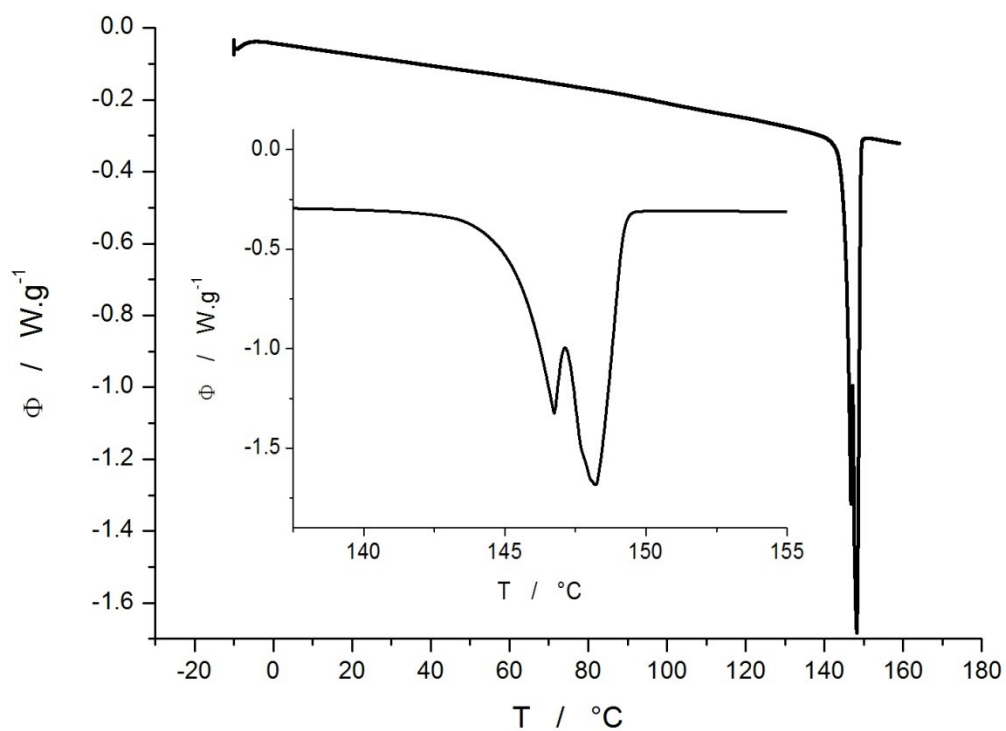


Supplemental online material – part 1

DSC curve for the 250 – 300 μm powder being annealed at 25 $^{\circ}\text{C}$ for six hours and then heated above T_m . Exothermic effects evolve in the upwards direction. The marked melting pre-peak indicates the presence of the NIM polymorphic form II.



Supplemental online material – part 2

It has been pointed out that the Kissinger method is not adequate to describe the kinetics of a process, and usually conceive its eventual complexity providing a single value of activation energy. Whereas the inadequacy of the Kissinger equation is perfectly valid in the case of certain following, competing and reversible reactions, it has been shown in [Is the original Kissinger equation obsolete today? R. Svoboda, J. Málek, J. Therm. Anal. Calorim. 115 (2014) 1961-1967] that the utilization of the Kissinger equation can be indeed very beneficial in the case of the overlapping independent or (majority of) consequent/following reactions. This is the case of the present (and majority of) glass-crystallization data. On the contrary, as has been shown in [Activation energy determination in case of independent complex kinetic processes. G. Luciano, R. Svoboda. Processes 7 (2019) 738] and in [Complex process activation energy evaluated by combined utilization of differential and integral isoconversional methods. R. Svoboda, G. Luciano. J. Non-Cryst. Sol. 535 (2020) 120003], it is the isoconversional methods, which can give biased and unreliable results, which can be difficult to interpret. In addition, the former of the two above-mentioned papers disproves the perceived supremacy of the recently derived isoconversional methods. In practical situations involving independent or following reactions, the accuracy of all differential isoconversional methods is similar, and the same holds also for all integral isoconversional methods (again compared with each other). It is however true, that some readers may still be interested in the course of the isoconversional data, these dependences calculated for the crystallization data are thus shown below.

Note that the integral isoconversional methods appear to agree slightly better with the E values determined via the Kissinger method (due to the results of the differential isoconversional methods being distorted by the deviations in the $d\alpha/dt$ values). Nonetheless, the actual courses of the E- α dependences are (as is often the case in the case of the real-life crystallization data) irregular, with no clear trends and no possibility to reliably extract any additional information. Below, each case will be commented individually. The non-monotonous trends in the differential methods increase with powders particle size due to the crystallization response being not averaged through so extensive number of crystallization centers compared to the finely powdered NIM grains.

In graph S2A, the isoconversional data for E- α and logA- α dependences obtained by the integral and differential isoconversional methods for the crystallization process in the 50 – 125 μm NIM powder are shown. In the α range 0.3 – 0.7, where the isoconversional E and A values are commonly averaged and the consistency of the process kinetics is considered, both quantities exhibit an insignificant change for the data series obtained at 1 – 20 $^{\circ}\text{C}\cdot\text{min}^{-1}$; the data series for the as-prepared non-degraded samples show a significantly decreasing trend, which however can be associated with the evident q^{+} -based change of the crystallization kinetics (see Fig. 3A). The same reason is also most probably the main reason for the large difference between the E and A values determined via differential and integral isoconversional methods, where the former takes into account the $d\alpha/dt$ signal that tend to distort the results due to e.g. imprecise subtraction of the thermokinetic background or due to the intrinsic changes of kinetic behavior. The values determined by the Kissinger method were 67 and 180 $\text{kJ}\cdot\text{mol}^{-1}$ for the 1 – 20 $^{\circ}\text{C}\cdot\text{min}^{-1}$ and 0.5&20 $^{\circ}\text{C}\cdot\text{min}^{-1}$ q^{+} ranges,

respectively. The integral isoconversional method provides almost identical values for the above-mentioned reasons. Overall, the isoconversional methods provided no added value in this case.

In graph S2B, the isoconversional data for $E-\alpha$ and $\log A-\alpha$ dependences obtained by the integral and differential isoconversional methods for the crystallization process in the 125 – 180 μm NIM powder are shown. In the α range 0.3 – 0.7, where the isoconversional E and A values are commonly averaged and the consistency of the process kinetics is considered, both quantities exhibit an insignificant change for the data series obtained at 1 – 20 $^{\circ}\text{C}\cdot\text{min}^{-1}$; the data series for the as-prepared non-degraded samples show a significantly decreasing trend, which however can be associated with the evident q^+ -based change of the crystallization kinetics (see Fig. 3B). The same reason is also most probably the main reason for the large difference between the E and A values determined via differential and integral isoconversional methods, where the former takes into account the $d\alpha/dt$ signal that tend to distort the results due to e.g. imprecise subtraction of the thermokinetic background or due to the intrinsic changes of kinetic behavior. The values determined by the Kissinger method were 110 and 183 $\text{kJ}\cdot\text{mol}^{-1}$ for the 1 – 20 $^{\circ}\text{C}\cdot\text{min}^{-1}$ and 0.5&20 $^{\circ}\text{C}\cdot\text{min}^{-1}$ q^+ ranges, respectively. The integral isoconversional method provides almost identical values for the above-mentioned reasons. Overall, the isoconversional methods provided no added value in this case.

In graph S2C, the isoconversional data for $E-\alpha$ and $\log A-\alpha$ dependences obtained by the integral and differential isoconversional methods for the crystallization process in the 180 – 250 μm NIM powder are shown. In the α range 0.3 – 0.7, where the isoconversional E and A values are commonly averaged and the consistency of the process kinetics is considered, both quantities exhibit an insignificant change for the data series obtained at 1 – 20 $^{\circ}\text{C}\cdot\text{min}^{-1}$; the data series for the as-prepared non-degraded samples show a mildly decreasing trend, which however can be associated with the evident q^+ -based change of the crystallization kinetics (see Fig. 3C). The same reason is also most probably the main reason for the large difference between the E and A values determined via differential and integral isoconversional methods, where the former takes into account the $d\alpha/dt$ signal that tend to distort the results due to e.g. imprecise subtraction of the thermokinetic background or due to the intrinsic changes of kinetic behavior. The values determined by the Kissinger method were 122 and 146 $\text{kJ}\cdot\text{mol}^{-1}$ for the 1 – 20 $^{\circ}\text{C}\cdot\text{min}^{-1}$ and 0.5&20 $^{\circ}\text{C}\cdot\text{min}^{-1}$ q^+ ranges, respectively. The integral isoconversional method provides almost identical values for the above-mentioned reasons. Overall, the isoconversional methods provided no added value in this case.

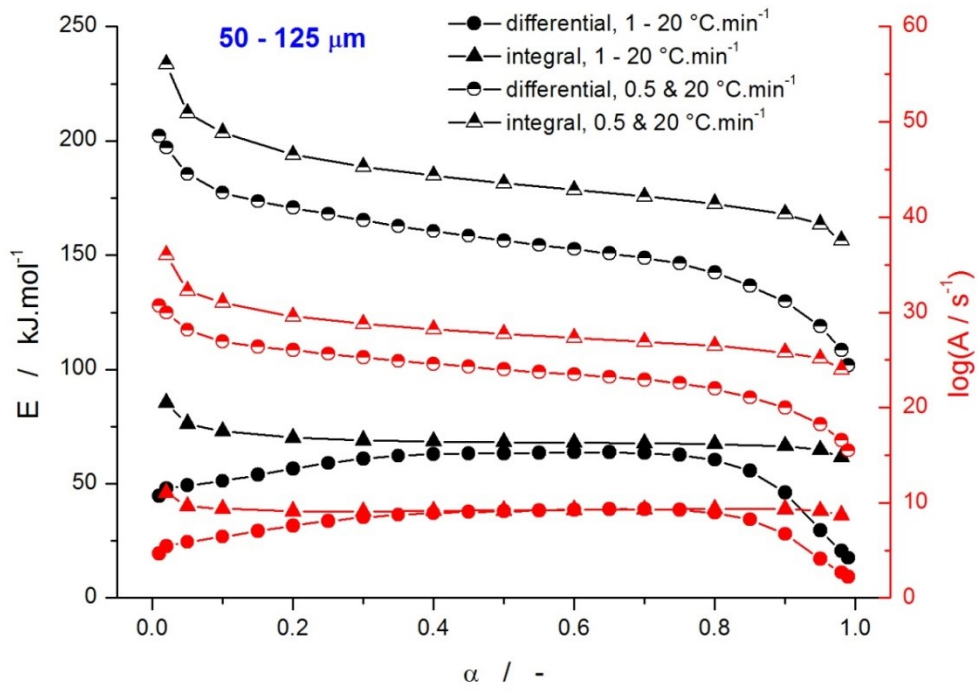
In graph S2D, the isoconversional data for $E-\alpha$ and $\log A-\alpha$ dependences obtained by the integral and differential isoconversional methods for the crystallization process in the 250 – 300 μm NIM powder are shown. In the α range 0.3 – 0.7, where the isoconversional E and A values are commonly averaged and the consistency of the process kinetics is considered, both quantities exhibit an insignificant change for the data series obtained at 1 – 20 $^{\circ}\text{C}\cdot\text{min}^{-1}$; the data series for the as-prepared non-degraded samples show a mildly decreasing trend from the integral method and non-monotonous trend from the differential method, which however can be associated with the evident q^+ -based change of the crystallization kinetics (see Fig. 3D). The same reason is also most probably the main reason for the significant difference

between the E and A values determined via differential and integral isoconversional methods, where the former takes into account the $d\alpha/dt$ signal that tend to distort the results due to e.g. imprecise subtraction of the thermokinetic background or due to the intrinsic changes of kinetic behavior. The values determined by the Kissinger method were 136 and 139 $\text{kJ}\cdot\text{mol}^{-1}$ for the 1 – 20 $^{\circ}\text{C}\cdot\text{min}^{-1}$ and 0.5&20 $^{\circ}\text{C}\cdot\text{min}^{-1}$ q^+ ranges, respectively. The integral isoconversional method provides almost identical values for the above-mentioned reasons. Overall, the isoconversional methods provided no added value in this case.

In graph S2E, the isoconversional data for E- α and logA- α dependences obtained by the integral and differential isoconversional methods for the crystallization process in the 300 – 500 μm NIM powder are shown. In the α range 0.3 – 0.7, where the isoconversional E and A values are commonly averaged and the consistency of the process kinetics is considered, both quantities exhibit an insignificant change for the data series obtained at 1 – 20 $^{\circ}\text{C}\cdot\text{min}^{-1}$; the data series for the as-prepared non-degraded samples show a significantly decreasing trend from the integral method and non-monotonous trend from the differential method, which however can be associated with the evident q^+ -based change of the crystallization kinetics (see Fig. 3E). The same reason is also most probably the main reason for the large difference between the E and A values determined via differential and integral isoconversional methods, where the former takes into account the $d\alpha/dt$ signal that tend to distort the results due to e.g. imprecise subtraction of the thermokinetic background or due to the intrinsic changes of kinetic behavior. The values determined by the Kissinger method were 109 and 152 $\text{kJ}\cdot\text{mol}^{-1}$ for the 1 – 20 $^{\circ}\text{C}\cdot\text{min}^{-1}$ and 0.5&20 $^{\circ}\text{C}\cdot\text{min}^{-1}$ q^+ ranges, respectively. The integral isoconversional method provides almost identical values for the above-mentioned reasons. Overall, the isoconversional methods provided no added value in this case.

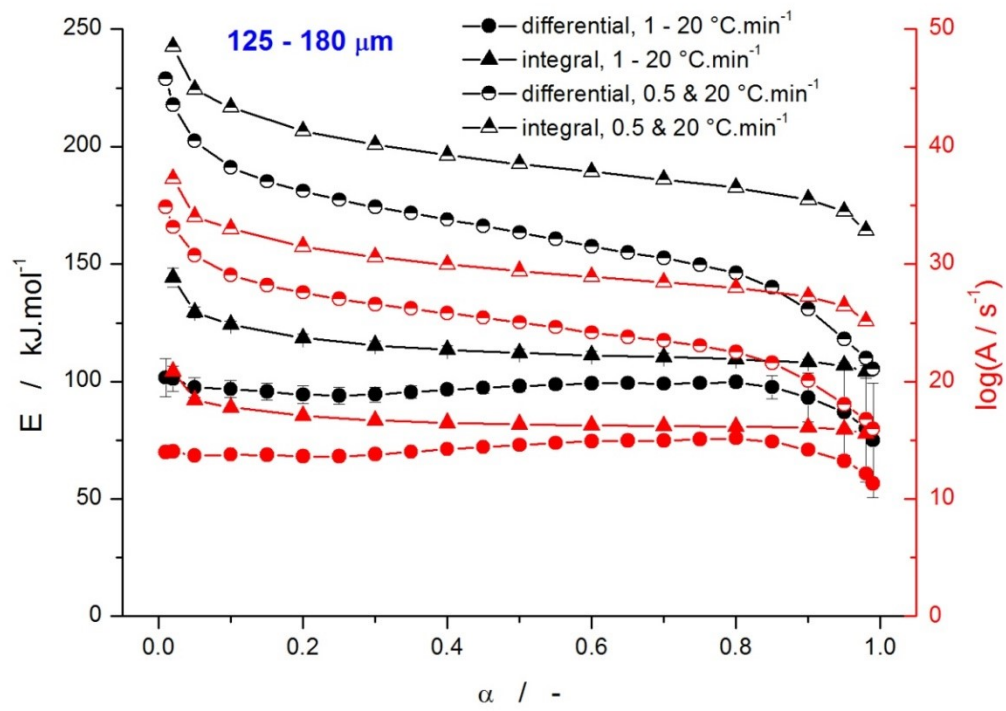
In graph S2F, the isoconversional data for E- α and logA- α dependences obtained by the integral and differential isoconversional methods for the crystallization process in the 500 – 1000 μm NIM powder are shown. In the α range 0.3 – 0.7, where the isoconversional E and A values are commonly averaged and the consistency of the process kinetics is considered, both quantities exhibit an insignificant change for the data series obtained at 1 – 20 $^{\circ}\text{C}\cdot\text{min}^{-1}$; the data series for the as-prepared non-degraded samples show a significantly decreasing trend from the integral method and non-monotonous trend from the differential method, which however can be associated with the evident q^+ -based change of the crystallization kinetics (see Fig. 3F). The same reason is also most probably the main reason for the significant difference between the E and A values determined via differential and integral isoconversional methods, where the former takes into account the $d\alpha/dt$ signal that tend to distort the results due to e.g. imprecise subtraction of the thermokinetic background or due to the intrinsic changes of kinetic behavior. The values determined by the Kissinger method were 120 and 123 $\text{kJ}\cdot\text{mol}^{-1}$ for the 1 – 20 $^{\circ}\text{C}\cdot\text{min}^{-1}$ and 0.5&20 $^{\circ}\text{C}\cdot\text{min}^{-1}$ q^+ ranges, respectively. The integral isoconversional method provides almost identical values for the above-mentioned reasons. Overall, the isoconversional methods provided no added value in this case.

Graph S2A

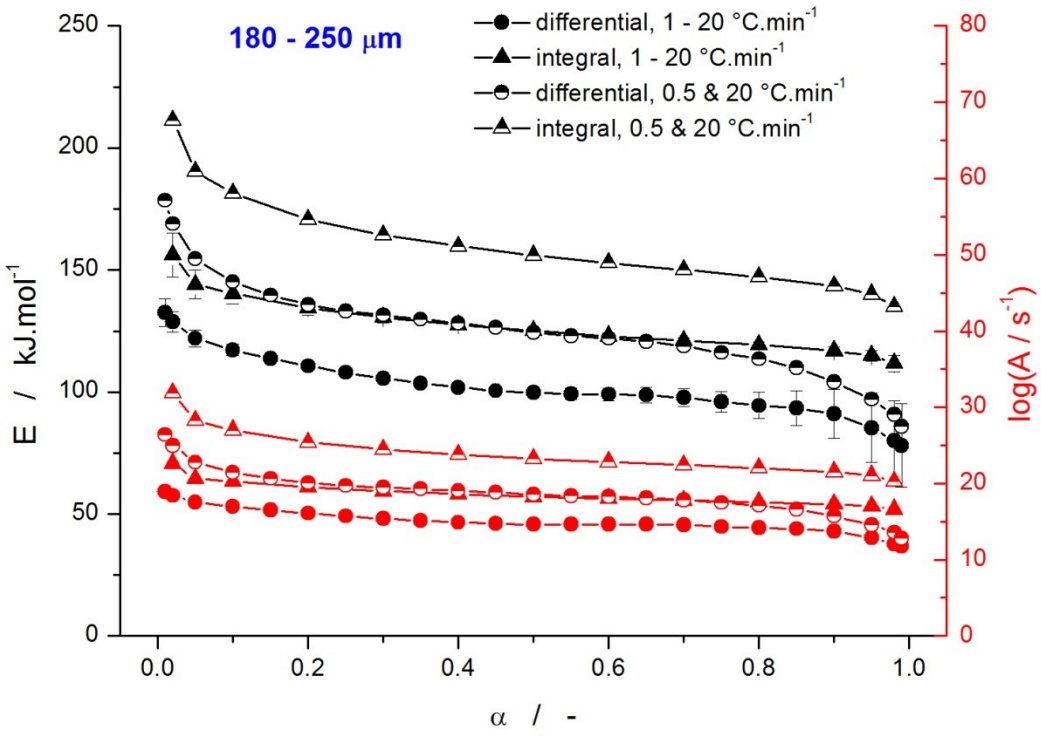


Graph

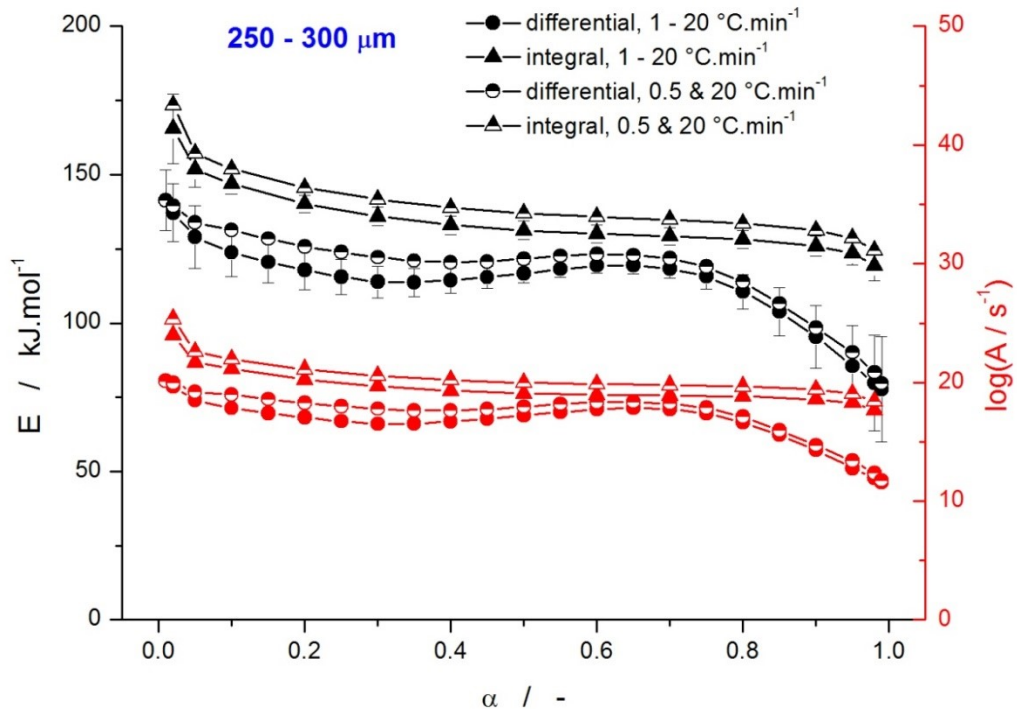
S2B



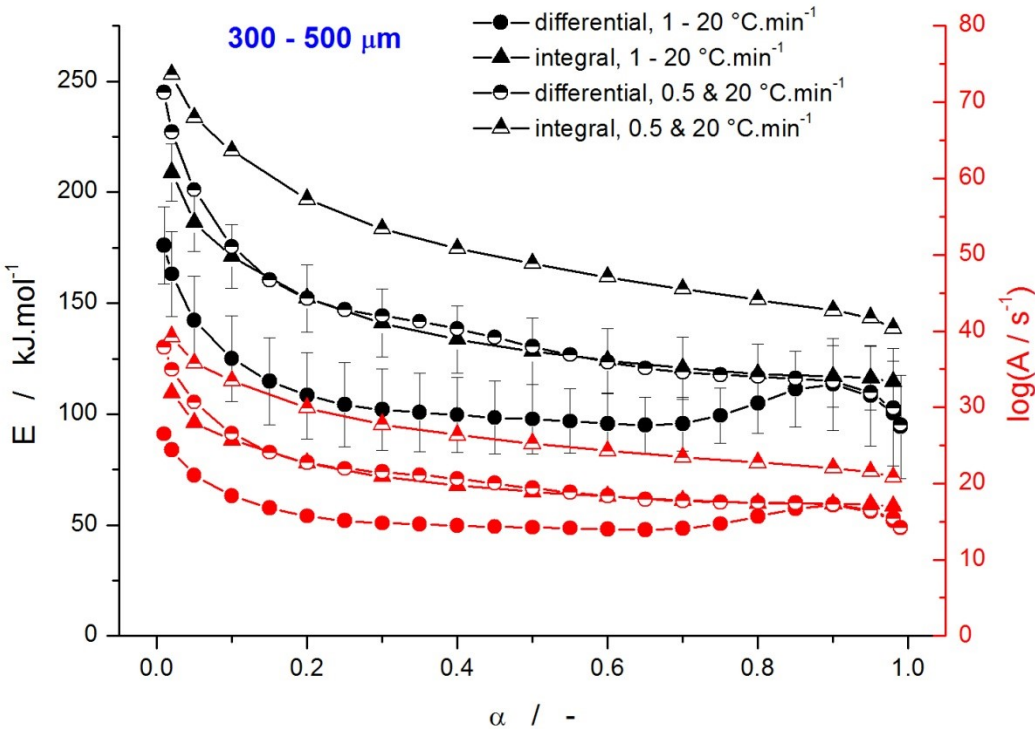
Graph S2C



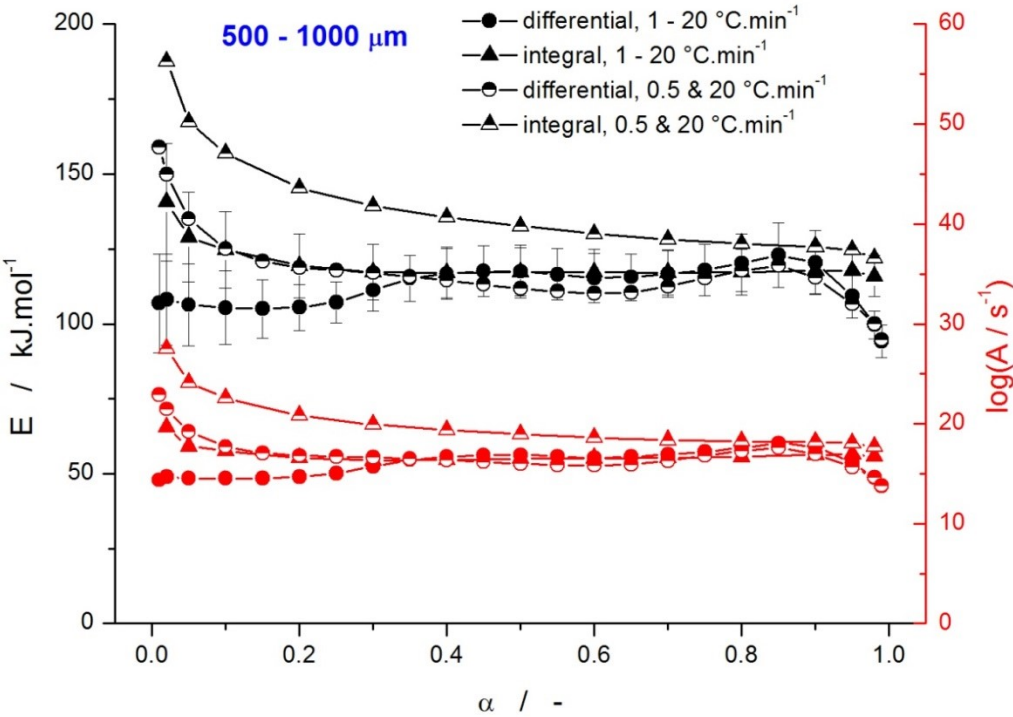
Graph S2D



Graph S2E



Graph S2F



Supplemental online material – part 3

The E - α and $\log A$ - α dependences obtained by the isoconversional methods for the decomposition process. In the α range 0.3 – 0.7, where the isoconversional E and A values are commonly averaged and the consistency of the process kinetics is considered, both quantities exhibit an insignificant change, the magnitude of which is lower than the error bars. Common interpretation of these E - α and $\log A$ - α courses would be that single process kinetics is encountered. However, by comparing this conclusion to the data from Figs. 6B and 10 from the main paper, it is obviously not true, as in reality, the decomposition exhibits a temperature-dependent kinetics. Nonetheless, the isoconversional E values averaged in the 0.3 – 0.7 α range are $100.3 \pm 2.0 \text{ kJ}\cdot\text{mol}^{-1}$ for the differential method and $102.0 \pm 0.4 \text{ kJ}\cdot\text{mol}^{-1}$ for the isoconversional method, which are consistent with the Kissinger method result of $102.4 \pm 13.8 \text{ kJ}\cdot\text{mol}^{-1}$. The error bars for the individual isoconversional evaluations were in the 9 – 12 $\text{kJ}\cdot\text{mol}^{-1}$ range, i.e., comparable to that for the Kissinger method. Hence, the no added value by the isoconversional methods compared to the result provided from the Kissinger method.

