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Ahmad Ali Joraid (✉ aaljoraid@taibahu.edu.sa)

Taibah University <https://orcid.org/0000-0001-9872-1428>

Rawda Mohammad Okasha

Taibah University

Mahdi A. Al-Maghrabi

Industrial College

Tarek H. Afifi

Taibah University

Christian Agatemor

University of Miami

Alaa S. Abd-El-Aziz

University of Prince Edward Island

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Thermodynamic Parameters of Nonisothermal Degradation of A New Family of Organometallic Dendrimer with Isoconversional Methods

Ahmad A. Joraid^{1,*}, Rawda M. Okasha², Mahdi A. Al-Maghrabi³, Tarek H. Afifi²,
Christian Agatemor⁴, Alaa S. Abd-El-Aziz⁵

¹Physics Department, Faculty of Science, Taibah University, Al-Madinah Al-Munawarah 30002, Saudi Arabia.

²Chemistry Department, Faculty of Science, Taibah University, Al-Madinah Al-Munawarah 30002, Saudi Arabia.

³Department of General Studies, Yanbu, Industrial College, Saudi Arabia.

⁴Chemistry Department, University of Miami, Coral Gables, FL, USA.

⁵Chemistry Department, Faculty of Science, University of Prince Edward Island, Charlottetown, Prince Edward Island C1A 4P3, Canada.

*Corresponding author

Abstract

The objective of this work is to obtain the thermodynamic parameters, namely, the changes of enthalpy, Gibbs free energy, and the entropy of two degradation steps observed in three of a new family of organometallic dendrimers. The isoconversional Flynn-Wall-Ozawa (FWO) model was employed to calculate the effective activation energy and pre-exponential factor. The changes of enthalpy and the entropy was consistent with the activation energy, whereas the change of Gibbs free energy remains positive during the entire degradation process, implying that the degradation is non-spontaneous and thus requires external heat supply.

Keywords: Dendrimers; Thermogravimetric analysis; Isoconversional methods; Nonisothermal kinetics; Thermodynamic parameters

1. Introduction

Dendrimers are large, monodisperse, highly branched molecules with precisely designed and defined homogeneous structures. Due to their unique chemical properties, dendrimers are emerging as very important materials and are actively researched in recent years. Their globular topology and tailored peripheral end groups enable their use in several applications like, pharmaceutical drug and gene delivery, chemotherapy, and diagnostic imaging [1-4]. While most dendrimers are organic macromolecules, great efforts are being made to incorporate inorganic main group elements, transition metals, and organometallic entities to create inorganic and organometallic dendrimers. This research merges the properties of the inorganic main elements and organometallic entities such as catalytic, electrochemical, optical and magnetic properties with the benefits generally attributed to dendrimers, such as site isolation, precise steric environments, recyclability and possible cooperative effects [5].

This study is a continuation to our previous degradation study on organometallic dendrimers exemplified by a new family of cross-linked organoiron dendrimers [4]. Understanding dendrimer degradation is very important because degradation informs dendrimer stability during syntheses, processing, fabrication, and applications. This importance, notwithstanding, research into dendrimer degradation lags syntheses and applications, creating a gap that could limit real life application. In contrast, polymer degradation have been extensively researched; indeed the kinetics and thermodynamics of the process has received a lot of attention.

In our previous work, we synthesized a class of organometallic dendrimers, a special class of polymers, and characterized the kinetics of the degradation process, specifically

determination of the kinetic triplets, the pre-exponential (frequency) factor, the effective activation energy, and the reaction model. To fully understand and optimize the degradation process, the thermodynamic parameters are required. The main goal of this article is to calculate the thermodynamic parameters, namely the changes of enthalpy, ΔH , Gibbs free energy, ΔG , and the entropy, ΔS . These parameters were calculated by using non-isothermal degradation of the organometallic dendrimers. The values of effective activation energy and the preexponential factor were calculated using the iso-conversional Flynn-Wall-Ozawa (FWO) method.

2. Materials and methods

2.1. Synthesis

The dendrimers were synthesized using our previously reported procedure [4]. The chemicals, and reagents used for the synthesis and the characterization of the all compounds and dendrimers as well as instruments for the characterization were previously reported [4]. The chemical structure of dendrimer 5, dendrimer 7 and dendrimer 8 synthesized are shown in Fig. 1.

2.2. Thermal analysis

Thermogravimetric analyses of the dendrimers were carried out by using a thermogravimetric analyzer (TGA) and differential scanning calorimeter (DSC) (TA Instruments DSC SDT Q600). A 3 mg the dendrimer was used at three different heating rates 10, 15 and 20 K min⁻¹ under dry nitrogen gas. The advanced thermokinetics software package AKTS-Thermokinetics, Ver. 4.15, was used for all kinetics analysis in this study.

2.3. Kinetic study

In iso-conversional methods, we used the theoretical kinetic equation combined with the Arrhenius expression, which interprets the DSC thermographs as a function of

temperature, T , expressed in term of the conversion fraction (the reaction progress), α , as follows [4,6,7]:

$$\frac{d\alpha}{dt} = k(T) f(\alpha) = A(\alpha) f(\alpha) \exp\left(\frac{-E}{RT}\right),$$

(1)

where, k , is the reaction rate constant, A (s^{-1}) is the pre-exponential (frequency) factor, E ($kJ\ mol^{-1}$) is the apparent (effective) activation energy describing the overall of the phase change process, R is the universal gas constant and $f(\alpha)$ is the reaction model, which describes the differential mechanism of various kinetic model functions.

In thermogravimetric analysis (TGA), α represents the weight loss fraction, which, can be determined from TG analysis as a fractional mass loss:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f},$$

(2)

where, m_0 , m_t and m_f represent the compound mass at the onset of degradation, at any time, t and at the completion of degradation, respectively.

For non-isothermal conditions and when T is dependent on the heating rate, β , and changes linearly with time ($T = T_0 + \beta t$), i.e.,

$$\beta = \frac{dT}{dt} = \text{constant},$$

(3)

Hence, the isothermal condition Eq. (1) can be given as a temperature-dependent:

$$\frac{d\alpha}{dT} = \frac{A(\alpha)}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha),$$

(4)

Integrating this equation gives:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A(\alpha)}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT,$$

(5)

where, $g(\alpha)$ is the integral form of the reaction model, which does not have an analytical solution, in nonisothermal experiments. Hence, to solve this equation several numbers of theoretical solution were obtained. The Ozawa and Flynn and Wall (FWO) method is one of these methods, which is measured at different, but constant, heating rates β_i [4,6,8,9].

$$\ln(\beta_i) = \ln\left(\frac{AE_\alpha}{R}\right) - \ln(g(\alpha)) - 5.3305 - 1.0518 \frac{E_\alpha}{RT_{\alpha,i}},$$

(6)

Therefore, plotting of $\ln(\beta_i)$ against $1/T_{\alpha,i}$ is a straight line, with a slope of $-E_\alpha/R$. The activation energy, E_α , and the pre-exponential A_α are then determined from the slope and the intercept of the line, respectively.

2.4. Thermodynamic Study

Thermodynamic parameters show an important role in better understanding of degradation of the organometallic dendrimer and their response to temperature and hence, their thermal stability. The thermodynamic parameters (ΔH , ΔG and ΔS) were calculated using the equations given below [10-16].

$$\Delta H = E_\alpha - RT_\alpha,$$

(7)

$$\Delta G = E_{\alpha} + RT \ln\left(\frac{K_B T}{hA}\right),$$

(8)

$$\Delta S = \frac{\Delta H - \Delta G}{T},$$

(9)

where, T is the absolute peak temperature, T_{α} is the temperature at the degree of conversion α , h is the Plank constant (6.626×10^{-34} Js) and K_B is the Boltzmann constant (1.381×10^{-23} JK⁻¹).

3. Results and discussion

3.1. The degradation behavior

The mass loss (TG) and derivative mass loss (DTG) curves were obtained under three different heating rates of 10, 15 and 20 °C min⁻¹. The samples were heated from room temperature to 973 K. Our previous study [4] showed that the three cross-linked organoiron dendrimers degradation exhibited different pyrolysis curves, but the overall changes were similar according to TG curves. The dendrimers degradations divided into two different steps. The low temperature degradation regime occurring at about 403-504 K accompanied by about 15% loss and the high temperature degradation regime occurring at about 542-862 K accompanied by about 60% loss. Therefore, each degradation peak will be treated as individual peaks. Henceforth, the first and second peaks are denoted as

LTD and HTD, respectively. Fig. 2 shows the TG and DTG curves of the three dendrimers under investigation.

3.2. Thermodynamic parameters

The FWO Eq. 6 discussed above was used to investigate the variation of the effective activation energy $E_{\alpha}(\alpha)$ with conversion fraction, α , and with temperature $E_{\alpha}(T)$, carried out at different heating rates β_i . Figs. 3, 4 and 5 present the calculated activation energies for the two steps LTD and HTD. Correspondingly, these figures show the variation of the logarithmic values of pre-exponential factor, $\ln(A_{\alpha})$, though, these values are in line with the values of the activation energy $E_{\alpha}(\alpha)$. These figures revealed a clear difference in the values of $E_{\alpha}(\alpha)$ and $E_{\alpha}(T)$ between the two steps LTD and HTD. For LTD step of dendrimer 5, there is a little increase (16-20 kJ mol⁻¹) in the activation energy between the initial and final stage of the degradation, while this increase is very high (50-140 kJ mol⁻¹) in HTD step. On the other hand, the variation of $E_{\alpha}(\alpha)$ for the LTD step of dendrimer 7 is the same as LTD step of dendrimer 5, while the HTD step is slightly decreases (43-34 kJ mol⁻¹) with increasing α or temperature. In contrast, for dendrimer 8, the value of $E_{\alpha}(\alpha)$ for HTD step is almost, constant with, α or temperature which is about 146 kJ mol⁻¹ exceptional at the terminal and final point. The value of LTD step is less than HTD step and decreases gradually with, α (51-26 kJ mol⁻¹). Using the effective activation energies, E_{α} , and the pre-exponential factor, A_{α} , derived from FWO model Eq. 6, the thermodynamic parameters (ΔH , ΔG and ΔS) were calculated according to Eqs. 7, 8 and 9 mentioned above.

3.2.1. The change in enthalpy

The change in enthalpy, ΔH , indicates the total heat transfer, which describes the total amount of heat required to decompose the dendrimer to LTD step then to HTD step. Figures 6 and 7 depict the variation of ΔH as a function of reaction progress, α , and temperature, respectively. As clear from these two figures, ΔH of dendrimers 5 and 7 is almost the same for LTD step; in addition, the variation of ΔH with α or T increases very slightly as the reaction progress go on. It is about 12 kJ mol⁻¹ at the beginning of the reaction and about 17 and 19 kJ mol⁻¹ for dendrimers 5 and 7, respectively at the reaction end. This means that a very low energy is required to decompose dendrimers 5 and 7 for LTD step. For dendrimer 8 the value of ΔH for LTD step is very high comparing with dendrimers 5 and 7 and almost constant, which is about 87 kJ mol⁻¹ at $\alpha = 0.5$. The LTD step may be attributed to the loss of cyclopentadienyl iron(II) moiety attached to the terminals of the structure [4,16]. The delay of degradation for dendrimer 7 and dendrimer 8, which occurred at a higher temperature compared to dendrimer 5 as clear from Figure 7 for LTD step, can be described in the basis of number of cationic iron centers [4]. In addition, the high increase in the value of ΔH for dendrimer 8, could be assigned to the size and number of the peripheral groups.

However, the thermal decomposition of HTD for all three dendrimers proceeds through different approach. As clear from Figures 6 and 7, ΔH increases strongly with increasing α or T for dendrimer 5. At the initial stage of the reaction, the value of ΔH for HTD step is about 39 kJ mol⁻¹, this value increases to about 134 kJ mol⁻¹ at the terminal stage, this means that a very high energy required as the reaction proceed. On the other hand, for dendrimers 7 and 8 ΔH was found to be a moderate value and gradually, decreases with increasing α or T . The values of ΔH for HTD are about 39 and 52 kJ mol⁻¹ at the initial stage, as the reaction grow these two values decrease to about 27 and 19 kJ mol⁻¹ at the terminal stage for values obtained for dendrimers 7 and 8, respectively. The

noticed shift to a high temperature and the increase to a high value of ΔH for dendrimer 5 can be ascribed to the breakage of the dendritic backbone and the presence of phenolic peripheral groups. This indicates a higher thermal stability of such structure compared to dendrimer 7 and dendrimer 8. The noticeable decrease in ΔH for dendrimer 7 can be ascribed to the existence of activated chloride terminal, which is considered as a good leaving group. In addition, due to the bifunctionality of the hydroquinone, which have a high possibility of crosslinking, suggest the decrease in ΔH for dendrimers 7 and 8. From Fig. 6 it is clear that the numbers of hydroquinone effect the values of ΔH , which are 31.81 and 25.12 kJ mol⁻¹ at $\alpha = 0.5$ for dendrimers 7 and 8, respectively, where the number of hydroquinone groups are 4 and 8 for the two compounds.

3.2.2. The change of the Gibbs free energy

The difference between the free energy of a compound and the free energies of its elements gives the change of the Gibbs free energy, ΔG , [13,14]. For the two steps LTD and HTD, Figures 8 and 9 show the variation of ΔG with reaction conversion and with temperature, respectively. It is clear from these two figures that ΔG is higher for HTD than for LTD and is almost within the same range for each step for the three dendrimers. Between the initial and final stages of the reaction and for LTD step, ΔG changes within the ranges 109-143, 119-154 and 128-148 kJ mol⁻¹ for dendrimers 5, 7 and 8, respectively. On the other hand, for HTD step, ΔG changes within the ranges 181-230, 159-236 and 159-253 kJ mol⁻¹ for the same dendrimers. Hence, ΔG was found to be positive during the whole process, this imply that the reaction is non-spontaneous and thus requires external heat supply.

3.2.3. The Entropy

Entropy, ΔS , is a physical property that is most associated with the state function of the reaction system, reflecting the disorder, randomness, or uncertainty of the system

[11,14]. Figures 10 and 11 show the variation of ΔS with the reaction conversion, α , and with temperature, respectively. First, the activation energy, the enthalpy and the entropy clearly have the same tendency; this is demonstrated in Fig. 12. Figure 10 shows that the values of, ΔS , for the two steps LTD and HTD proceed through different approach. On the other hand, the figure indicates that the values of ΔS are negative for all samples under investigation for both LTD and HTD steps, this means that the system is becoming less disordered, and the degradation will not occur spontaneously. Negative values of ΔS are observed in many studies [4,10-14]. Finally, Tables 1, 2 and 3 summarize the thermodynamic parameters for the two steps LTD and HTD for all three dendrimers under investigation.

4. Conclusions

The experimental results of TGA curves showed two phases of mass loss for all three dendrimers under study, with about 15% and 60% loss for first and second degradation. The effective activation energies, and the pre-exponential factors, derived from the Ozawa and Flynn and Wall (FWO) model were used to calculate the thermodynamic parameters namely the changes of enthalpy, Gibbs free energy, and the entropy. For LTD steps of all three dendrimers the two thermodynamic parameters, the changes of enthalpy and the entropy, almost showed a constant trend with a higher conversion fraction, α or temperature, which suggested that the degradations were constant to proceed along the time. On the other hand, and for HTD step for dendrimer 5 these two parameters showed a clear and noticeable increasing trend with increasing, α , or temperature, which suggested that the degradation was harder to proceed along the time. While, for dendrimers 7 and 8 the changes of enthalpy and the entropy for HTD steps slightly showed a decreasing trend with a higher conversion fraction, α , or temperature, which suggested that the degradation of for both dendrimers were easier to proceed along the time. For all three dendrimers the change of the Gibbs free energies, ΔG , for the two steps were found

to be positive during the whole process, indicating that the degradations are non-spontaneous and thus require external heat supply.

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Figures legend

Fig. 1. The chemical structure of dendrimer 5, dendrimer 7 and dendrimer 8.

Fig. 2. TG and DTG curves of dendrimer 5, dendrimer 7 and dendrimer 8 at heating rates 10, 15 and 20 °C min⁻¹.

Fig. 3. The values of $E_{\alpha}(\alpha)$, $\ln(A_{\alpha})$ and $E_{\alpha}(T)$ of the two steps LTD and HTD for dendrimer 5.

Fig. 4. The values of $E_{\alpha}(\alpha)$, $\ln(A_{\alpha})$ and $E_{\alpha}(T)$ of the two steps LTD and HTD for dendrimer 7.

Fig. 5. The values of $E_{\alpha}(\alpha)$, $\ln(A_{\alpha})$ and $E_{\alpha}(T)$ of the two steps LTD and HTD for dendrimer 8.

Fig. 6. The variation of the change of enthalpy, ΔH , as a function of reaction progress, α , of the two steps LTD and HTD for dendrimer 5, 7 and 8.

Fig. 7. The variation of the change of enthalpy, ΔH , as a function of temperature of the two steps LTD and HTD for dendrimer 5, 7 and 8.

Fig. 8. The variation of the change of Gibbs free energy, ΔG , as a function of reaction progress, α , of the two steps LTD and HTD for dendrimer 5, 7 and 8.

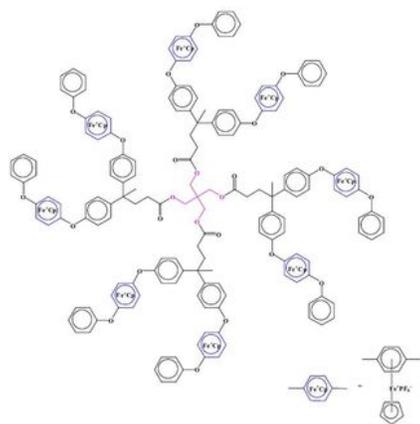
Fig. 9. The variation of the change of Gibbs free energy, ΔG , as a function of temperature of the two steps LTD and HTD for dendrimer 5, 7 and 8.

Fig. 10. The variation of the entropy, ΔS , as a function of reaction progress, α , of the two steps LTD and HTD for dendrimer 5, 7 and 8.

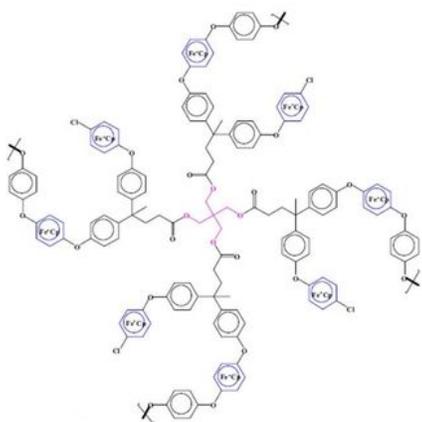
Fig. 11. The variation of the entropy, ΔS , as a function of temperature of the two steps LTD and HTD for dendrimer 5, 7 and 8.

Fig. 12 shows that the activation energy, the enthalpy and the entropy have the same tendency.

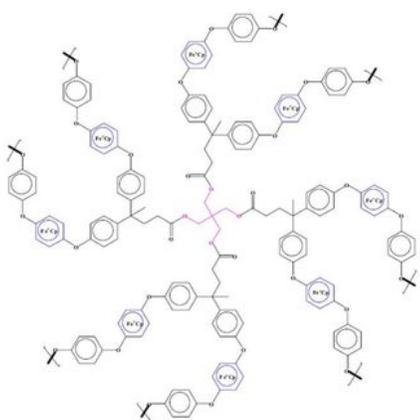
Figures



Dendrimer 5



Dendrimer 7



Dendrimer 8

Figure 1

The chemical structure of dendrimer 5, dendrimer 7 and dendrimer 8.

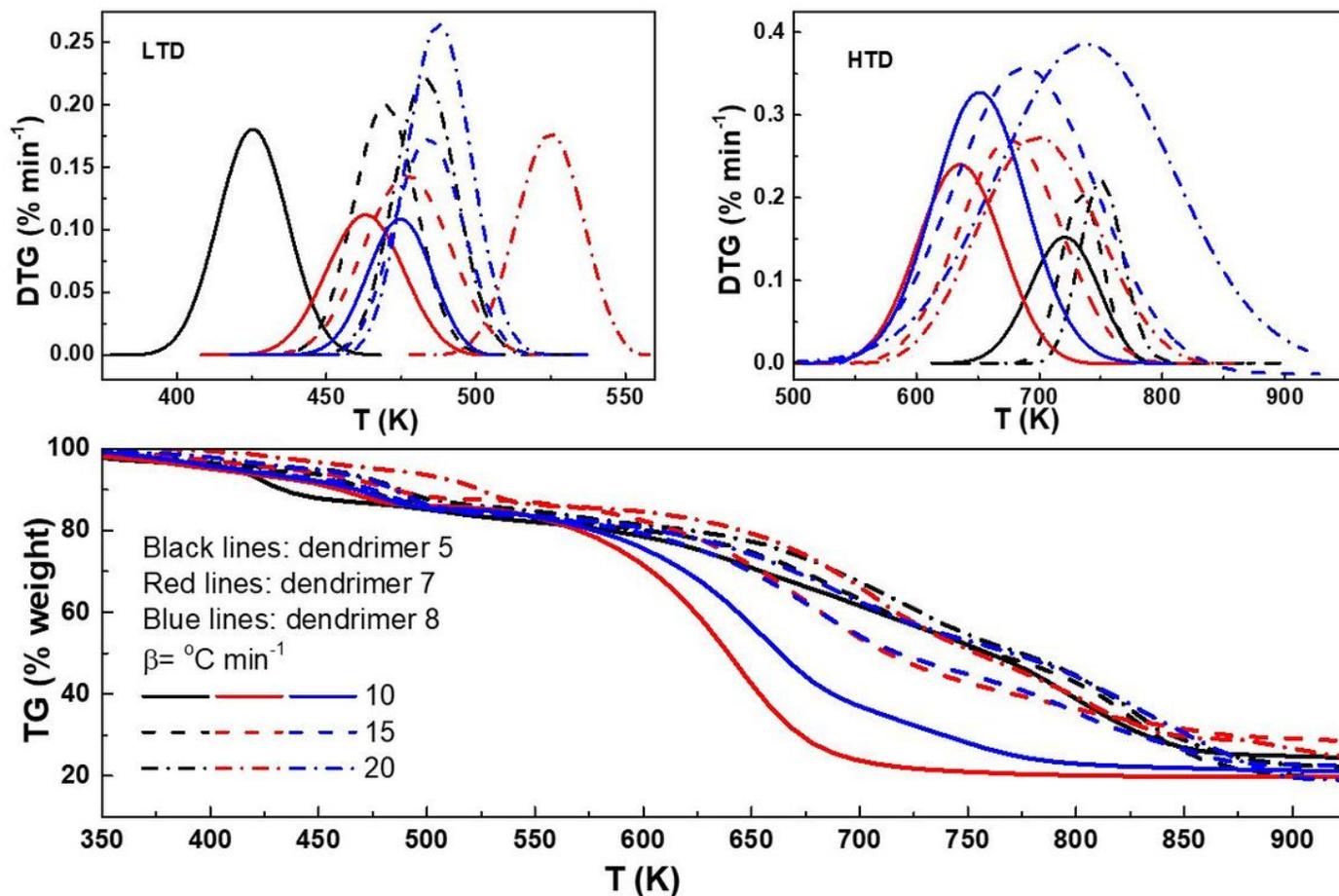


Figure 2

TG and DTG curves of dendrimer 5, dendrimer 7 and dendrimer 8 at heating rates 10, 15 and 20 °C min⁻¹.

Figure 3

Please see the Manuscript file for the complete figure caption.

Figure 4

Please see the Manuscript file for the complete figure caption.

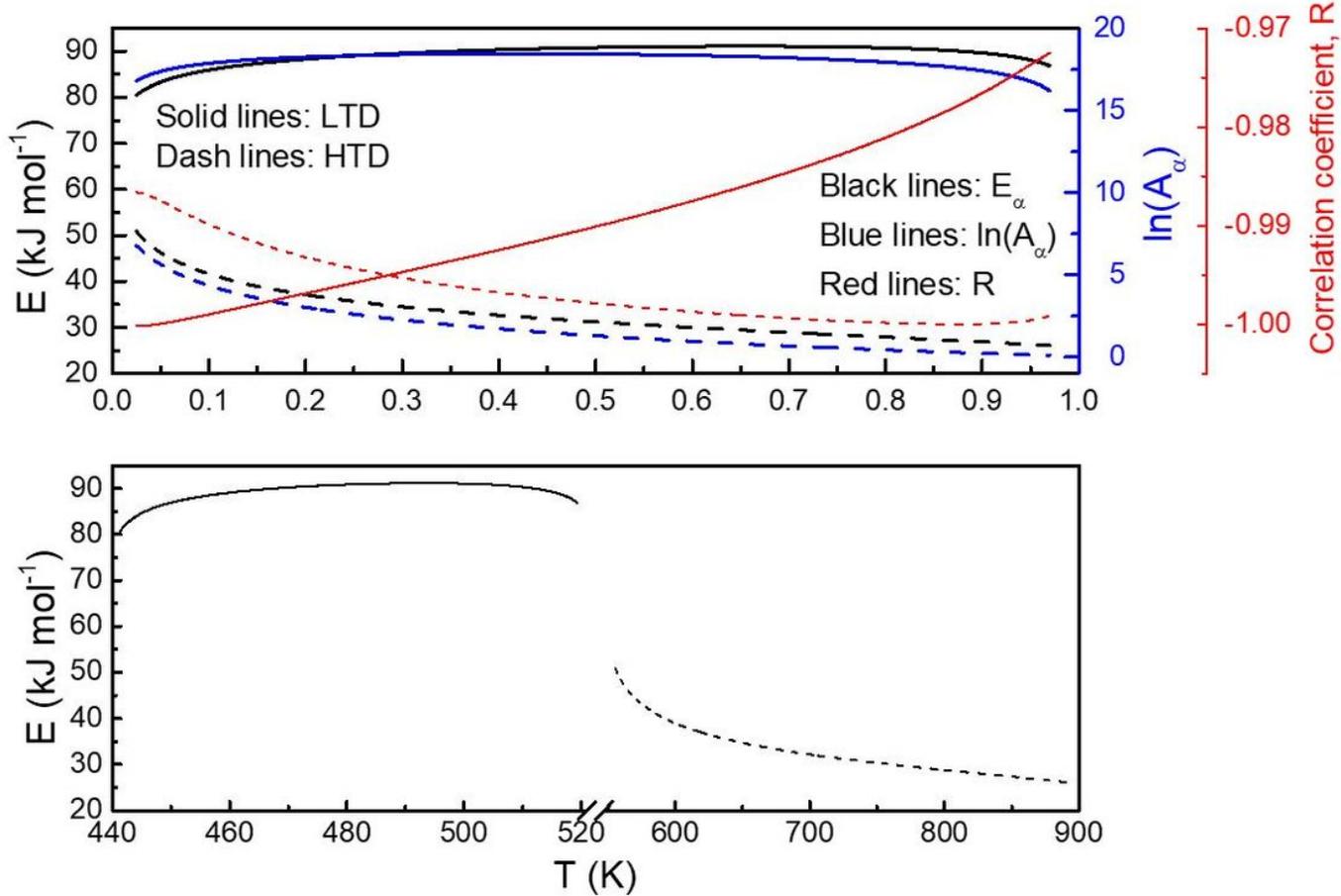


Figure 5

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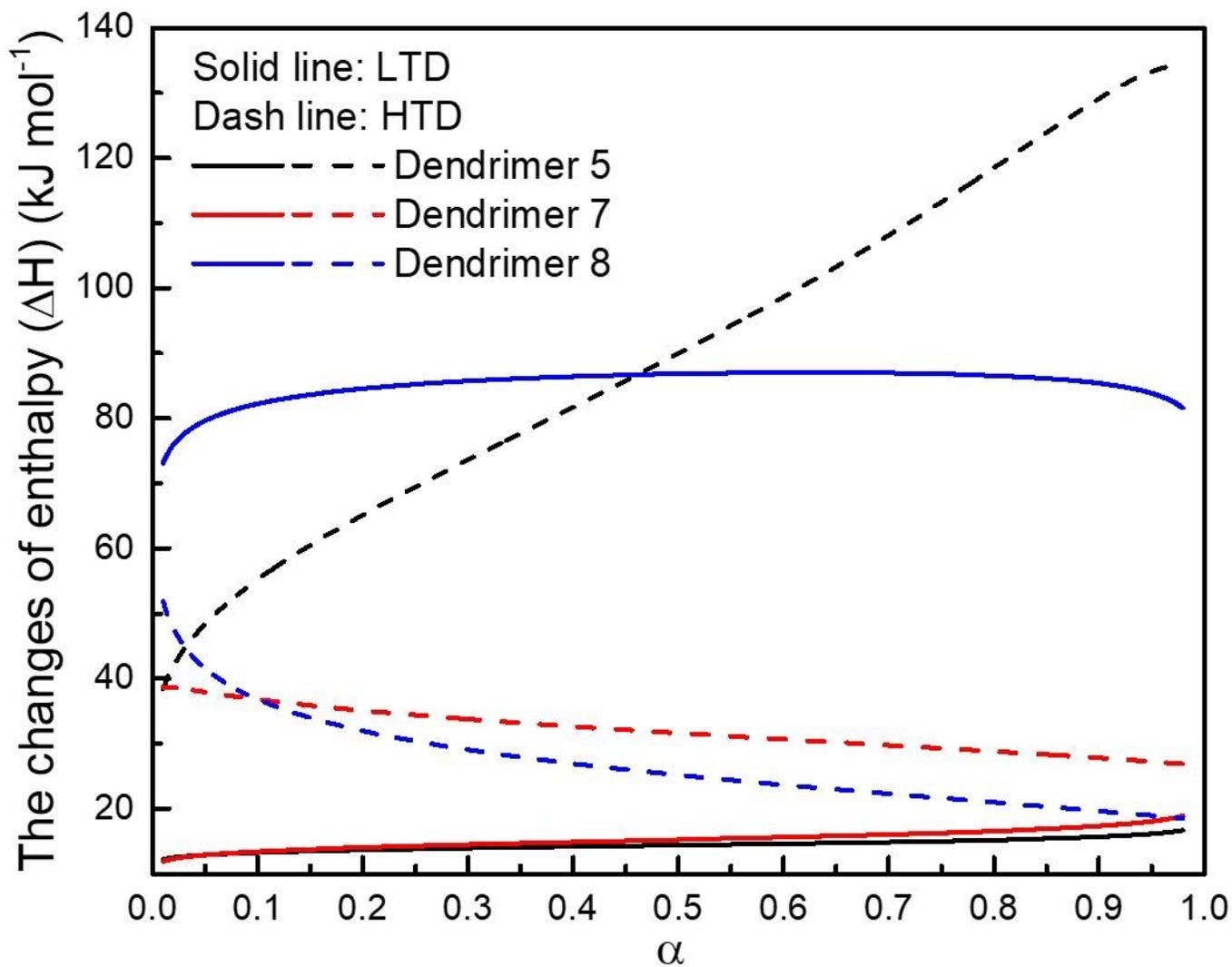


Figure 6

The variation of the change of enthalpy, ΔH , as a function of reaction progress, α , of the two steps LTD and HTD for dendrimer 5, 7 and 8.

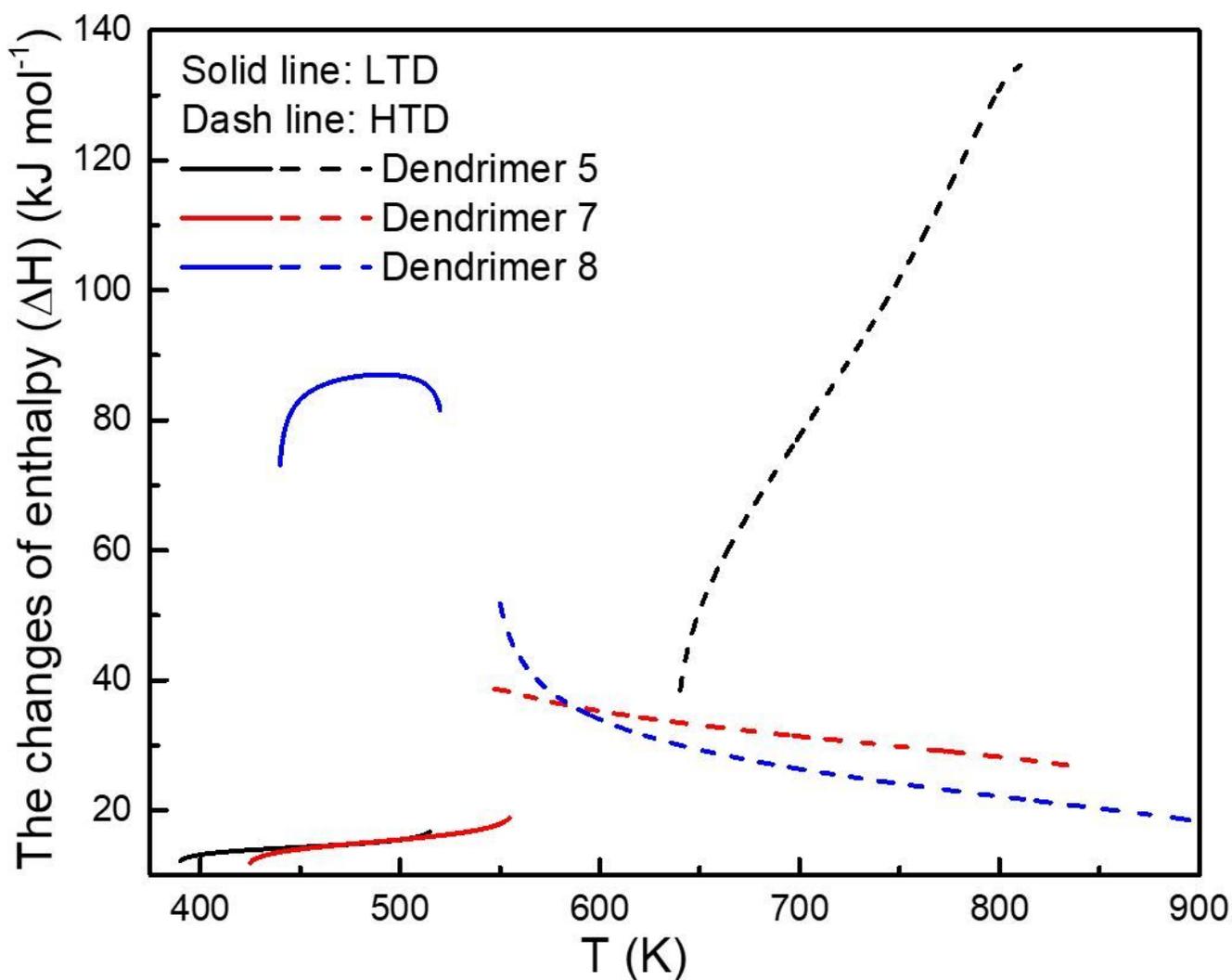


Figure 7

The variation of the change of enthalpy, ΔH , as a function of temperature of the two steps LTD and HTD for dendrimer 5, 7 and 8.

Figure 8

The variation of the change of Gibbs free energy, ΔG , as a function of reaction progress, a , of the two steps LTD and HTD for dendrimer 5, 7 and 8.

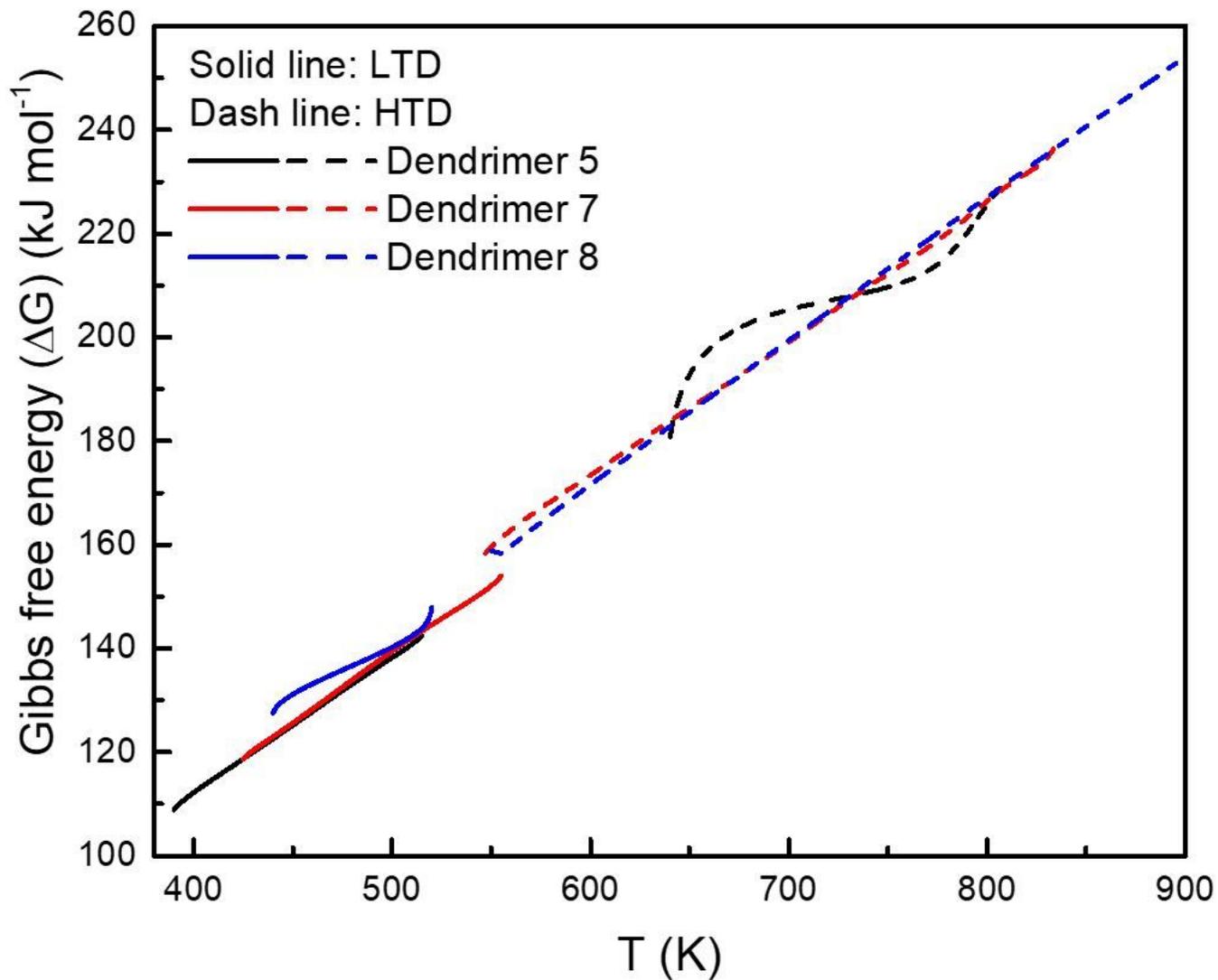


Figure 9

The variation of the change of Gibbs free energy, ΔG , as a function of temperature of the two steps LTD and HTD for dendrimer 5, 7 and 8.

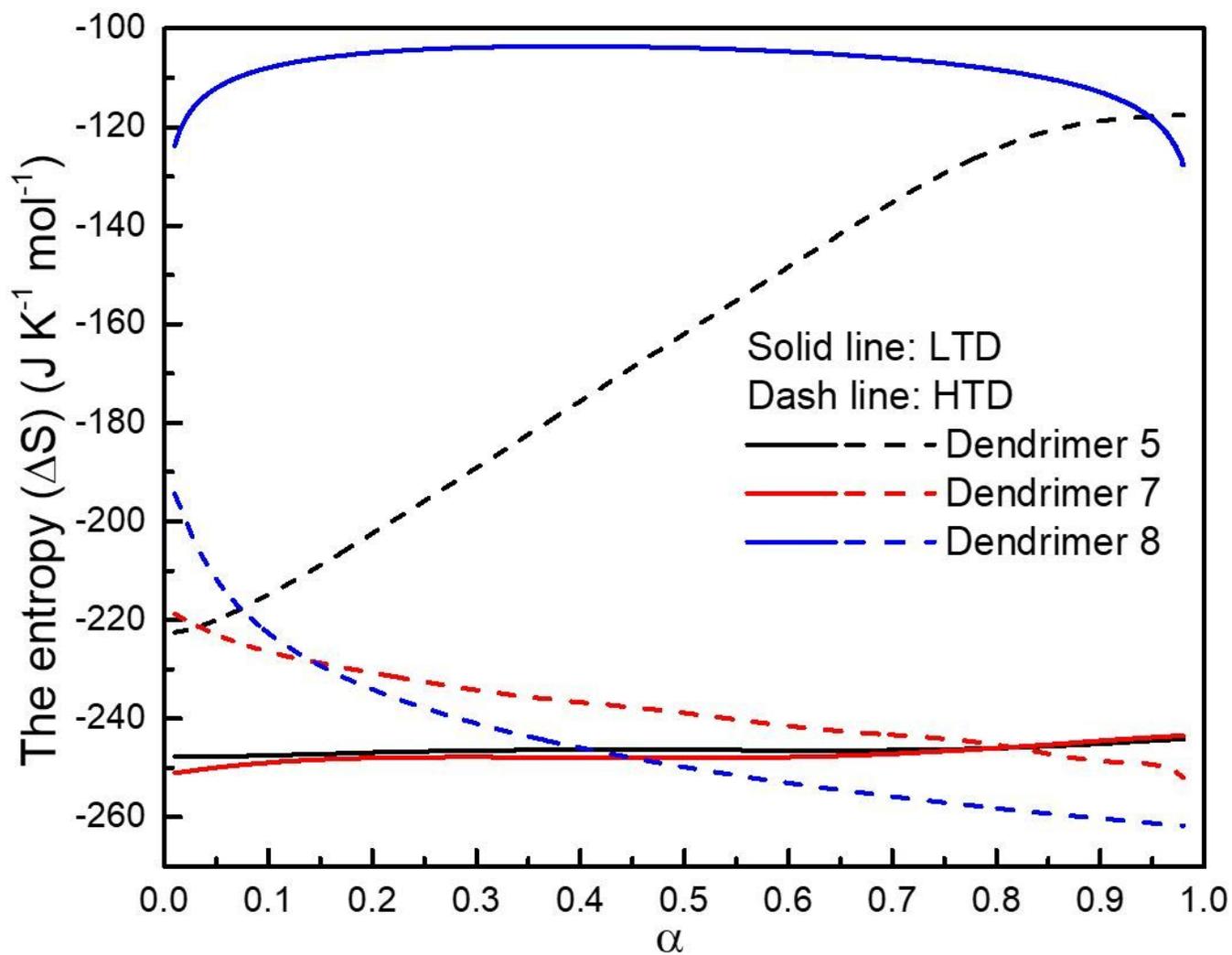


Figure 10

The variation of the entropy, ΔS , as a function of reaction progress, α , of the two steps LTD and HTD for dendrimer 5, 7 and 8.

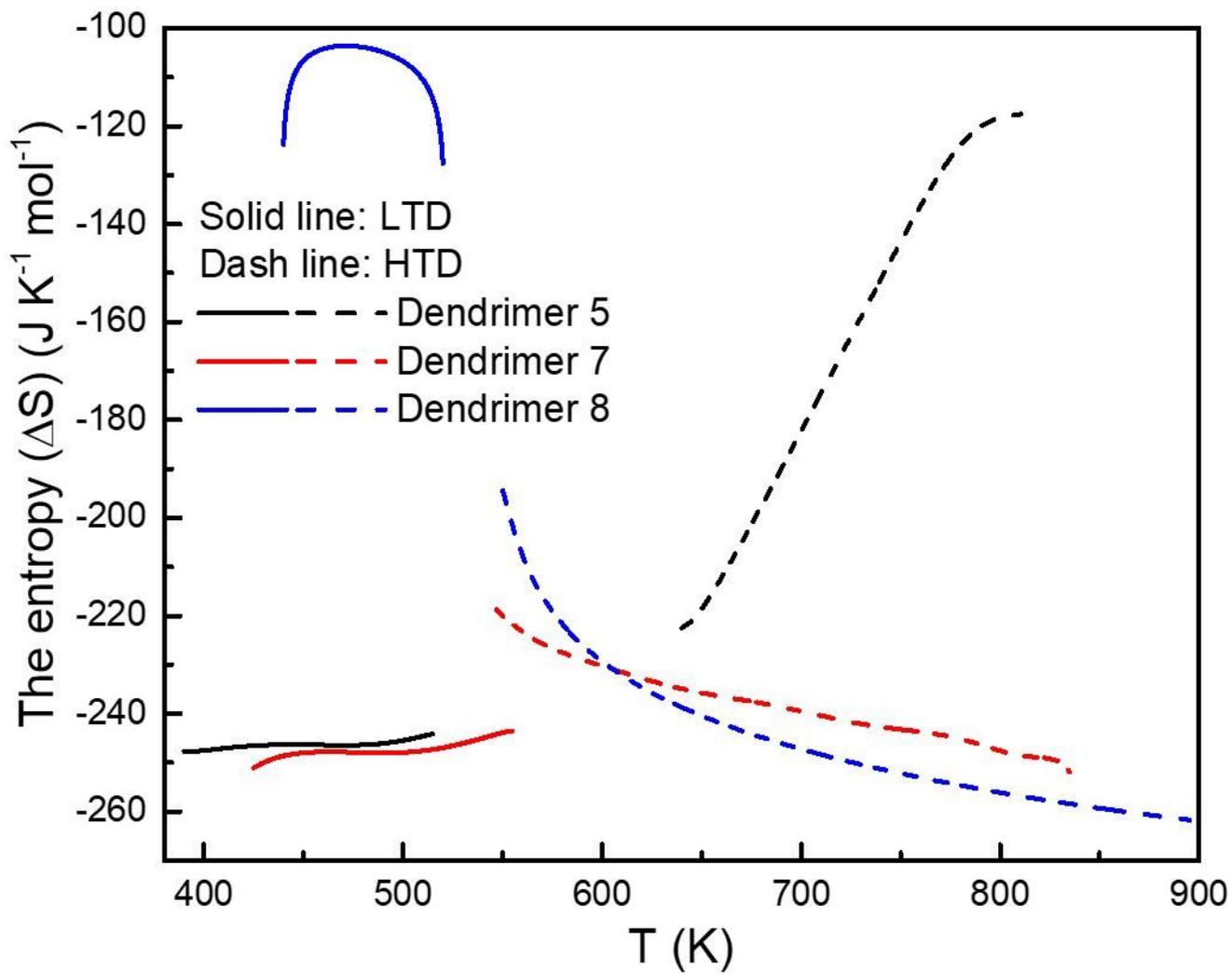


Figure 11

The variation of the entropy, ΔS , as a function of temperature of the two steps LTD and HTD for dendrimer 5, 7 and 8.

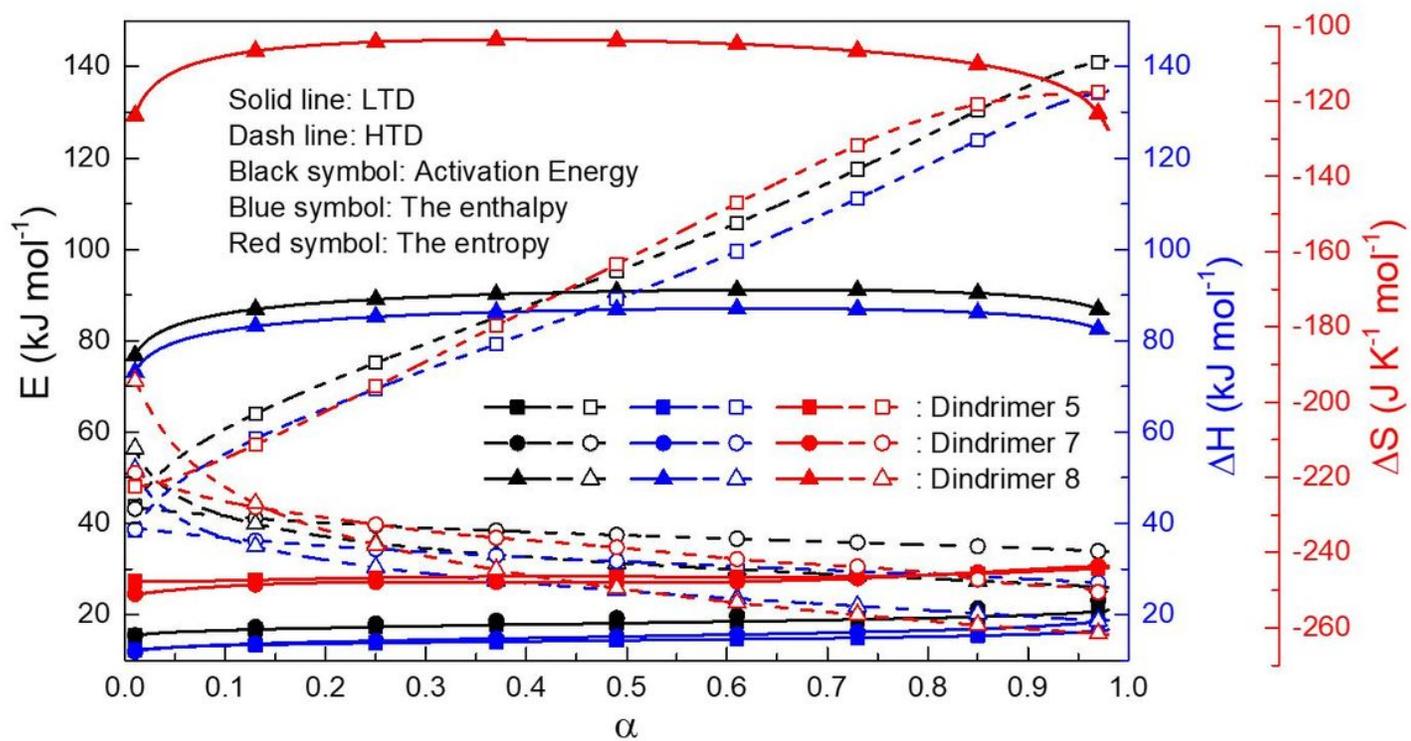


Figure 12

shows that the activation energy, the enthalpy and the entropy have the same tendency.