Thermochimica Acta 490 (2009) 32–36

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

# Decomposition kinetics of nylon-6/graphite and nylon-6/graphite oxide composites

Kevin Scully, Rabin Bissessur*

*Department of Chemistry, University of Prince Edward Island, Charlottetown, PEI, Canada C1A 4P3*

ARTICLE INFO

*Article history:*
Received 6 November 2008
Received in revised form 22 January 2009
Accepted 27 January 2009
Available online 6 February 2009

*Keywords:*
Chemical kinetics
Composite materials
Graphite
Graphite oxide
Thermogravimetric analysis

ABSTRACT

Composite materials of nylon-6/graphite oxide and of nylon-6/graphite were synthesized and their decomposition kinetics determined by thermogravimetric analysis (TGA). Our research shows that both graphite and graphite oxide can be used as fillers to enhance the thermal stability of the polymer. The activation energy for the decomposition of pure nylon-6 itself was found to be 165.4 kJ/mol. The presence of graphite as a filler material produced the greatest enhancement in the thermal stability of the polymer when present at 15 wt.%. The activation energy for the decomposition of the resulting composite was 195.4 kJ/mol, an enhancement of 30.0 kJ/mol over the pure polymer. On the other hand, when present at only 5 wt.%, graphite oxide was shown to significantly enhance the thermal stability of the nylon-6. The activation energy of the resulting material was determined to be 191.1 kJ/mol, an enhancement of 25.7 kJ/mol when compared to the pure polymer.

## 1. Introduction

Recently, exfoliated composites have gained a considerable amount of interest in the scientific community [1,2]. A great number of applications for exfoliated composites have been found in places such as the automotive industry and aerospace industry [3]. An exfoliated composite usually refers to a hybrid material containing a small amount of filler, e.g. a layered structure dispersed in a polymer matrix. Materials of this type received highlight in the 1990s when a team of researchers at the Toyota Central Research Laboratories released results showing the extraordinary mechanical integrity of nylon-6/clay hybrids [4]. Aside from their remarkable strength, exfoliated composites are lightweight, thus making them ideal for applications where stringent weight restrictions would apply.

While most applications of exfoliated materials are due to their high strength and low weight characteristics, there is research evidence demonstrating that they could also be utilized as selective permeable membranes for separation/purification purposes [5,6]. The permeability of these materials could be used in the petroleum refining industry to aid in the purification process [6]. The literature also supports that exfoliated composites show significant enhancement in flame retardancy and decomposition temperatures [7]. These properties have been attributed to the formation of a transient protective barrier. Essentially the filler material generates deposits of stable char which temporarily shields the composite [8,9].

Our interests in graphite arise from the fact that it has been shown to significantly improve the performance of polymeric materials when dispersed throughout the polymer matrix. However, the incorporation of graphite into most polymeric materials is difficult to achieve due to its incompatibility/insolubility with most common organic solvents.

Therefore, alternative methods have to be devised in order to generate exfoliated composites consisting of graphite. To this end, we first and foremost resort to the oxidation of graphite-to-graphite oxide (GO), a hydrophilic-layered material compatible with nylon-6, the polymer matrix chosen in this study. While the precise structure of graphite oxide is not known, FTIR studies confirm that it contains functional groups such as COC, COOH, C=O and OH [10]. It has generally been accepted that the carboxyl and carbonyl functionalities tend to be located near the edges of the graphite oxide, while other functionalities such as epoxides and hydroxyl groups tend to be located on the basal planes of the graphite oxide [11]. The increased polarity of GO allows for better dispersion in polar organic solvents. The graphite oxide can then be reduced back to graphite through the use of reducing agents such as hydrazine [11]. Although there have been studies performed into some of the properties of nylon-6/graphite hybrids [6], to date there has been practically no kinetic data published on the decomposition aspects of these materials. In this paper we report on the solvent-based synthesis and characterization of both nylon-6/graphite oxide and nylon-6/graphite hybrids. The synthesis of exfoliated composites often relies on techniques such as melt intercalation, melt

---

* Corresponding author. Tel.: +1 902 566 0510 fax: +1 902 566 0632.
*E-mail address:* rabissessur@upei.ca (R. Bissessur).

0040-6031/$ – see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.tca.2009.01.029

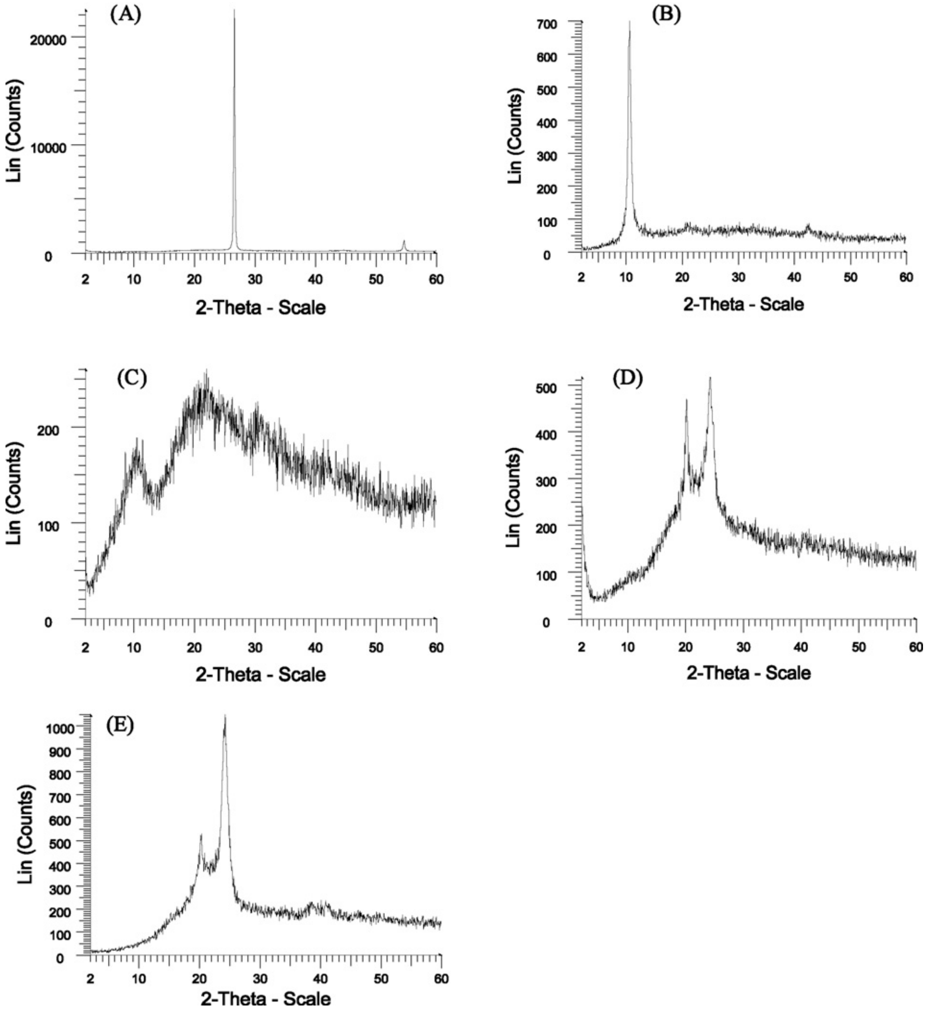

**Fig. 1.** (A) XRD of pristine graphite, (B) XRD of GOX1, (C) XRD of GOX2, (D) XRD of nylon-6/graphite 15%, and (E) XRD of nylon-6 film.

extrusion and mold injection [12–14]. Each of these methods requires significantly more complex experimental setup. By utilizing solvent chemistry methods to synthesize the exfoliated composites, there is no need for processing equipment. The resulting materials were characterized by powder X-ray diffraction, and their decomposition kinetics were determined by thermogravimetric analysis (TGA).

## 2. Materials

Nylon-6 (ultra high molecular weight), with particle size of 3.00 mm was purchased from Aldrich Chemical Company. Synthetic graphite powder (particle size 1–2 μm), hydrazine (1.0 M solution in THF) and 2,2,2-trifluoroethanol were also purchased from Aldrich Chemical Company. Hydrogen peroxide (30%, ACS grade) was bought from EM Science. All reagents and solvents were used as received, with no further purification.

## 3. Instrumentation

Powder X-ray diffraction (XRD) was run on a Bruker AXS D8 Advance diffractometer equipped with a graphite monochromator, variable divergence slit, variable antiscatter slit, and a scintillation detector. Cu(Kα) radiation (λ = 1.542 Å) was utilized and the data collection was carried out at room temperature. Samples were run in air as thin films with a scan range of 2–60°.

Thermogravimetric analyses (TGA) were performed on a TA instruments Q 500 model. Scans were performed up to 600 °C. All runs were performed under an inert nitrogen atmosphere with a flow rate of 60 mL/min. Each sample was run four times at selected heating rates of 5, 10, 20 and 40 °C/min.

## 4. Experimental

### 4.1. Synthesis of graphite oxide

The synthesis of graphite oxide was carried out following the Hummers' method. [15]. Graphite powder (10 g) was placed in a 6-L Erlenmeyer flask. Concentrated sulfuric acid (230 mL) was cooled to 0 °C, and added to the graphite. Potassium permanganate (30 g) was then carefully added to the resulting dark slurry. During the addition of the permanganate, the temperature was maintained below 20 °C. The reaction mixture was then cooled to 0 °C, and stirred for 30 min. Afterwards, 230 mL of deionized water was added to the reaction flask. A rise in temperature was observed, and care was taken to maintain the temperature of the reaction mixture below 90 °C. After 20 min of stirring, an additional 1.4 L of deionized water was added. Immediately following this step, 100 mL of hydrogen peroxide (30%) was rapidly added. The reaction flask was then allowed to sit overnight, with no agitation.

The following morning the excess liquid was decanted. The remaining content was then purified via dialysis. Dialysis was

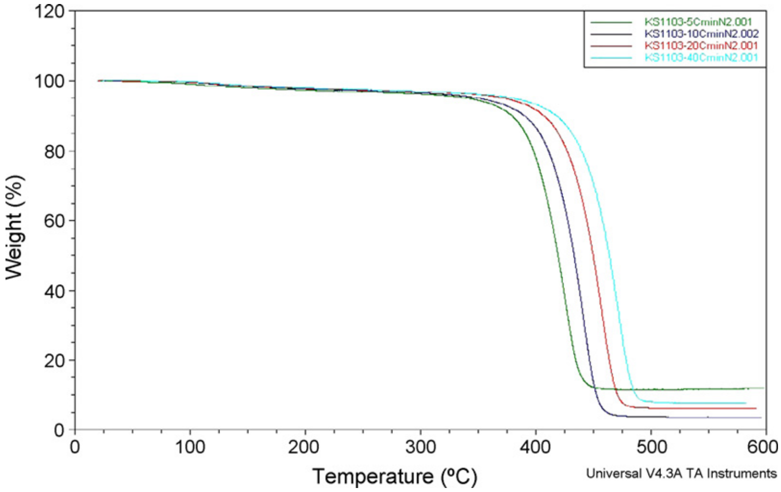

**Fig. 2.** TGA spectra of nylon-6/graphite 10%.

judged complete when no precipitate of $BaSO_4$ was observed upon addition of an aqueous solution $BaCl_2$. The remaining water was then removed via freeze-drying. The final product was a dark brown powder, and was designated as GOX1. The GOX1 underwent the same exact procedure as outlined above, and the resulting product was denoted as GOX2.

### *4.2. Synthesis of nylon-6/graphite, and nylon-6/graphite oxide thin films*

Nylon-6 (100 mg) was transferred to a 125 mL round bottom flask. 2,2,2-trifluoroethanol (5 mL) was added to the round bottom flask to dissolve the polymer. The dissolution was assisted by magnetically stirring the solution while refluxing. Graphite oxide, GOX2 (1 mg) was transferred to a 25 mL Erlenmeyer flask. 2,2,2-trifluoroethanol was then added to disperse the graphite oxide. This was followed by 20 min of ultrasonication to fully disperse the graphite oxide. The graphite oxide suspension was transferred to the hot nylon-6 solution. The reaction mixture was then refluxed for several hours.

The graphite oxide was allowed to undergo *in situ* reduction through the addition of hydrazine to the reaction medium. This was associated with a change in the color of the reaction medium from brown to black. The reaction mixture was allowed to reflux for several hours in order to allow reduction of the GOX2. The hot reaction mixture was then cast on a heated glass plate. This resulted in the formation of a thin polymeric film, with the amount of graphite present at 1 wt.%. The film was readily peeled off from the glass substrate. The procedure as described above was repeated in order to prepare a series of films with varying graphite composition (5, 10, 15, and 20 wt.%). Thin films containing varying amounts of graphite oxide, GOX2 (1, 5, 10, 15, and 20 wt.%) were also prepared as described above, with the only difference that no hydrazine was added to the reaction mixtures.

## 5. Results and discussion

Pristine graphite showed an intense peak near 27° in its X-ray diffractogram (Fig. 1A). This angle corresponds to an interlayer spacing of 3.35 Å which is expected for graphite. After undergoing oxidation, the diffraction peak shifts to a lower angle (Fig. 1B) which corresponds to an interlayer spacing value of 7.89 Å. This interspacing value is in good agreement with previously reported values [16].

The graphite oxide (GOX1) was then subjected to a second oxidation using the Hummers' method. It was visually observed that the second oxidation produces a material (GOX2) which is lighter brown in color, and with a finer particle size. Powder X-ray diffraction (Fig. 1C) showed that GOX2 is amorphous compared to GOX1. The broadening of the low angle peak can be interpretated as an increase in the number of functional groups in the material. This is further supported by the GOX2s superior dispersion in polar solvents, and thus GOX2 was used in the preparation of the composite films.

Powder X-ray diffraction of the resulting hybrids (nylon-6/graphite and nylon-6/graphite oxide) resembles that of the pure polymer. This is understandable because of the greater proportion of the polymer in the hybrids. As an illustration the powder pattern of nylon-6/graphite 15% is presented in Fig. 1D. For comparison, the powder pattern of pure nylon-6 is depicted in Fig. 1E.

The activation energy ($E_a$) for the decomposition of the various nylon-6 composites was determined following the Ozawa's method [17]. The thermograms of these composites were collected at varying heating rates. As an example, the compilation of thermograms at different heating rates for nylon-6/10% graphite is illustrated in Fig. 2. Fig. 3 depicts TGA spectra at 10 °C/min of nylon-6 mixed with graphite at 1, 10 and 20 wt.% (Table 2).

The data in Fig. 2 were used to generate complimentary plots of conversion ($\alpha$). Conversion ($\alpha$) is the ratio of the actual weight loss

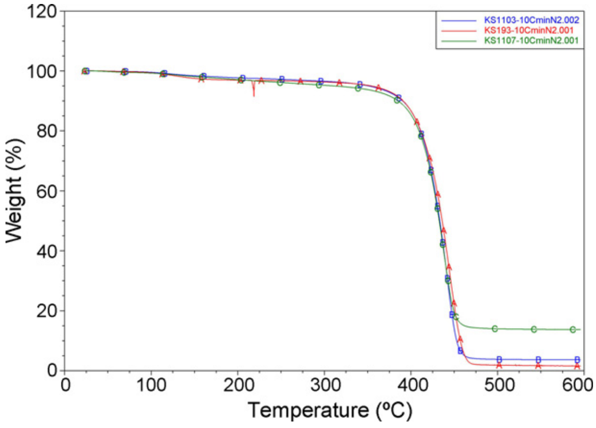

**Fig. 3.** TGA spectra at 10 °C/min: (A) nylon-6/graphite 1%, (B) nylon-6/graphite 10%, and (C) nylon-6/graphite 20%.

**Table 1**
Activation energy of decomposition for nylon-6/graphite and nylon-6 graphite oxide composites.

| Wt.% of filler | $E_a$ with graphite filler (kJ/mol) | $E_a$ with graphite oxide filler (kJ/mol) |
|---|---|---|
| 1 | 187.3 | 168.9 |
| 5 | 184.6 | 191.1 |
| 10 | 181.7 | 177.9 |
| 15 | 195.4 | 182.2 |
| 20 | 184.2 | 169.4 |

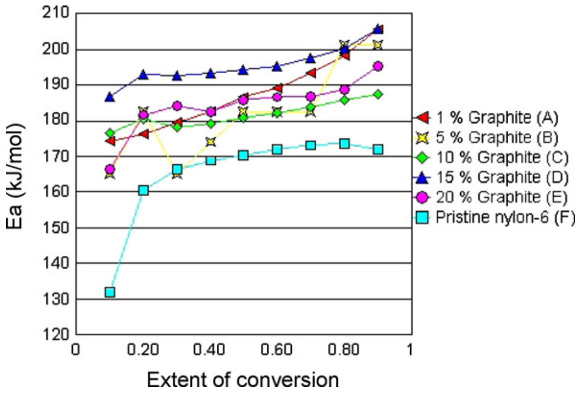

**Fig. 4.** Activation energy ($E_a$) versus conversion plots: (A) nylon-6/graphite 1%, (B) nylon-6/graphite 5%, (C) nylon-6/graphite 10%, (D) nylon-6/graphite 15%, (E) nylon-6/graphite 20%, and (F) pristine nylon-6.

to the total weight loss. Mathematically conversion is expressed as

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \tag{1}$$

where $m_0$ is defined as the initial weight before any decomposition of the composite, and $m_\infty$ as the final weight remaining at the end of the decomposition process. The $m$ term represents the actual weight at any temperature. Using Eq. (1) and the data from the thermal decomposition curves, plots of conversion against temperatures was generated.

From the conversion curves, an Ozawa plot for each of the samples was constructed. This is accomplished by plotting the log of the heating rate ($\beta$) against the inverse of temperature in K. This was performed for nine selected points of conversion. The results were nine lines with similar slopes. The Ozawa plot was then used to calculate the activation energy for the decomposition of the composite, by making use of the relationship [17]

$$E_a = -\text{slope} \times \left(\frac{R}{0.457}\right) \tag{2}$$

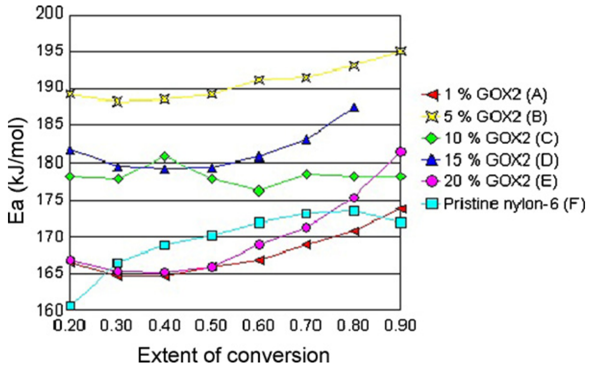

**Fig. 5.** Activation energy ($E_a$) versus conversion plots: (A) nylon-6/graphite oxide 1%, (B) nylon-6/graphite oxide 5%, (C) nylon-6/graphite oxide 10%, (D) nylon-6/graphite oxide 15%, (E) nylon-6/graphite oxide 20%, and (F) pristine nylon-6.

**Table 2**
Onset of decomposition temperatures from TGA.

| Wt.% filler | Onset temperature of decomposition at 10 °C/min with graphite as filler (°C) | Onset temperature of decomposition at 10 °C/min with graphite oxide as filler (°C) |
|---|---|---|
| 1 | 414 | 410 |
| 5 | 400 | 419 |
| 10 | 414 | 422 |
| 15 | 414 | 415 |
| 20 | 411 | 415 |

Pristine nylon-6 onset of decomposition: 398 °C.

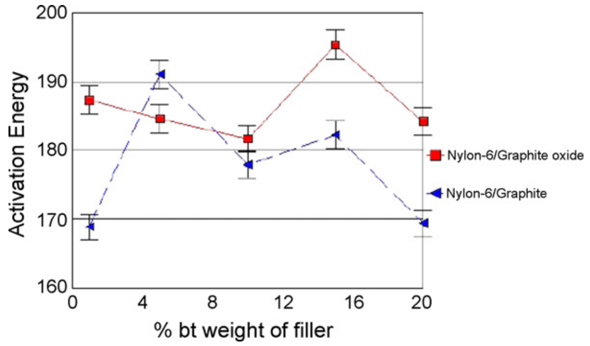

**Fig. 6.** Plot of activation energy versus wt.% of filler material.

where $E_a$ is the activation energy and $R$ the molar gas constant. The slope of each line in the Ozawa plot was determined by performing linear regression.

The Ozawa plots were used to calculate the activation energy associated with each line in the Ozawa plot. The activation energies were then averaged to obtain a more accurate value. This procedure was used to calculate the activation energy for the decomposition of all samples prepared, and the data are summarized in Table 1.

The activation energy for the decomposition of pure nylon-6 was found to be 165.4 kJ/mol. The experimental data in Table 1 show that both filling materials considerably enhance the activation energy for the decomposition of nylon-6. Graphs of activation energy versus conversion plots for all composites, including virgin nylon-6 is shown in Figs. 4 and 5. Graphite containing composites showed maximum enhancement in activation energy when composed of 15 wt.% graphite. The maximum enhancement in graphite oxide containing composites was observed at 5 wt.%. Graphite oxide composites also showed a second enhancement in activation energy at 15 wt.% which overlaps with data from the graphite composites. The effect can be illustrated by plotting activation energy versus the percentage of filler by weight (see Fig. 6). The maximum enhancement in activation energy was slightly higher for the graphite composites, and this may be attributed to the greater ability for graphite to char as the nylon-6 decomposes. The formation of char may form a protective barrier which prevents further decomposition of the polymer [8,9]. However, other mechanisms as described in reference 18 cannot be ruled out [18].

## 6. Conclusions

We have shown that both graphite and graphite oxide fillers significantly enhance the activation energy of decomposition of the nylon-6 host matrix. The activation energy for the decomposition of the pure polymer was found to be 165.4 kJ/mol. The presence of graphite at 15 wt.% resulted in the greatest enhancement in the activation energy of the polymer matrix, with a value of 195.4 kJ/mol. On the other hand, for the graphite oxide/nylon-6 composite series, the maximum enhancement in the activation energy of the polymer host was observed at 5 wt.% of the graphite oxide. The ability of graphite to slightly outperform graphite oxide as a filler material may be attributed to the formation of char during the decomposition phase of the nylon-6.

## Acknowledgments

The authors would like to thank the Natural Sciences and Engineering Research Council of Canada (NSERC), Canada Foundation for Innovation (CFI), Atlantic Innovation Fund of Canada (AIF), Materials Technology Network for Atlantic Canada (MatNet), and UPEI for financial support.

## References

[1] S.S. Ray, M. Okamoto, Prog. Polym. Sci. 28 (2003) 1539–1641.
[2] F. Hussain, M. Hojjati, M. Okamoto, R.E. Gorga, J. Compos. Mater. 40 (2006) 1511–1575.
[3] J. Golebiewski, A. Rozanski, J. Dzwonkowski, A. Galeski, Eur. Polym. J 44 (2008) 270–286.
[4] A. Okada, M. Kawasumi, A. Usuki, Y. Kojima, T. Kuraughi, O. Kamigaito, Mater. Res. Soc. Symp. Proc. 171 (1990) 45–50.
[5] L. Lu, H. Sun, F. Peng, Z. Jiang, J. Membr. Sci. 281 (2006) 245–252.
[6] M. Yoshikawa, H. Shimada, K. Tsubouchi, Y. Kondo, J. Membr. Sci. 177 (2000) 49–53.
[7] C.E. Powell, G.W. Beal, Curr. Opin. Solid-State Mater. Sci. 10 (2006) 73–80.
[8] S. Bourbigot, J.W. Gilman, C.A. Wilkie, Polym. Degrad. Stab. 84 (2004) 483–492.
[9] F. Gong, M. Feng, C. Zhao, S. Zhang, M. Yang, Polym. Degrad. Stab. 84 (2004) 289–294.
[10] R. Bissessur, S.F. Scully, Solid State Ionics 178 (2007) 877–882.
[11] S. Stankovich, D.A. Dikin, R.D. Piner, K.A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S.T. Nyguyen, R.S. Ruoff, Carbon 45 (2007) 1558–1565.
[12] N.N. Bhiwankar, R.A. Weiss, Polymer 47 (2006) 6684–6691.
[13] G.M. Russo, V. Nicolais, L.D. Maio, S. Montesano, L. Incarnato, Polym. Degrad. Stab. 92 (2007) 1925–1933.
[14] W.-J. Lee, S.-E. Lee, C.-G. Kim, Compos. Struct. 76 (2006) 406–410.
[15] W.S. Hummers Jr., R.E. Offeman, J. Am. Chem. Soc. (1958) 1339.
[16] P. Liu, K. Gong, P. Xiao, M. Xiao, J. Mater. Chem. 10 (2000) 933–935.
[17] T. Ozawa, J. Therm. Anal. 2 (1970) 301–324.
[18] K. Chen, C.A. Wilkie, S. Vyazovkin, J. Phys. Chem. B 111 (2007) 12685–12692.