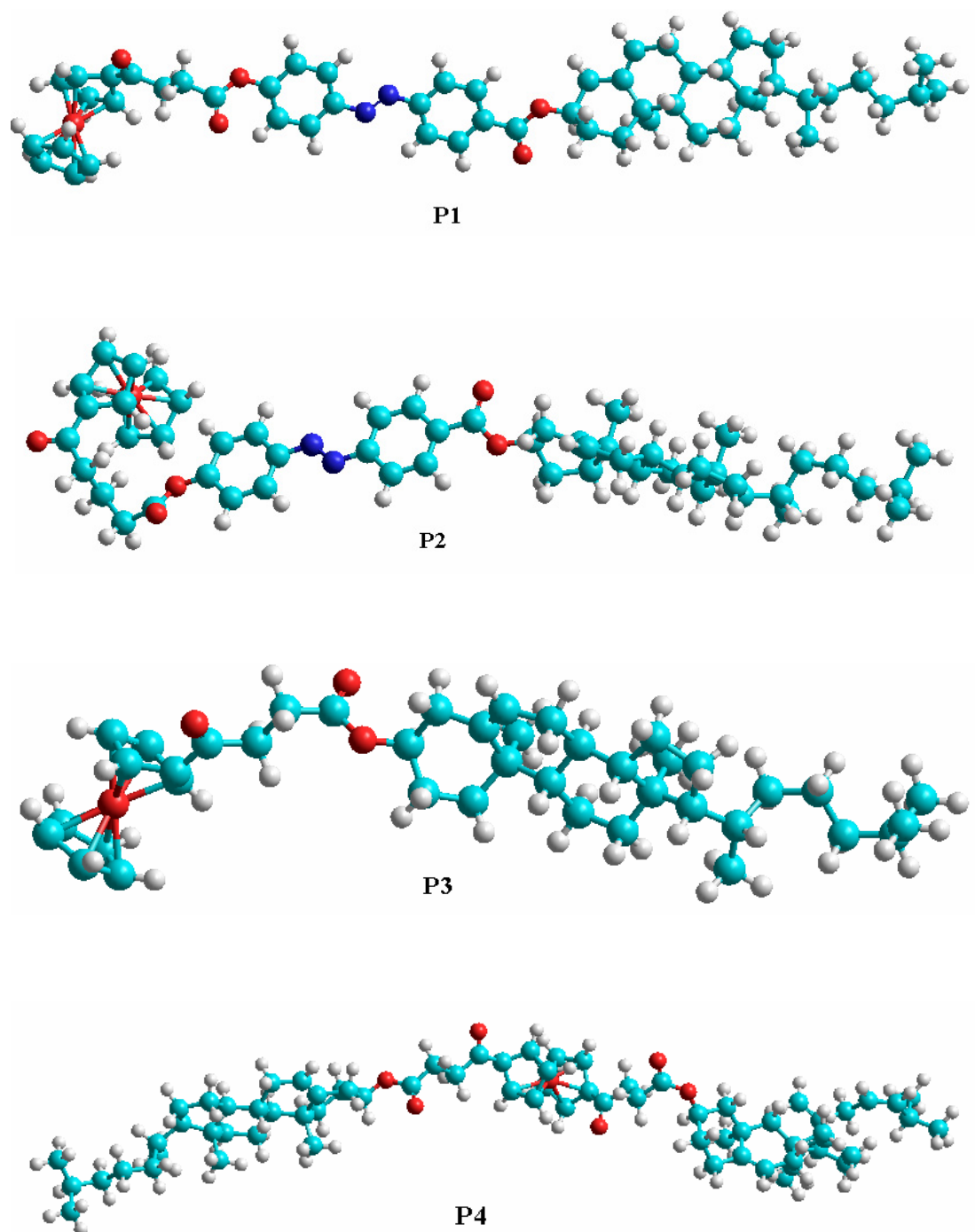
Figure 6. *Geometry of the symmetrically monosubstituted and disubstituted ferrocene derivatives*

Table 3. *Molecular descriptors obtained via molecular modeling*

Sample	Approximate surface [Å^2]	Volume [Å^3]	Polarizability [Å^3]	Molar mass [Da]	Asymmetry parameter[*] S = L/d
P1	1113.4	2433.7	93.1	878.9	2.7
P2	1087.7	2425.1	94.9	893.0	3.9
P3	830.0	1852.2	69.2	654.7	1.9
P4	1443.6	3149.7	123.2	1119.4	2.5

[*] The asymmetry parameter was calculated via the relation between the length of the molecule and its diameter

A well defined structure is generated in order to calculate the molecular descriptors. After the drawing of the molecules and the minimization of the system energy via optimization, one calculates the "single point" properties of a molecule. The optimized structure can be used in molecular dynamics simulation. The Molecular Mechanics force field (MM+) was applied for the optimization of the preliminary structure and for the study of the conformational behavior of each ferrocene derivative. It has been proven that molecular mechanics produces more realistic geometric values for the majority of organic molecules due to the fact that it is much parameterized.

The comparative analysis of the chemical structure of the analyzed compounds by taking into consideration the onset temperature of the degradation led to a series of observations concerning the thermal stability of the analyzed organic compounds. Thus, if one compares the thermal stability of compound **P1** with the thermal stability of the ferrocene derivative **P2,** which has an extra methylene group in the flexible part of the molecule, one may notice an increase by almost 10 °C of the thermal stability of the latter compound and a high value of the asymmetry parameter. If one takes into consideration the shape of the DTA peaks in Figure 7 (the first stage), the initiation of the thermal decomposition for the first two samples probably occurs in the azo group, which, according to some previous studies, is more labile [16]. This statement is also supported by the fact that, for the symmetrically monosubstituted (**P3**) or disubstituted (**P4**) ferrocene derivatives which do not contain the azoaromatic unity, thermal stability increases by approximately 40 °C when compared to compounds **P1** and **P2.**

If one compares the thermal stability of compound **P3** with its homolog, which comprises the azoaromatic unit **P1,** one may notice a rise by 36 °C of the onset temperature of thermal degradation, but the value of the asymmetry parameter and of polarizability decreases, which leads to the impossibility of arranging the ferrocene derivative **P3** in the crystalline liquid stage.

As concerns the compound **P4**, which is a symmetrically distributed ferrocene derivative, its thermal stability improves by approximately 30 °C when compared with its monosubstituted homolog. A possible explanation would be a much higher polarizability of the molecule, as well as the intensification of the strong reactions between the hydrogen atoms and the aliphatic chains of cholesterol.
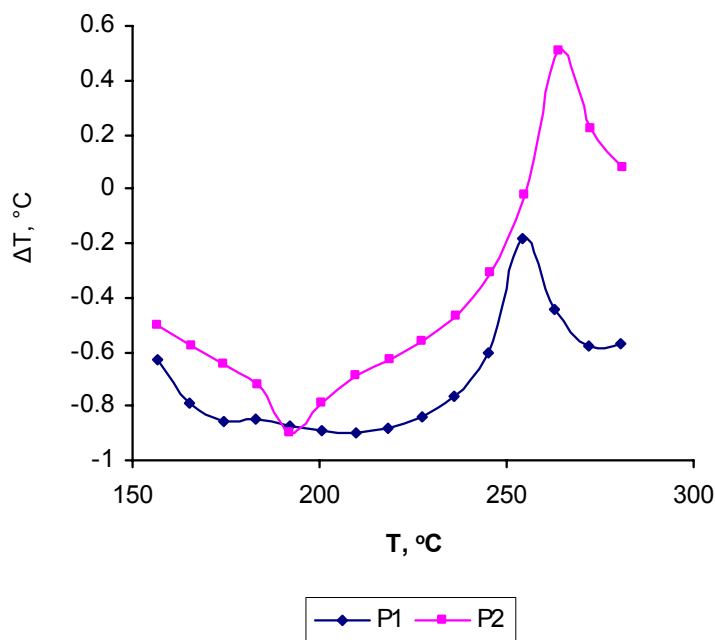
Figure 7. *DTA curves for compounds **P1** and **P2***

CONCLUSIONS

The characterization via thermal methods emphasized the structure – thermal stability dependence, more specifically the influence of the length of the flexible part, of the azoaromatic unit and of the presence of the cholesteryl unit on thermal stability. The remarks concerning the structure – thermal stability dependence, found in this paper, reveal the possibility of guiding synthesis for the purposes of obtaining compounds with liquid crystal properties and with a certain degree of thermal stability.

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