

Investigations on thermal stability of some ferrocene liquid crystals bearing azo, ferrocenyl and cholesteryl units

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Ferrocene liquid crystals received a great attention in the last years, mainly because of its interesting properties and the combination between liquid crystals properties with metals properties. Only few examples of ferrocene liquid crystals bearing either cholesteryl or azo aromatic unit could be found in the literature. The presence of each of three groups contribute by specific properties to the obtaining of materials capable of responding in electric or magnetic field or to UV light exposure. The azo aromatic units are photo-sensitive due to cis-trans photoisomerization and can be used as switchers in liquid crystals devices. On the other hand, the cholesteryl unit induces chiral mesophases with the advantage of fast response on stimuli, high birefringence and the presence of physical colors. Since mesomorphic behavior for the thermotropic liquid crystals are due to the increasing of temperature in the system, it is easy to understand the importance of thermal stability for such kind of systems. The purpose of the paper is the study the thermal stability of some ferrocene liquid crystals bearing both azo and cholesteryl and to evaluate the influence of each structural factor such as: ferrocenyl, cholesteryl, azo units and the length of the flexible chain on the thermal stability of these compounds.

(Received January 18, 2006; accepted March 23, 2006)

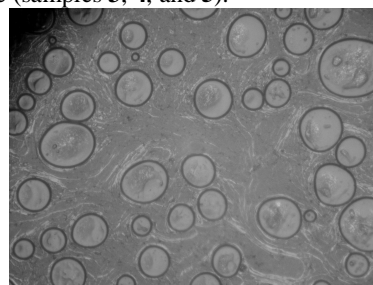
Keywords: Ferrocene, Liquid crystal, Ferrocene units, Cholesteryl unit

1. Introduction

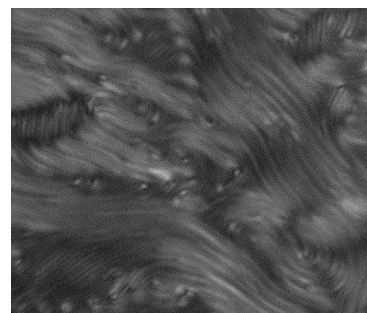
Liquid crystals are materials in which the mesomorphic properties appear in a certain temperature domain. The mesophases can be identified by their individual birefringent textures when viewed between crossed polarisers under a light microscope or by differential scanning calorimetry (DSC) by identifying the transition temperatures and the level of enthalpy from one phase to another [1]. Ferrocene is a bulky unit so that the appearance of liquid crystals phases of ferrocene derivatives is limited both by sterical factors and polarity. Any minor change on the shape and structure of the molecules might have a major influence upon the type of mesophase and mesomorphic domain [2]. This molecule is having instead the advantage that is combining the properties of metals with those of organic compounds [3]. When ferrocene derivatives contain both azo and chiral units, new materials capable of responding in magnetic and electric field or to UV-light exposure can be obtained [4]. For finding new properties, thermal stability of the compounds is one of the most important requirements. Because liquid crystals are materials in which mesomorphic properties appears at a certain temperature domain it is easy to understand the important role played by thermal stability for such compounds. For example, in the case of liquid crystals with the clearing point above the decomposition temperature a study of thermo degradation process is requested [5].

The present paper is a study of the thermal stability of some ferrocene liquid crystals derivatives (compounds **1** and **2**) by comparing their stability with simple and similar

compounds in which minor changes of the structure has been made (samples **3**, **4**, and **5**).



sample 1 at 183 °C

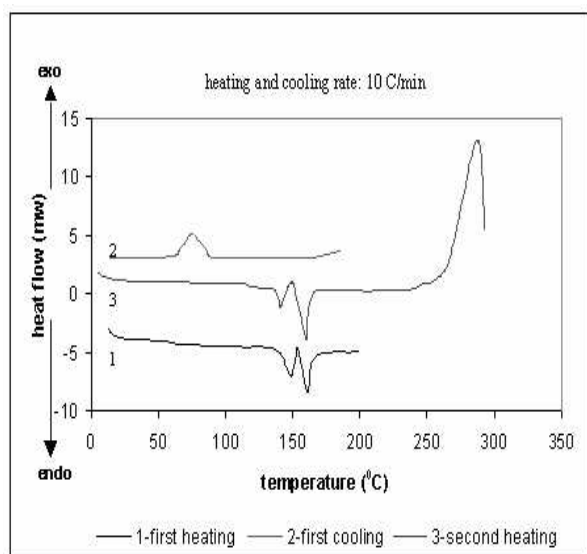


sample 2 at 203 °C

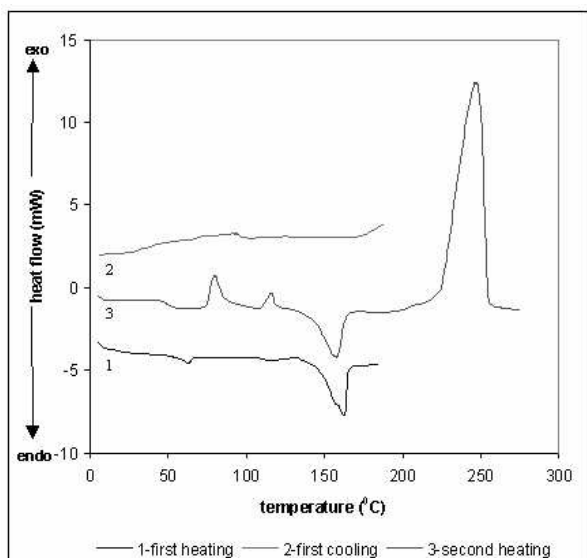
Fig. 1. Textures of samples 1 and 2 observed on the POM.

Liquid crystals behavior of samples **1** and **2** by both POM and DSC measurements are presented in Fig. 1 and 2. The DSC curves of samples **1** and **2** reveal the property of polymorphism, resulting from the different arrangements of the ferrocene in the solid state. As it is well known, conformational polymorphism occurs when a

molecule is able to adopt different shapes, due to internal degrees of freedom (ferrocene is connected to the mesogenic unit by a flexible chain). Besides that, the two cyclopentadienyl rings of the ferrocene may be easily reoriented by small rotations of the rings, even in solid state, with a low requested energy [6]. Both samples present a wide mesomorphic domain, from 161 °C and 163 °C, respectively, up to 250 °C and 300 °C. Over these temperatures, the degradation process begins. The study of these samples by optical polarized microscopy reveals the chiral liquid crystalline textures on a wide range (Fig. 1).



a



b

Fig. 2. DSC curves of sample 1 (a) and sample 2 (b).

2. Experimental

Thermal behaviour of some ferrocene liquid crystals with azo and cholesteryl units (table 1) has been studied by using a MOM-Budapest Derivatograph, which allows simultaneous recording of thermogravimetric, derivative thermogravimetric and differential analysis, in statically air conditions.

Kinetic processing of thermogravimetric data of the studied compounds was established using Coats-Redfern integral method [7].

Table 1. Chemical structure of the analyzed compounds.

Sample	Chemical structure
1	
2	
3	
4	
5	

3. Results and discussion

The recorded thermograms, by maintaining constant the operational parameters, are presented in Figs. 3, 4 and 5.

From thermograms, one can observe the complexity of the thermal decomposition of the compounds with azo and cholesteryl units. Thus, in the case of the samples 1, 2 and 3, the degradation takes place in three stages; in turn, the degradation process of 4 and 5 takes place in two stages, which are in fact a sequence of two processes that are not completely separated.

Table 2 reveals the thermogravimetric data such as: the interval of temperature in which the degradation takes place for each stage, weight loss (w, %), corresponding for each stage and DTA characteristics of the process (endo or exo).

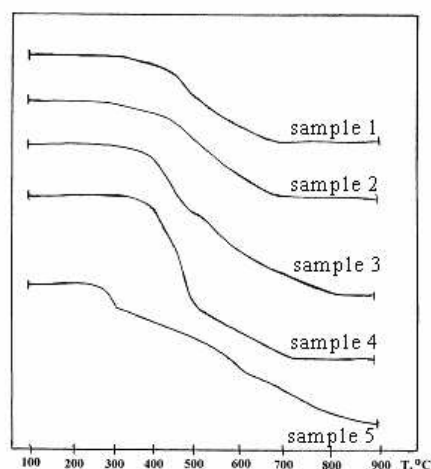


Fig. 3. The TG curves.

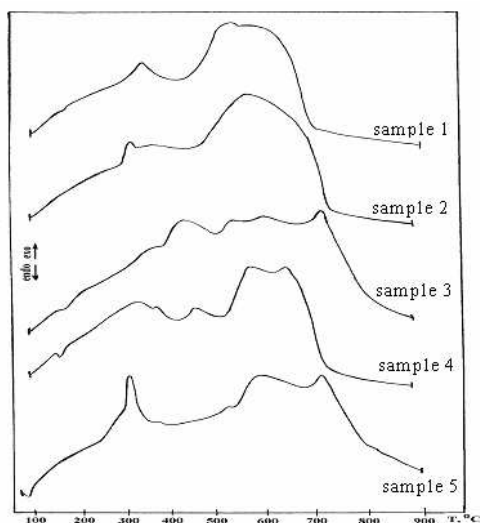


Fig. 4. The DTA curves.

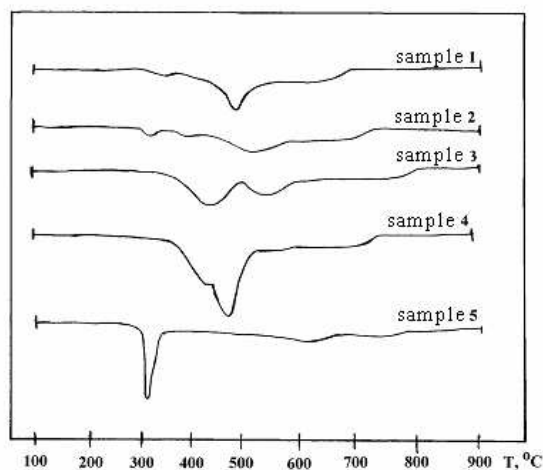


Fig. 5. The DTG curves.

By analyzing the data from Table 2, one can observe that the thermal degradation process of the investigated compounds starts at a higher temperature than 310 °C, an exception being only for the case of sample 5, for which $T_i = 260$ °C, which proves the high thermal stability. The weight loss on each stage is depending on the chemical structure of each compound and is situated between different temperature intervals.

In the first stage, thermal degradation of samples 3 and 4 is much slower as compared with the other compounds, if refer to the interval of temperature in which the process takes place (190 °C and 180 °C, respectively).

Using as thermal stability criteria the initial temperature of decomposition (T_i), the thermal stability series was established as being the following:

$$4 > 1 > 2 \approx 3 > 5$$

Among the compounds with one esteric joint, the cholesterol ester (4) presents a much higher thermal stability than those with azophenol (5), so that the azo group is less stable than the esteric one.

Table 2. Thermogravimetric and thermal characteristics.

Sample	Stage of thermal degradation	DTA characteristic	Temperature domain	Weight loss (W%)
1	I	exo	340-440	13.33
	II	exo	440-520	33.33
	III	exo	520-680	45.00
	residue			8.34
2	I	exo	310-450	15.15
	II	exo	450-600	57.57
	III	exo	600-700	24.24
	residue			3.04
3	I	exo	310-500	39.28
	II	exo	500-600	17.85
	III	exo	600-840	26.78
	residue			16.09
4	I	exo	350-530	56.25
	II	exo	540-740	25.00
	residue			18.75
5	I	exo	260-315	12.72
	II	exo	510-880	67.27
	residue			20.01

The presence of strong electron-withdrawing groups next to the ferrocene unit (keto group) is having the same effect of decreasing of thermal stability (compounds 3 and 4).

In the purpose of getting some information regarding the degradation mechanism, a kinetic processing of the data, by using the Coats-Redfern integral method, has been made. The obtained results: reaction order (n), activation energy (E_a) and pre-exponential factor ($\ln A$) are presented in Table 3.

Table 3. Kinetic characteristics in non-isotherm conditions.

Sample	Stage of thermal degradation	Ea(kJ/mol)	n	lnA	r ²
1	I	74.86	1	16.62	0.999
	II	280.36	1	46.82	0.998
	III	113.07	1	17.11	0.995
2	I	85.46	1	19.14	0.999
	II	136.38	1	22.11	0.999
	III	199.12	1	28.84	0.996
3	I	99.24	1	18.83	0.998
	II	171.15	1	27.19	0.999
	III	84.05	1	12.35	0.998
4	I	129.27	1	22.43	0.999
	II	81.23	1	12.89	0.997
5	I	177.85	1	40.35	0.999
	II	138.67	1	20.40	0.999

Closely values of the activation energy for the samples **2** and **3** in the first stage of degradation process indicate a similar thermostability, which is in a good correlation with the observations obtained from the T_i values. The kinetic characteristics suggest the complexity of the thermal degradation through successive reactions, accompanied by exothermal processes, respectively thermo-oxidative reactions.

4. Conclusions

The paper presents a comparative study regarding thermal stability of some ferrocene derivatives with azo and cholesteryl units, whose structures differs by the nature of the functional groups attached to the molecule. By analyzing the thermogravimetric data, the following series of thermal stability: **4** > **1** > **2** \cong **3** > **5** has been established. In conclusion, ferrocene derivatives without

azo unit are more stable than those with a connecting azo group; the compounds with strong electron-withdrawing groups (samples **2** and **3**) are less stable than samples **1** and **4**. A complex mechanism of thermal degradation, through successive reactions has been also detected.

References

- [1] P. Collings, M. Hird, "Introduction to liquid crystals", Taylor & Francis, (1997).
- [2] T. Chuard, R. Deschenaux, *Chimia* **57**, 597 (2003); S. Campidelli, E. Vazquez, D. Milic, M. Prato, J. Barbera, D. M. Guldi, M. Marcaccio, D. Paolucci, F. Paolucci, R. Deschenaux, *J. Mater. Chem.* **14**, 1266 (2004).
- [3] C. Imrie, C. Loubser, P. Engelbrecht, C. W. J McClelland, *Chem. Soc., Faraday Trans.* **1**, 2513 (1999).
- [4] a) N. Tamaoki, AV. Parfenov, A. Masaki, H. Matsuda, *Adv. Mater.* **9**, 1102 (1997). b) N. Tamaoki, G. Kruk, H. Matsuda, *J. Mater. Chem.* **9**, 2381 (1999) c) G Kruk, N Tamaoki, H Matsuda, Y Kida, *Liq. Cryst.* **26**, 1687 (1999) d) N Tamaoki, S Song, M Moriyama, H.Matsuda, *Adv. Mater.* **12**(2), 94 (2000). e) M Moriyama, S Song, N.Tamaoki, *J. Mater. Chem.* **11**, 1003 (2001) f) M Moriyama, N. Tamaoki, *Chem. Lett.* **114**, 2 (2001).
- [5] D. Apreutesei, G. Lisa, N. Hurduc, D. Scutaru, *CEJC* **2**(4), 553 (2004).
- [6] J. Bernstein Conformational Polymorphism. In *Organic Solid State Chemistry*, Desiraju GR (ed) Elsevier: Amsterdam, 1987, p. 471 and refs. therein.
- [7] A. W. Coats, J. P. Redfern, *Nature* **201**, 68 (1964).

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