

INVESTIGATIONS ON THE THERMAL BEHAVIOR OF SOME FERROCENE DERIVATIVES WITH LIQUID CRYSTALLINE PROPERTIES

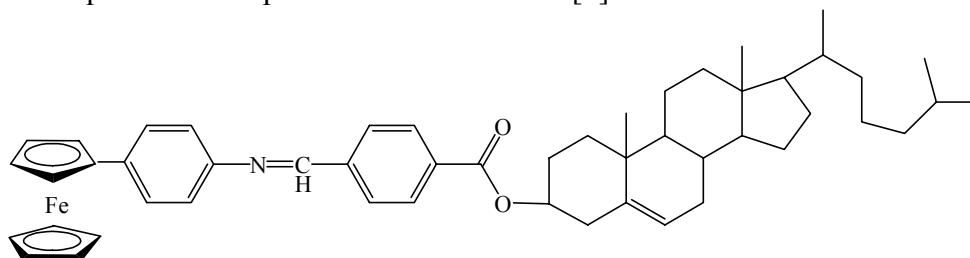
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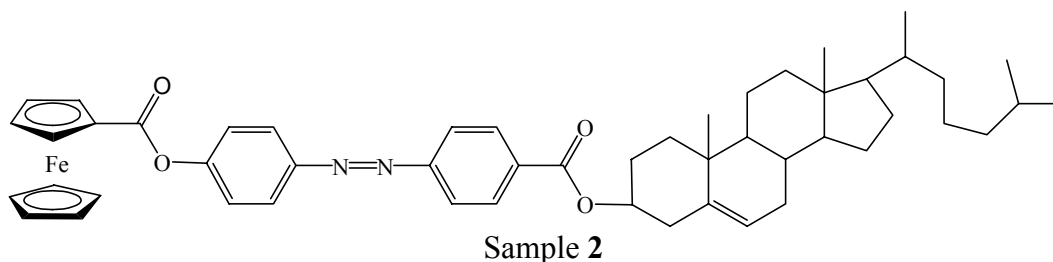
Abstract: Thermal stability depends on the nature of functionalities within a molecule. Such considerations are of great importance for industrial applications, especially when processing at high temperature is required. In the case of organometallic molecules, the major factor in inducing special properties is the presence of a metal, which might confer not only its properties but also geometries rarely found in purely organic compounds. Kinetics of thermal behavior, at three heating speeds 6.5, 10 and 14.5 K/min of sample 1 and sample 2 have been studied [1]:



Sample 1

The thermostability has been established by applying thermal criterions. The processing of ATG data by integral methods was carried out, following the

activation energy – transformation degree dependence and the evolution of the nucleation process.



Keywords: *ferrocene derivatives, thermogravimetry, kinetic parameters*

INTRODUCTION

Thermal stability is an important factor which affects the use of a new compound in industry, especially in fields where processing at high temperature is required [2-4]. In the case of liquid crystals, besides the necessary physical properties as fluidity, optical anisotropy and low viscosity, the compounds should be also stable in the temperature domain at which mesomorphic properties are present. When the clearing point is above the decomposition temperature, the thermal stability of these compounds is of interest. The paper presents a thermal stability study of some liquid crystalline ferrocene derivatives, with different substituents attaching the ferrocene unit to the mesogen. The degradation process is complex and depends on the nature of the substituents linked to the ferrocenyl unit.

EXPERIMENTAL

The thermal behavior of ferrocene derivatives was studied using a MOM-Budapest derivatograph, which allows simultaneous recording of thermogravimetric analysis, derivative thermogravimetry and differential thermal analysis, in static air conditions. The experiment was carried out using Al_2O_3 as reference material heated at 1000 °C, platinum sample crucibles and heating speeds of 6.5, 10 and 14.5 °C/min. Kinetic processing of the thermogravimetric data was made by the Coats-Redfern integral method [5] and the method proposed by Vyazovkin [6], which offers information concerning the nucleation process and growth mechanism of nuclei.

RESULTS AND DISCUSSIONS

The thermograms recorded at 10°C/min heating speed, keeping other operational parameters constant, are presented in the figures 1 and 2.

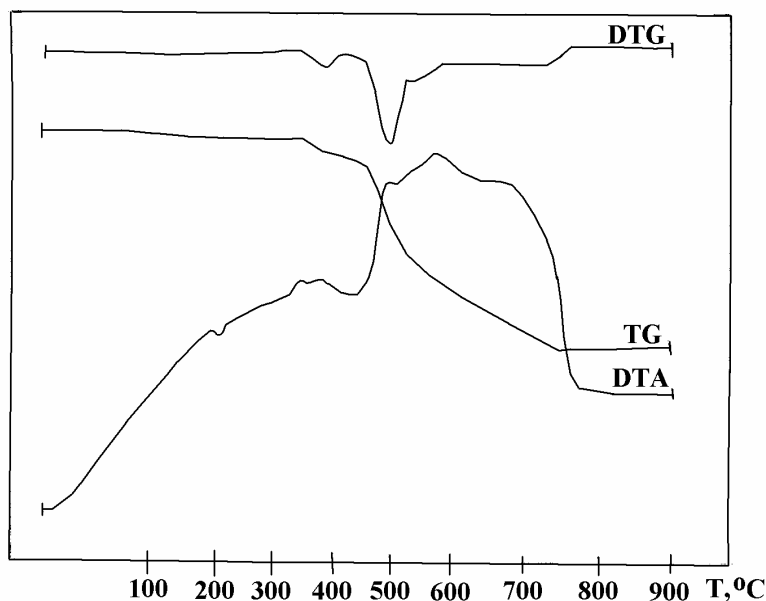


Figure 1. DTG, DTA and TG curves for sample 1

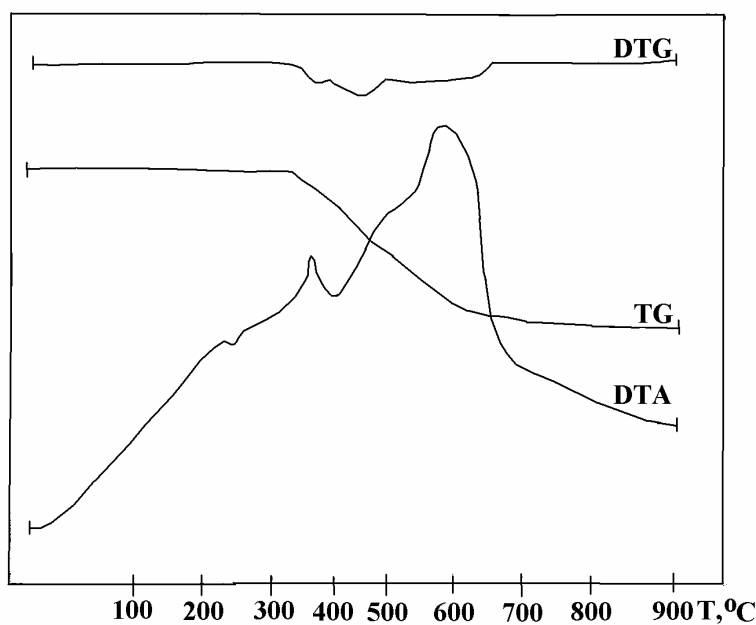


Figure 2. DTG, DTA and TG for sample 2

As can be seen from Figures 1 and 2, the thermal degradation of ferrocene derivatives is complex. Thermal degradation of sample **1** takes place in four steps while sample **2** degraded in only two.

The first stage of thermal degradation of sample **2** is, in fact, a succession of two processes, which are not completely separate.

The thermogravimetric and thermal data, respectively T_i – the temperature when the degradation process starts, T_f – the temperature when the degradation process is finished, for each stage, and the percentage of weight loss are presented in Table 1. The endo or exo character of the processes is also underlined. The thermal characteristics

indicate a good thermal stability, the initial temperature of degradation being higher than the clearing point.

Table 1. Thermal characteristics for sample 1 and 2 (10 °C/min heating speed)

Sample	Stage of thermal degradation	T _i (°C)	T _f (°C)	DTA characteristic	Weight loss (%)
1	I	345	375	exo	9.38
	II	452	500	endo	26.27
	III	502	560	exo	18.76
	IV	562	740	exo	30.03
	residue				15.56
2	I	335	460	exo	34.46
	II	462	620	exo	43.07
	residue				22.47

Table 1 shows that the degradation processes for ferrocene derivatives begin at 335°C for sample 2 and at 345°C, in the case of sample 1. The most significant weight loss was recorded in the final stage of thermal degradation for both ferrocene derivatives. On observe that, in the last stage, the thermal degradation of sample 1 is much slower as compared with sample 2, if the interval in which the process takes place (178 °C) is considered. So, considering the initial temperature of degradation (T_i) as criteria of thermal stability, sample 1 is more stable than sample 2.

In order to elucidate further insight into the degradation process, kinetic processing of data was carried out using the Coats-Redfern (C-R) integral method. Table 2 presents reaction order (n), activation energy (E_a), preexponential factor (ln A) and correlation coefficient (r²).

For the first stage of degradation, smaller values of the activation energy were observed for sample 2 as compared with sample 1, in accordance with the observations derived from thermogravimetric data. The kinetic characteristics suggest the complexity of the thermal degradation through successive reactions, generally exothermic ones, more specifically thermal-oxidation processes. In the case of sample 1, values of the reaction order confirm the complexity of the degradation reactions, especially the influence of diffusion. For establishing the influence of the heating speed on the thermal stability, thermograms at three heating speeds of 6.5, 10.0 and 14.5 °C/min were recorded.

The discussions are based on the kinetic model of “the reaction order”. A rigorous study includes the nucleation process. As a consequence, the Vyazovkin method has been used [6]. The dependence of activation energy versus the conversion degree of ferrocene derivatives is presented in Figures 3 and 4.

On observe that the values of the apparent activation energy vary between 100-170 kJ/mol, which confirms the complexity of the degradation mechanism. The increase in activation energy in the last stage suggests that the fragmentation of the aromatic rings occurs at temperatures over 500 °C. A model of the thermal degradation for each stage of the two ferrocene derivatives has been established, by applying Vyazovkin method [6]. The results obtained are presented in the Figures 5 - 10.

Table 2. The kinetic characteristics in non-isothermal conditions

Sample	Stage	n	E _a (kJ/mol)	ln A	r ²
1	I	1	160.07	32.77	0.98
	II	0	163.56	30.09	0.99
	III	0	153.99	26.60	0.98
	IV	1	125.15	17.43	0.98
2	I	1	110.52	20.64	0.99
	II	2	138.23	18.42	0.98

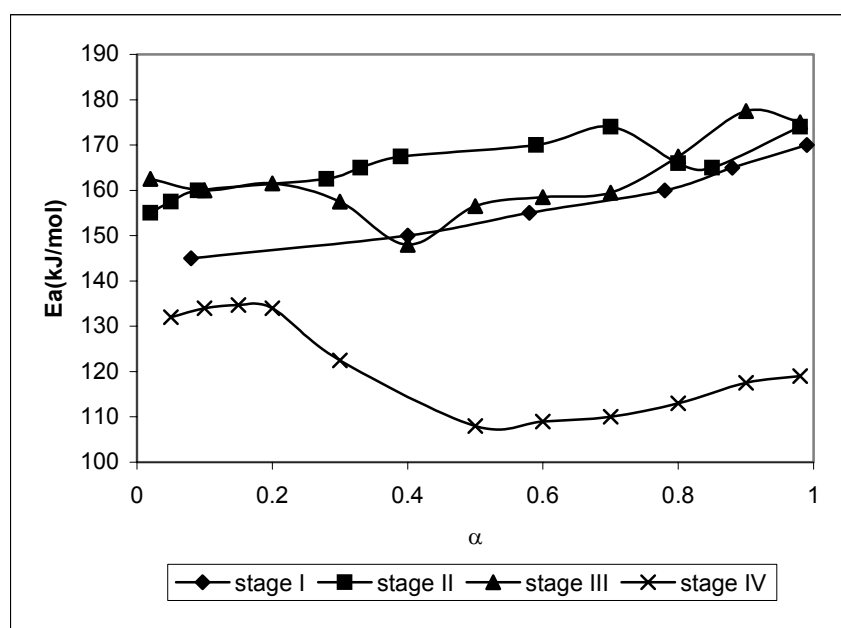


Figure 3. The dependence of activation energy versus transformation degree for sample 1

The kinetic model of sample 1 for the II and III stages of thermal degradation is Avrami-Erofeev. This model shows that the reactions are controlled by diffusion and the growth of the nuclei takes place in volume [7]. For the same sample, in the first and the last stage, a power law model has been obtained suggesting a nucleation followed by a growth in volume. The power law model suggests that the decomposition mechanism of sample 1 under isothermal conditions takes place by multi-step nucleation, which pointed out that the formation of a stable growth nucleus required successive molecular decompositions [8]. In the case of sample 2, by respecting the kinetic low characteristic to the bimolecular reactions, for both degradation stages, a randomized nucleation has been observed.

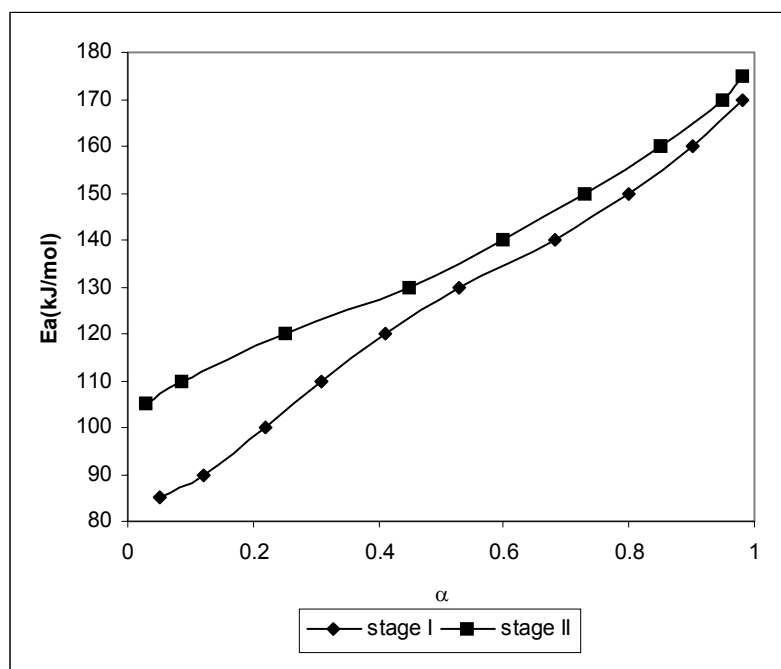


Figure 4. The dependence of activation energy versus transformation degree of sample 2

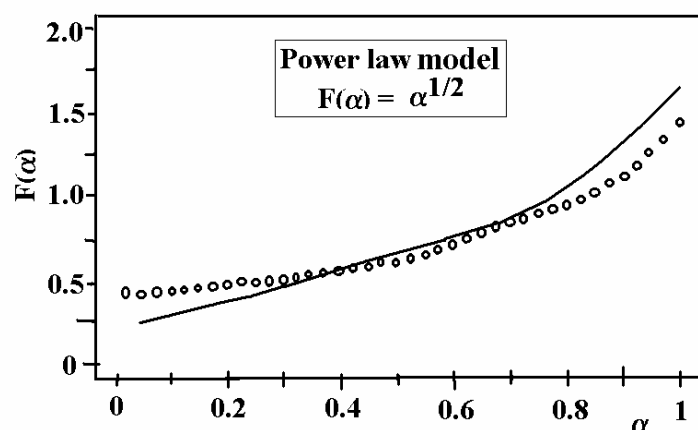


Figure 5. The model of thermal degradation for the sample 1 (stage I)

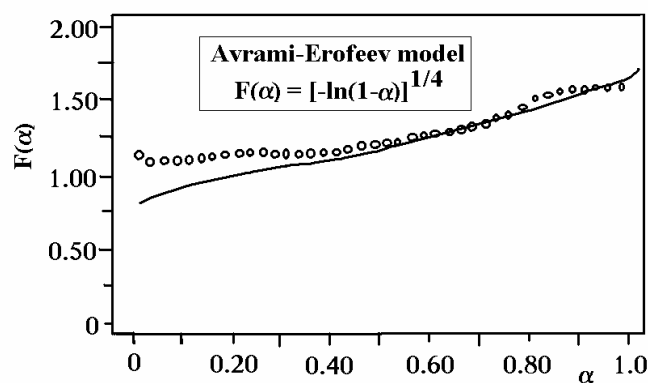


Figure 6. The model of thermal degradation for the sample 1 (stage II)

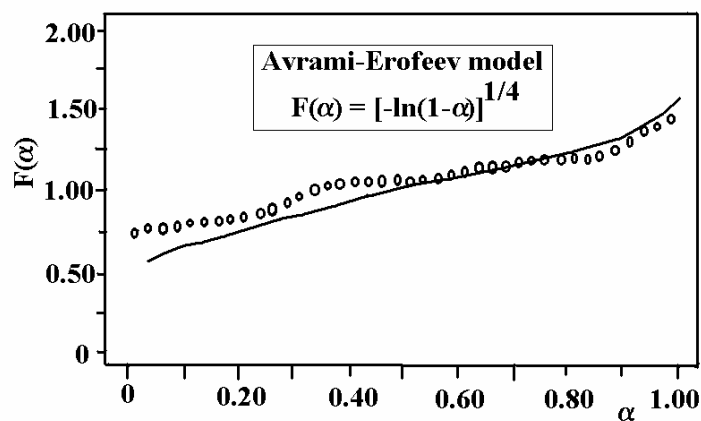


Figure 7. The model of thermal degradation for the sample 1 (stage III)

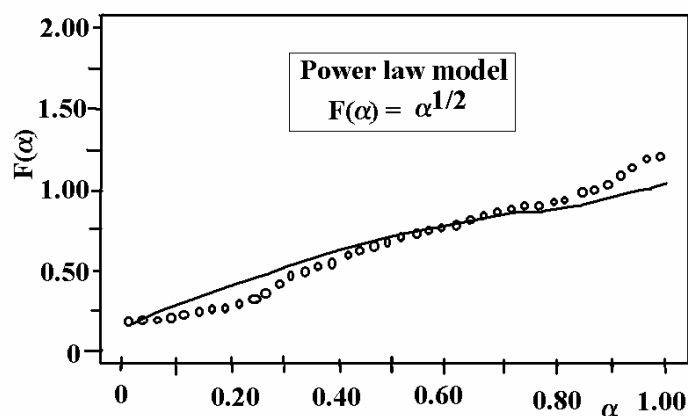


Figure 8. The model of thermal degradation for the sample 1 (stage IV)

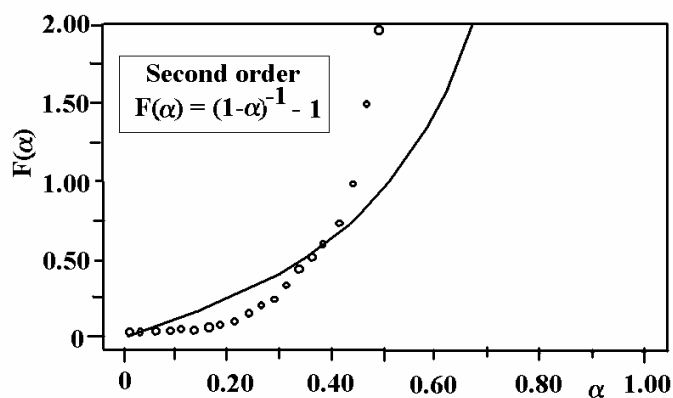


Figure 9. The model of thermal degradation for the sample 2 (stage I)

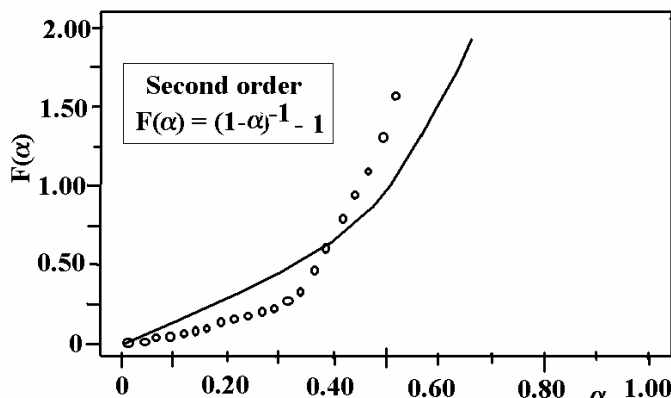


Figure 10. The model of thermal degradation for the sample 2 (stage II)

CONCLUSIONS

- The thermal and kinetic characteristics indicate a good thermal stability, much higher than the clearing point (approximate 100 °C).
- The presence of an azo group determines the decreasing of thermal stability, confirmed by the value of the apparent activation energy.
- The mechanism of degradation is complex, by successive reactions.
- The process of nucleation is complex and influenced by the chemical structure of the compounds.
- In the case of sample 1, corresponding for all four degradation stages, the nuclei appear superficially and a growth in volume (II and III stages) follows; finally the appearance of the nuclei is randomized.
- In the case of sample 2, the nucleation is simpler, probably determined by the higher degree of diffusion, when the nuclei for each particle appear randomized.

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