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An electrical conductivity study of a cyano-substituted polyamide and of the corresponding diamide derived from 1,4-bis(2-cyano-2-carboxyvinyl)benzene: the effect of pyrolysis temperature and pyrolysis duration

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The electrical conductivity of a pyrolysed cyano-substituted polyamide and of the corresponding diamide, prepared from 1,4-bis(2-cyano-2-carboxyvinyl)benzene, was studied. In particular, the a.c. conductivity of the unpyrolysed polymer, in the form of a thin film with a thickness of 3000 Å, was investigated at room temperature over the frequency range from 40 Hz to 100 kHz. The observed frequency dependence suggests the existence of interfacial polarizations between the bulk and the electrodes, or within the bulk. The d.c. conductivity of the polymer and the corresponding diamide, in the form of pellets, both unpyrolysed and pyrolysed, was investigated over the temperature range from 100 to 600 K. The pyrolysis temperature covered the range from 550 up to 900°C. The effect of pyrolysis duration was also studied at pyrolysis temperatures of 550 and 750°C. The results show that the conductivity of the pyrolysed samples increases enormously with increasing pyrolysis temperature up to 750°C, reaching a value of 2.857 Ω^{-1} cm^{-1} at room temperature, while further increase in the pyrolysis temperature results in a decrease of the conductivity. For a pyrolysis temperature of 900°C the conductivity at room temperature has a value of 1.613×10^{-1} Ω^{-1} cm^{-1}. The effect of pyrolysis at high temperatures suggests the promotion of formation of a multiphase system, which could also be responsible for the observed behaviour of the conductivity at prolonged, moderately high pyrolysis temperatures. X-ray profiles, recorded for all samples, both unpyrolysed and pyrolysed, support the interpretation of the conductivity results.

(Keywords: electrical conductivity; cyano-substituted polyamide; pyrolysed polyamide)

INTRODUCTION

Recently, the electrical conductivity at three different pyrolysis temperatures of a cyano-substituted polyamide, derived from 1,4-bis(2-cyano-2-carboxyvinyl)-benzene, has been reported[1]. Despite the limited number of temperatures at which the conductivity was measured, the results showed that the conductivity increased dramatically as the pyrolysis temperature increased, and that the pyrolysed polyamide showed semiconducting behaviour, whereas the unpyrolysed material had insulating properties. This transition from an insulating to a semiconducting form by increasing the pyrolysis temperature has been known for various related classes of polymers for some time[2]. Furthermore, the effect of pyrolysis duration has been reported to increase the conductivity of the same polymers[2].

In order to shed further light on the electrical behaviour of the polyamide the a.c. conductivity of the unpyrolysed polymer in the form of a thin film was studied at room temperature. In addition, the d.c. conductivity was investigated at different pyrolysis temperatures, covering the range from 550 to 900°C. The effect of pyrolysis duration on the conductivity was also studied at 550 and 750°C. For comparison, the electrical behaviour of the model diamide was also investigated, following pyrolysis in the same temperature region. In order to relate the observed electric behaviour with the structure, X-ray diffraction spectra were recorded for the unpyrolysed polyamide, as well as for all of the pyrolysed samples and the model diamide.

EXPERIMENTAL

Details regarding the preparation of the polymer and the model diamide can be found in ref. 3. *Schemes 1* and *2* summarize the reaction steps required for

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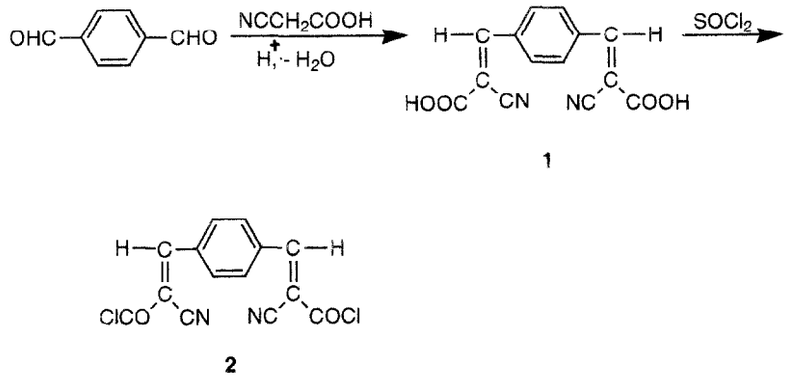
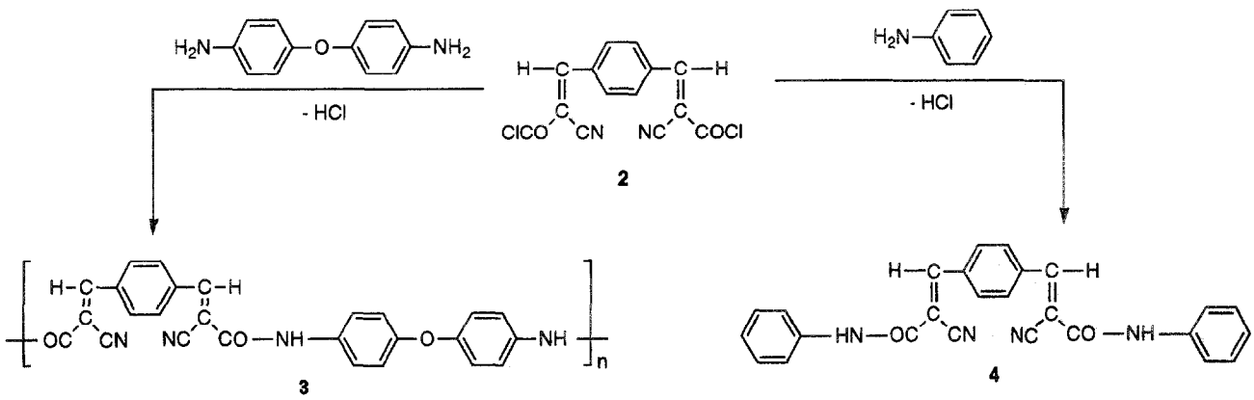


Scheme 1



Scheme 2

obtaining the monomer (**2**), the polymer (**3**) and the model diamide (**4**).

The a.c. conductivity of the unpyrolysed polymer (**3**) was measured in the form of a thin film capacitor. First an aluminium electrode was thermally evaporated on to a meticulously cleaned glass substrate and then a drop of a solution of the polymer in *N,N*-dimethylformamide (DMF) was put on the substrate. The thin film was formed by the spin coating method. Following this process, the glass substrate was put in a vacuum oven and the sample was dried for 24 h at 140°C under vacuum in order to evaporate the solvent. A second aluminium electrode was then evaporated on to the substrate, the resulting capacitor having a cross-section of $3 \times 3\,mm^2$. The evaporations were performed under vacuum using a Leybold–Heraeus ultra high vacuum system. The pressure during the evaporation process was of the order of 10^{-7} mbar. The thickness of the thin film was measured with a Varian Å-Scope Interferometer (Model 980-4020) and found to be equal to 3000 Å. The a.c. conductivity measurements were taken with a Keithley LCZ-meter (Model 3330); this was driven by a computer program so that the voltage drop along the thin film capacitor was kept constant, and the current, voltage, phase angle, conductance, impedance and capacitance of the resulting thin film capacitor were recorded automatically over the frequency range from 40 Hz to 100 kHz.

For the d.c. investigations, the powder from the unpyrolysed material was pressed to form pellets, having a diameter of 10 mm and an average thickness of ~ 1 mm. The pellets were then pyrolysed at temperatures ranging from 550 to 900°C, in steps of 50°C. The resistivity of the pyrolysed samples was measured by applying the Van der Pauw method[4]. The apparatus used for this has been described in detail in the work of Krontiras *et al.*[1]. The crystallinity of the pyrolysed samples was investigated by recording X-ray diffraction profiles with a Phillips PW1840 Diffractometer, using the CuKβ line (40 kV, 30 mA).

RESULTS AND DISCUSSION

X-ray diffraction

A meaningful interpretation of the experimental results requires the determination of the structure of the unpyrolysed and pyrolysed polyamide **3**, i.e. whether they are amorphous or crystalline. The recorded X-ray profiles are shown in *Figure 1*. The unpyrolysed polymer shows two strong peaks at $2\theta = 38$ and 45°, and a third peak at 66°, whose intensity is lower. As the pyrolysis temperature is increased the intensity of all peaks is reduced. As a result of this the weak peak disappears. The other two peaks are still present, even at the highest pyrolysis temperatures. However, additional peaks manifest themselves, as can be seen from *Figure 1*.

No attempt has been made to further analyse the X-ray profiles. However, the results suggest that there is crystallinity in the samples, and this is present up to 700°C. The presence of additional peaks at higher

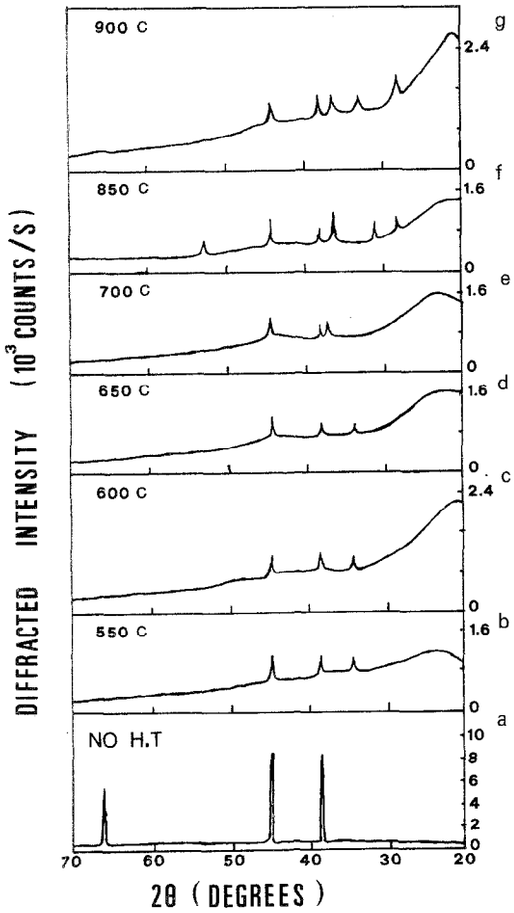


Figure 1 X-ray profiles of polyamide 3 after pyrolysis at different temperatures

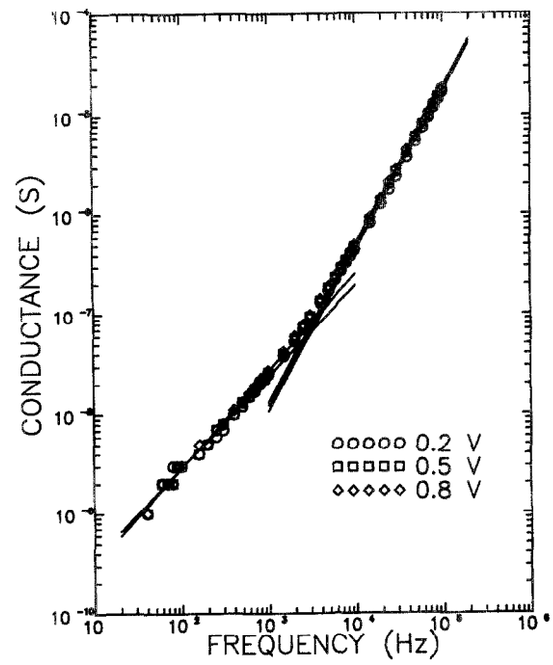


Figure 2 Frequency dependence of the conductance of polyamide 3 for three different applied voltages

pyrolysis temperatures may be attributed to the formation of a new crystalline phase. The presence of a multiphase has been observed by other workers[5,6].

A.c. conductivity

Figure 2 shows, in a log–log form, the real part of the a.c. conductance G at room temperature of the thin polymeric film, as a function of the frequency f for different applied voltages in the range from 40 Hz to 100 kHz. In order to avoid overcrowding of the experimental points, only the results obtained for 0.2, 0.5 and 0.8 V are plotted. This figure suggests that the a.c. conductivity is independent of the applied voltage, i.e. the system behaves linearly with the applied voltage. It is clearly shown that in the frequency ranges from 40 to 5.0×10^2 Hz and from 7.0×10^3 to 1.0×10^5 Hz the conductivity follows within each particular range the *universal dielectric response*[7], which is expressed by the following relationship:

$$\sigma = b(2\pi f)^n = b\omega^n \quad (1)$$

where b and n are constants with different values in each region. By applying a non-linear, least-squares computer program the results were fitted to equation (1) in the low and high frequency regions, respectively, yielding values of 1.0 and 1.6 for the exponent n in these respective regions.

Figure 3 shows the logarithmic representation of the complex impedance. This behaviour is typical of cases where a barrier region exists in series with the bulk. This effect is known as the Maxwell–Wagner effect and is related to the interfacial polarizations of the bulk material with the electrodes, or within the bulk between the grains[7,8]. The intense, sharp peaks in the X-ray diffraction profile of the unpyrolysed polymer (*Figure 1a*) suggest the existence of a crystalline phase and therefore supports this behaviour.

D.c. conductivity

Figure 4 shows the temperature dependence of the resistivity of polyamide **3**, shown for samples pyrolysed at different temperatures.

The effect of the pyrolysis temperature was also investigated for the model diamide **4**. *Figure 5* shows the results of the temperature dependence of the resistivity of the model diamide **4**, pyrolysed at 550 and 750°C. For comparison, the resistivity data for polyamide **3**, pyrolysed at the same temperatures, are also shown in the same figure. It is obvious from this figure that diamide **4** has a higher resistivity than polyamide **3** when pyrolysed at the same temperature. This confirms that the transition from diamide **4** to polyamide **3** increases the conjugation of the π-electron system of the molecule and thus, the conductivity.

Bearing in mind that these resistivity results for polyamide **3** resemble those reported in other studies[1,9–11], the results from this present work were fitted to the following relationship:

$$\rho = \rho_0 \exp\left(\frac{\Delta E}{kT}\right) \quad (2)$$

by applying to the two distinct temperature regions that are observed, the same non-linear least-squares computer fitting program which was used in the previous

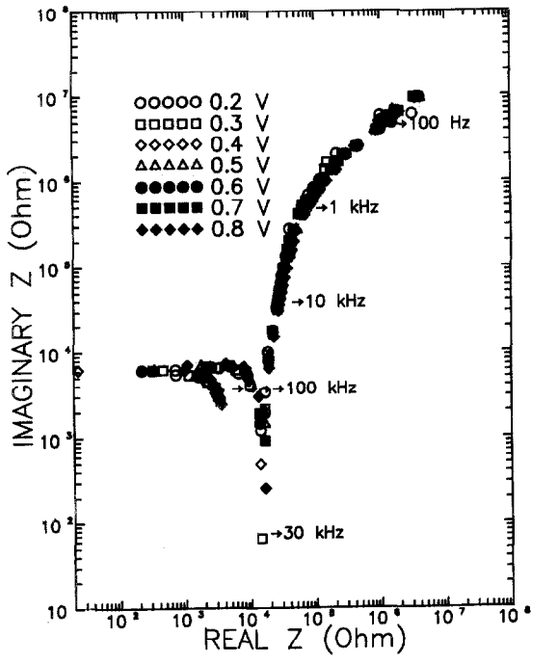


Figure 3 Logarithmic representation of the complex impedance of polyamide **3**

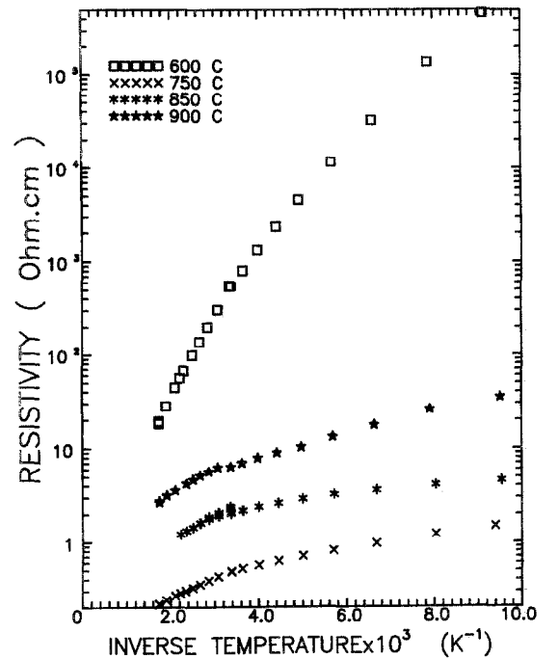


Figure 4 Temperature dependence of the electrical resistivity of polyamide **3** after pyrolysis at different temperatures

Table 1 Values of ρ_0 and ΔE for the lower and higher temperature regions for polyamide **3**

Pyrolysis temperature (°C)	Region			
	Low temperature		High temperature	
	ρ_0 (Ω cm)	ΔE (eV)	ρ_0 (Ω cm)	ΔE (eV)
550	1.18×10^3	0.13	8.191	0.26
600	1.29×10^1	0.10	4.88×10^{-1}	0.18
650	1.444	0.04	2.63×10^{-1}	0.08
700	5.03×10^{-1}	0.03	1.09×10^{-1}	0.06
750	2.57×10^{-1}	0.02	8.67×10^{-2}	0.05
850	1.678	0.01	3.41×10^{-1}	0.05
950	2.544	0.03	8.89×10^{-1}	0.06

work. The results of this fitting are summarized in *Table 1*, where ρ_0 and the values for the activation energy ΔE for the two different temperature regions are given. These two activation energies are associated with the intramolecular and intermolecular conducting processes. Specifically, the lower values of ΔE are associated with the intermolecular conduction process, while the higher values are related to the intramolecular conduction process.

The activation energies for the model diamide **4** are given on *Figure 5* and can be compared with the activation energies of polyamide **3** for the same pyrolysis temperatures, which are given in *Table 1*. Both sets of activation energies, namely those for the intermolecular and intramolecular conductivities for both pyrolysis temperatures have values greater than the corresponding activation energies obtained for polyamide **3.**

From *Figure 5* it is observed that for pyrolysis temperatures higher than 750°C, namely 850 and 900°C, the resistivity shows an increase as the pyrolysis temperature is increased. This effect is shown clearly in *Figure 6*, where the conductivity at room temperature is

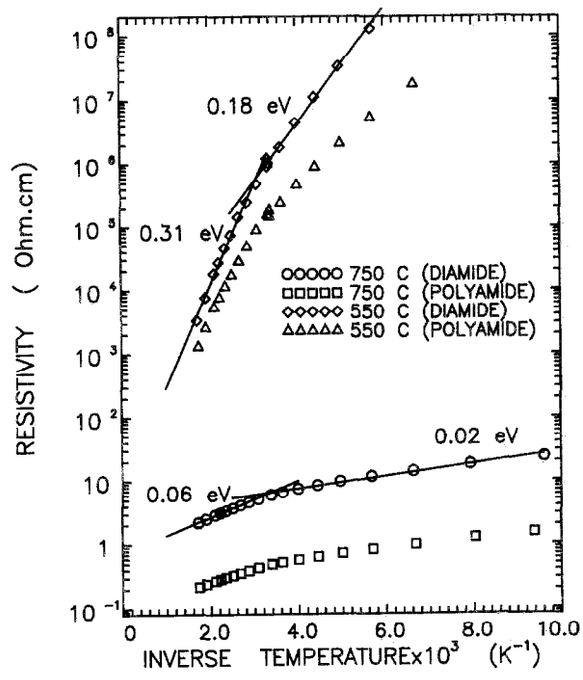


Figure 5 Temperature dependence of the electrical resistivity of polyamide **4** pyrolysed at 550 and 750°C; for comparison, the resistivity data of polyamide **3**, pyrolysed at the same temperatures, are also shown

plotted as a function of the pyrolysis temperature. From *Table 1*, it is concluded that both activation energies decrease as the pyrolysis temperature increases up to 750°C, in accordance with the fact that by increasing the pyrolysis temperature one would expect an increase in the amount of crosslinking. However, for temperatures higher than 750°C, the activation energies increase as the pyrolysis temperature increases. The increase in resistivity and activation energy for both the intermolecular

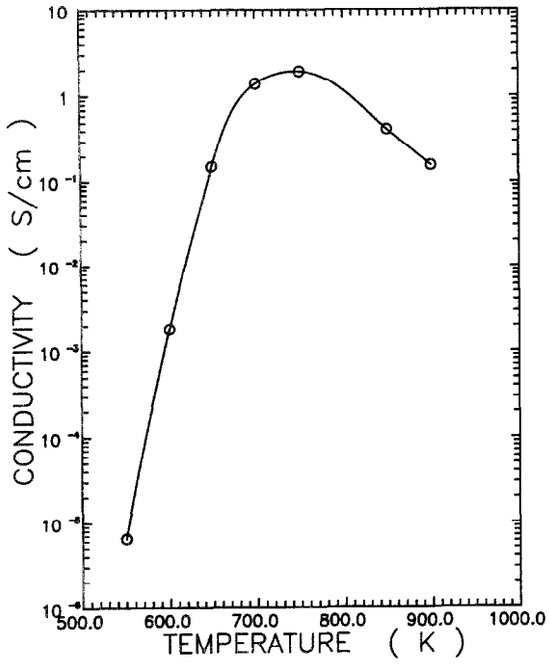


Figure 6 Room temperature conductivity of polyamide **3** plotted as a function of the pyrolysis temperature

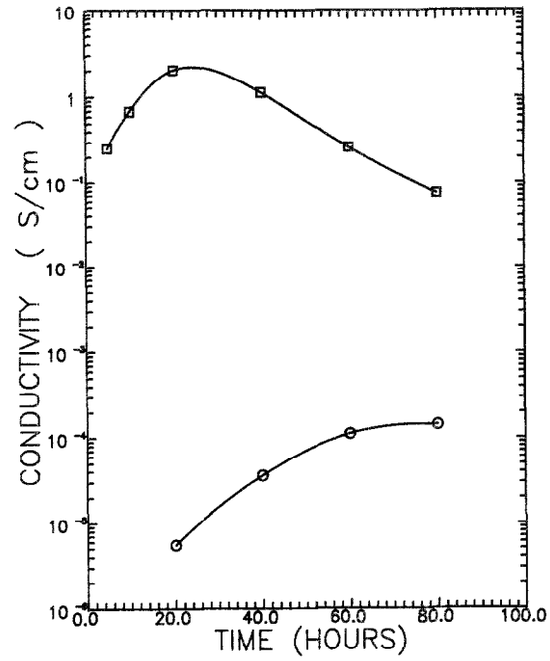


Figure 7 Room temperature conductivity of polyamide **3** plotted as a function of the pyrolysis duration for samples pyrolysed at different temperatures: O, 550; □, 750°C

and intramolecular processes should be associated with the additional crystalline phase which is observed for samples pyrolysed at 850 and 900°C. This is easily confirmed by comparing *Figures 1b–1d* with *Figures 1f* and *1g*. The observed crystallinity of the samples justifies the application of equation (2) to the analysis of the resistivity results, and not the variable range hopping model, either one-dimensional or three-dimensional[12], or the model using a distribution of barrier heights[13], since these models apply to amorphous materials.

Figure 7 shows the effect of the duration of pyrolysis at two different pyrolysis temperatures, namely 550 and 750°C, on the conductivity of polyamide **3** at room temperature. The solid line drawn through the experimental points is the result of a computer curve fitting program using splines, and it is drawn to show the trend, rather than the actual dependence of the conductivity on the pyrolysis duration. The effect of the duration of pyrolysis at 550°C is to increase the conductivity as the pyrolysis duration increases, whereas a maximum is observed for the conductivity of the sample pyrolysed at 750°C. This may be attributed to the formation of a multiphase system as a result of prolonged pyrolysis at high temperatures. Since such a multiphase system has been observed for pyrolysis temperatures of 850 and 900°C, this may be explained by the fact that such a system is formed in less than 20 h at these temperatures, a time interval used as a standard for all pyrolysis temperatures.

CONCLUSIONS

The a.c. conductivity of polyamide **3** has been investigated at room temperature in the form of thin films and has shown the existence of interfacial polarizations between the bulk and the electrodes or within the bulk. This behaviour is supported by X-ray studies of the polyamide.

The temperature dependence of the resistivity of polyamide **3** and the model diamide **4** has been investigated as a function of pyrolysis temperature and pyrolysis duration. Both materials show semiconducting behaviour, which is thermally activated with distinct intermolecular and intramolecular conduction processes. Upon increasing the pyrolysis temperature up to 750°C the conductivity increases whereas for higher temperatures it decreases. This is associated with the formation of a multiphase system, as suggested by the corresponding X-ray profiles. The behaviour of the conductivity of polyamide **3** as a function of pyrolysis duration is also attributed to the formation of a multiphase system.

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