Thermal stability of some self-assembling hydrogen-bonded polymers and related model complexes

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ABSTRACT

The thermal stability of polymers is of fundamental importance both in processing and in many applications (e.g.: injection moulding, hot melts). As part of an investigation to determine the suitability of supramolecular polymers for novel applications in Materials Science, the thermal behaviour of two model compounds representing the principal classes of supramolecular polymer has been studied in some detail. *p*-Methoxybenzoic acid was complexed with 1,2-di(4-pyridyl)ethylene in 2:1 ratio as a model compound representing liquid-crystal association chain supramolecular polymers. It is proposed that the model compound degrades as a single species obeying first-order kinetics; the activation energy (E_{act}) of the degradation process was calculated to be 127 kJ/mol. A model ureidopyrimidinone dimer degraded in two steps, also following first order kinetics, with E_{act} = 71.5 kJ/mol. The dimer was unaffected by annealing, suggesting that related polymers may be used at elevated temperatures. Polymer analogues of both model compounds were synthesised and their thermal behaviour was found to parallel that of the models. In light of these results, the implications for processing both supramolecular polymers are also considered.

KEYWORDS

Liquid-crystal association chain polymers, Ureidopyrimidinone polymers, Thermal stability, Degradation

INTRODUCTION

Supramolecular Polymer Science has advanced to the stage where a variety of systems have been reported whose chemistry is well understood.[1-3] We are currently studying the principal classes of supramolecular system to establish their suitability for novel applications in Materials Science. Given the fundamental importance of thermal stability

both in processing and in many applications (e.g.: injection moulding, hot melts) it was considered worthwhile to begin by examining the thermal behaviour of appropriate model compounds in some detail. Two systems were selected for initial study: liquid crystalline complexes of benzoic acid derivatives with dipyridyls and ureidopyrimidinone assemblies, linear supramolecular polymers that display novel temperature-dependent rheological behaviour.

Benzoic acid-dipyridyl model complexes are representative of a large class of liquid-crystal association chain polymers supramolecular polymers. Association of these functions has been used to form a wide range of supramolecular assemblies: main- and side- chain liquid crystals, grafting side groups onto a conventional polymer, and network structures.[4, 5]

More recently, ureidopyrimidinone systems have been developed with the aim of promoting self-assembly solely through hydrogen bonding. It has been speculated that this feature may give rise to unique properties: for example, Sijbesma and Meijer[6] claimed that these materials should exhibit the same flow behaviour as small molecules at elevated temperatures, yet form rugged networks upon cooling.

EXPERIMENTAL

Synthesis

The model 2:1 complex **1** was prepared by recrystallising *p*-methoxybenzoic acid and 1,2-di(4-pyridyl)ethylene from freshly-distilled methanol (1 g acid/1.669 g 1,2-di(4-pyridyl)ethylene/25 ml methanol) Needle-like caramel-coloured crystals were recovered in 66 % yield. Peaks at 2500 and 1900 cm^{-1} (double-minimum type hydrogen bonds) in the product's infrared spectrum replaced the broad 3500-3000 cm^{-1} band (-OH) of *p*-methoxybenzoic acid, confirming that the complex formed as expected.[7] Tetraethyleneglycoxy bis(4-benzoic acid) - 1,2-di(4-pyridyl)ethylene 1:1 complex **2** was prepared according to published procedures.[8]

N,N-1,6-hexanediyl(2-ureido-6-methyl-4-pyrimidone) **3** was synthesised following the general procedure outlined by Sijbesma and co-workers.[6] 2.875 g (23 mmol) 6-methylisocytosine was added to a 500 ml three-necked flask, then suspended in 250 ml dry pyridine and heated with mechanical stirring. 1.83 ml (11 mmol) 1,6-hexane diisocyanate was added dropwise by syringe and the whole refluxed for 4 hours. Aliquots were drawn from the

reaction mixture at regular intervals and their infrared spectra recorded to ensure complete reaction of the starting materials. After cooling to room temperature, the reaction mixture was quenched into n-hexane (500ml). The resulting precipitate was filtered, washed with three 100 ml portions of n-hexane and dried overnight in a vacuum oven. Recrystallisation from hot 5:2 chloroform/ethanol gave the required product in 88 % yield. Comparing the infrared spectrum of the final product with those of its dimer analogue **4** and previously reported ureidopyrimidinones[9] confirmed that the synthesis was successful. 2-Butylureido-6-methyl-4-pyrimidinone **4** was synthesised as reported by Beijer and co-workers.[6, 9] All other reagents were of analytical grade, purchased from Merck or Sigma-Aldrich and used as received. Pyridine was dried sequentially over 10 % w/v 4 Å molecular sieve; all other solvents were dried sequentially over 5 % w/v 3 Å sieves.

Spectroscopy

Infrared spectra were recorded as KBr discs (1 % sample w/w) on a Perkin Elmer Spectrum 2000 FTIR spectrophotometer. The range 4000-400 cm^{-1} was scanned 16 times, averaged and normalised using Perkin Elmer's Spectrum v1.30 software to give the spectra shown.

Thermal Analysis

Differential Scanning Calorimetry (DSC) experiments were conducted using a Perkin Elmer DSC-6 at heating rates of 10 ºC/min. A TA Instruments model 951 thermobalance was used for thermogravimetric analysis (TGA), at heating rates of 5 ºC/min. The sample chambers were purged with flowing oxygen-free nitrogen during all thermal analyses. Degradation mechanisms were determined by repeated the TGA experiments, recovering samples at each stage identified. The samples' infrared spectra were recorded for comparison with the starting material. Samples for hot-stage microscopy were prepared by depositing a 0.1M solution of **3** in dry chloroform (4.1845 g / 100 ml) onto glass slides. Evaporating the chloroform slowly allowed the bifunctional urediopyrimidinones to self-assemble into a thin film. These samples were then examined under an Olympus BX60 microscope fitted with a Reichert stage capable of heating to 300ºC.

Degradation rates were determined by equilibrating the thermobalance at a range of temperatures between 140 and 240 ºC, then holding samples of the 2:1 complex isothermally until they reached the limit of the TGA's sensitivity.

The activation energy and temperature dependence were obtained by calculating the rate constants and fitting them to the Arrhenius equation, $\ln k = \ln A - E_{act} / RT$.

<u>Annealing Study</u>

0.8 g samples of **4** were placed in a Lenton furnace at 100 ºC for 24 hours, then allowed cool to room temperature. Samples of annealed dimer and control (untreated dimer) alike were ground to a powder and pressed into discs using ethyl cellulose as filler. X-Ray powder diffractograms (XRD) were recorded on a Phillips Xpert diffractometer (Cu Kα radiation, spinning sample stage, PC-APD v4.0b software). The 2θ range 5 – 50 º was scanned (0.040 º step size, 1 second/step) at ambient temperature for both the annealed and control samples.

RESULTS AND DISCUSSION

<u>Acid-Dipyridyl Complexes</u>

Table 1 lists the model complex's thermal events, which fell midway between those of its components, as expected. DSC (Figure 2) showed that **1** underwent a sharp melting transition at 171 ºC. In TGA experiments, **1** underwent thermal degradation in a single event between 150 and 250 ºC, losing 98.5 % of the initial sample mass (Figure 3). The infrared spectra of samples recovered at 160, 180 and 200 ºC during the degradation process agreed well with that of the complex as synthesised (Figure 4), suggesting that the complex degrades as a single species. The model complex's polymer analogue, **2**, showed comparable behaviour; it melted at 178 ºC and began to degrade at 163 ºC, losing 72 % of the initial sample mass by 450 ºC.

Table 2 shows the isothermal hold data, which in every case was found to fit a first-order rate law with correlation factors $\geq$ 96 %. For example, 9.29 mg of dimer was held at 429 K for 120 minutes, after which 3.64 mg of sample remained. A straight-line plot of ln (mass/initial mass) = -kt was obtained by linear regression with a correlation factor of 99.7 %, giving a rate constant, $k = 1 \times 10^{-4}$ s^{-1}. At this temperature, the half-life ($t\frac{1}{2} = \ln2/k$) was found to be 6900 seconds. An Arrhenius plot (Figure 5) was prepared from these k values, at 99 % correlation and the activation energy was calculated from the slope (E_{act} / R) as 123 kJ/mol.

Ureidopyrimidinones

In a previous study, dimeric 2-Butylureido-6-methyl-4-pyrimidinone **4** was chosen as a model compound in order to study the thermal stability of ureidopyrimidinone supramolecular polymers.[10] The dimer underwent thermal degradation once heated to its melting point of 225 ºC. The kinetics of the degradation process were determined and a degradation mechanism proposed whereby the dimer's butane-1-isocyanate 'tail' cleaves first, followed by the isocytosine 'head' breaking down between 244 and 299 ºC. Reaction rates ranged from 1.2×10^{-3} to 6.2×10^{-3} s^{-1} and the activation energy was calculated to be 71.5 kJ/mol.

The DSC trace in Figure 6 shows the polymer's melting transition at 234 ºC, preceded by rearrangement of the polymer's crystalline structure as indicated by the shoulder at 216 ºC. To verify this, a film of **3** was cast from chloroform solution and examined under a hot stage microscope. Above 180 ºC, its structure became more ordered. These ordered domains melted in turn, the last at 235 ºC, leaving an oily brown droplet. TGA of **3** (Figure 7) showed that 68 % of the ureidopyrimidone polymer's mass was lost between 216 ºC and 420 ºC, and 17 % between 216 ºC and 475 ºC, leaving a residue of 15 % of the original sample. As the hexamethylene spacer and isocytosine 'heads' account for 40.2 % and 29.9 % of the polymer's molecular weight respectively, these steps correspond to the loss of the spacer and one head, followed by loss of the second head. Isocytosine rings were identified as the primary species present in the infrared spectrum of a sample recovered at 290 ºC. Taken together, this suggests that the polymer degrades following a mechanism which parallel that of the dimer. First, the urea linkage within the spacer cleaves, causing it to pyrolize, then the isocytosine rings break down, leaving a carbonaceous char.

Another potential obstacle to using ureidopyrimidinone polymers at elevated temperatures is that ureidopyrimidinones are known to undergo keto-enol tautomerism.[9] Figure 8 shows the X-Ray diffractograms of annealed **4** and a control sample, which agreed closely. As the crystal structure of the ureidopyrimidinone hydrogen-bonding function was not affected adversely by annealing, it is reasonable to expect that the polymer's material properties should not be affected either.

CONCLUSION

Both model compound studies show that the thermal behaviour of acid-dipyridyl and ureidopyrimidinone supramolecular polymers is closer to that of low-molecular weight species than conventional polymers: their melting transitions, in particular, are remarkably sharp. A degradation mechanism is proposed for acid-dipyridyl assemblies and the kinetics of this process have been elucidated. While the activation energies for thermal degradation of both model compounds are lower than those of typical conventional polymers, they remain completely stable to temperatures exceeding those of the common polymers. However, once thermal degradation begins, it proceeds rapidly in both model compounds.

The thermal behaviour of the acid-dipyridyl and ureidopyrimidinone supramolecular polymers is in keeping with that of the model compounds. Although neither may be safely heated above their melting points during processing or in service, this need not restrict their use unduly. Rather, successful application of supramolecular polymers will most likely follow from investigating alternative techniques such as processing in solution or in-situ assembly.

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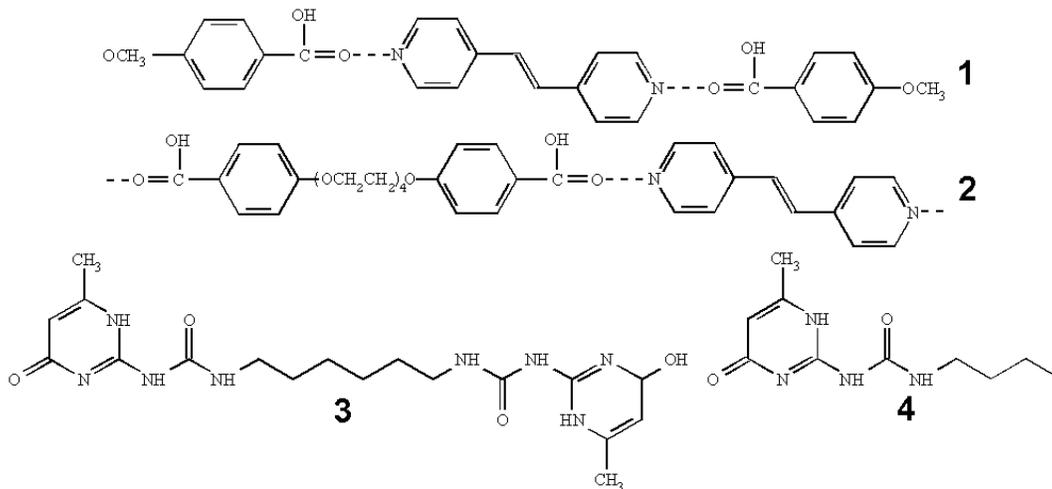
FIGURES AND TABLES

Figure 1: Structures of *p*-Methoxybenzoic acid-1,2-Di(4-pyridyl)ethylene 2:1 complex (1), Tetraethyleneglycoxy bis(4-benzoic acid)-1,2-di(4-pyridyl)ethylene 1:1 complex (2), *N,N*-1,6-hexanediyl(2-ureido-6-methyl-4-pyrimidone (3) and 2-Butylureido-6-methyl-4-pyrimidinone (4)
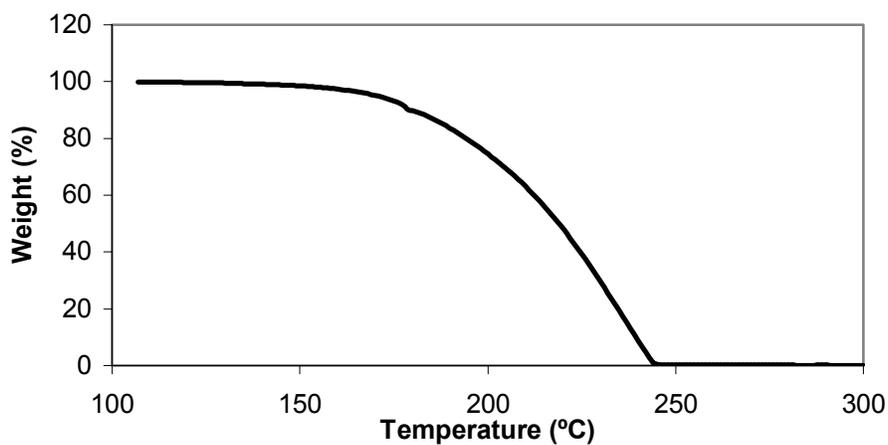
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Figure 3: TGA trace of model complex **1**

Figure 4: Infrared spectra of **1** as synthesised (A), after heating to 160 ℃ (B), 180 ℃ (C) and 200 ℃ (D)

Figure 5: Arrhenius plot for model complex **1**

Figure 6: DSC trace of *N,N*-1,6-hexanediyl(2-ureido-6-methyl-4-pyrimidone **3**

Figure 7: TGA trace of *N,N*-1,6-hexanediyl(2-ureido-6-methyl-4-pyrimidone **3**

Figure 8: XRD of control (top) and annealed (bottom) ureidopyrimidinone dimer **4**

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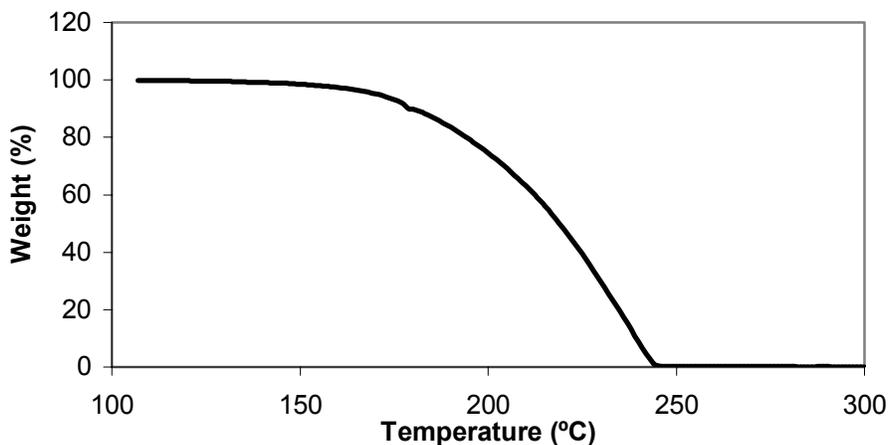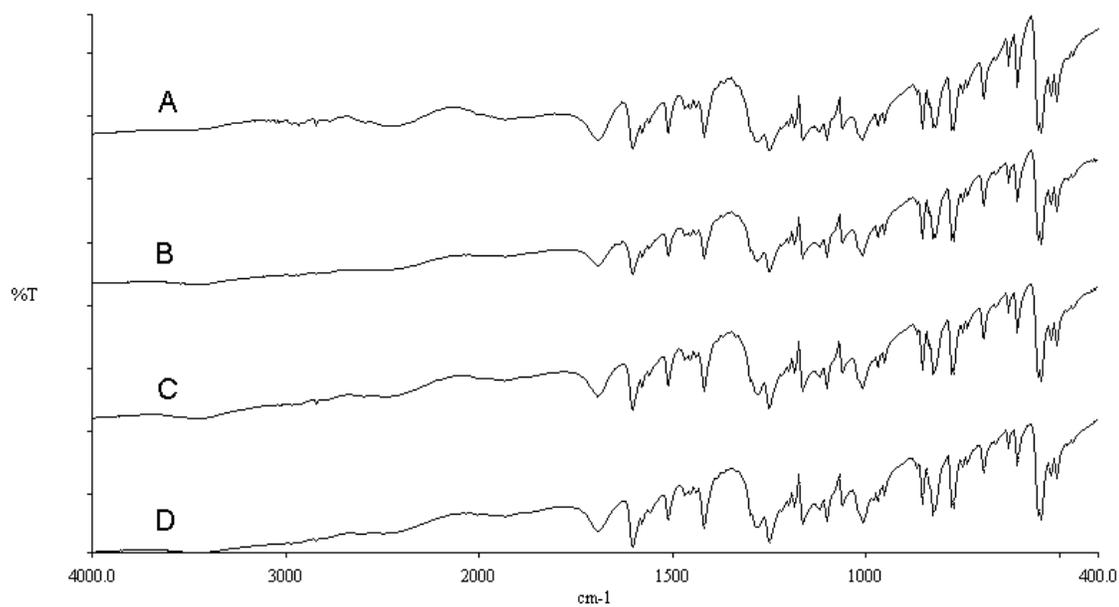**Figure 2:** DSC trace of model complex **1**

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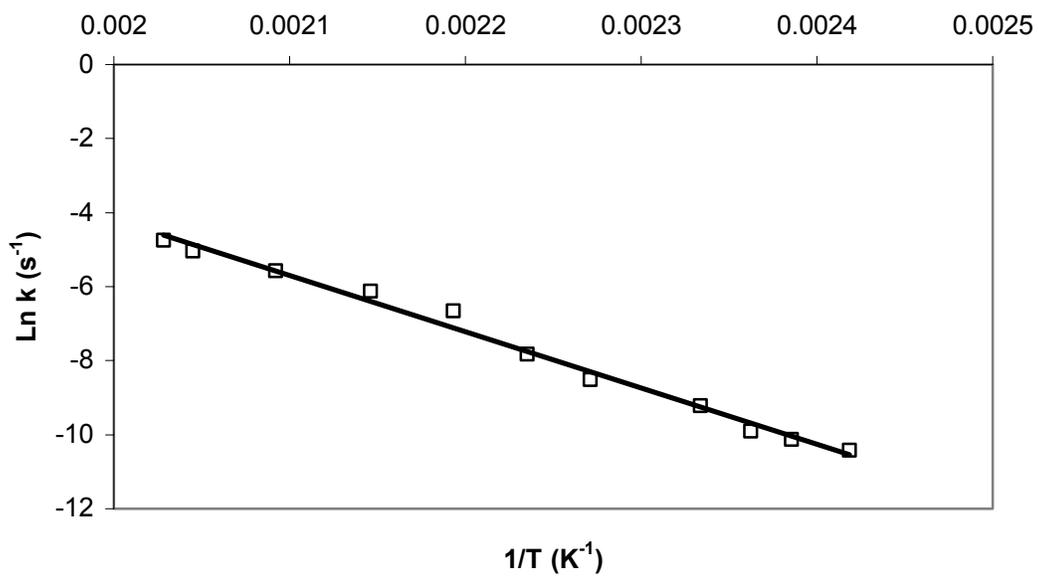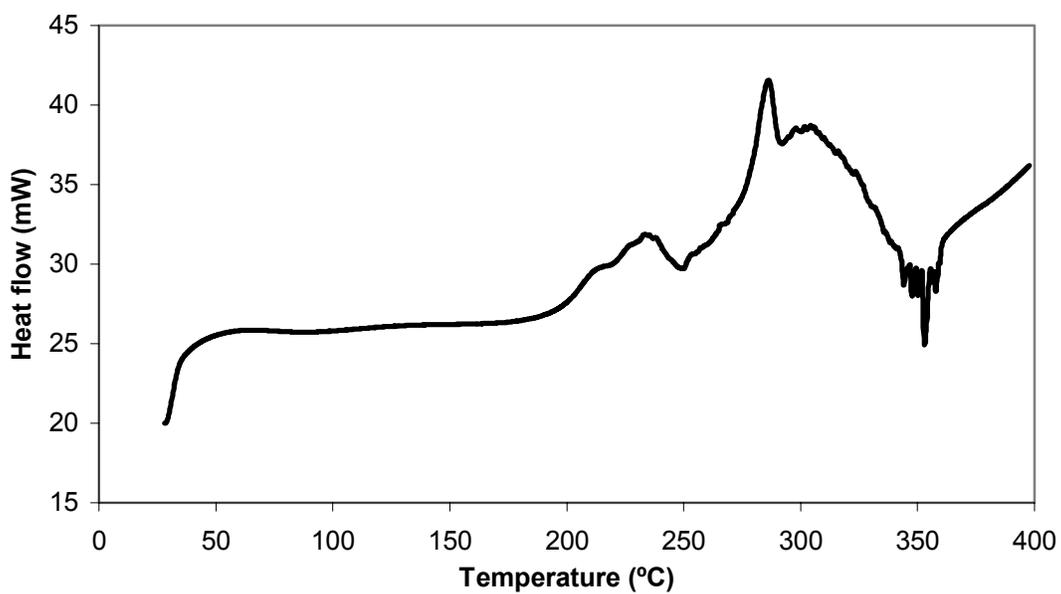

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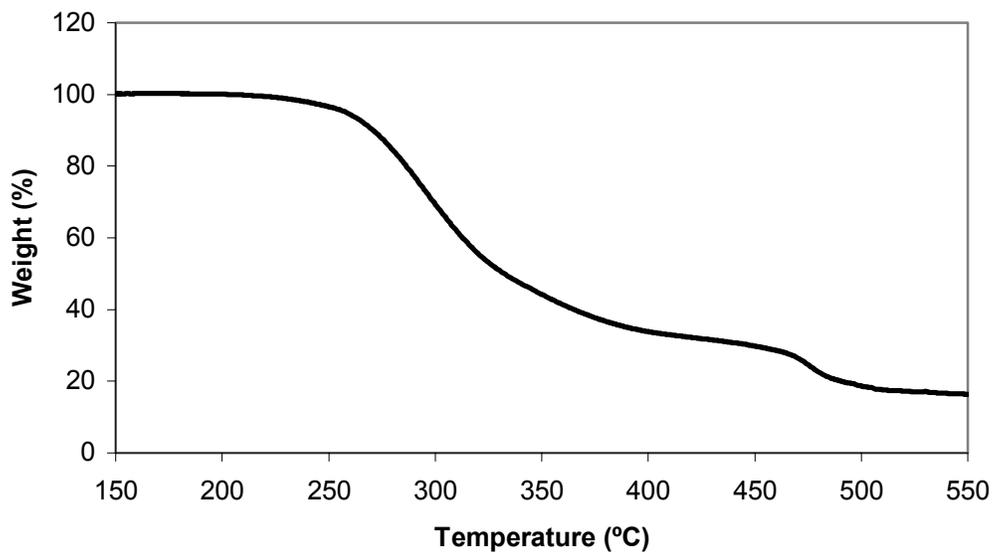

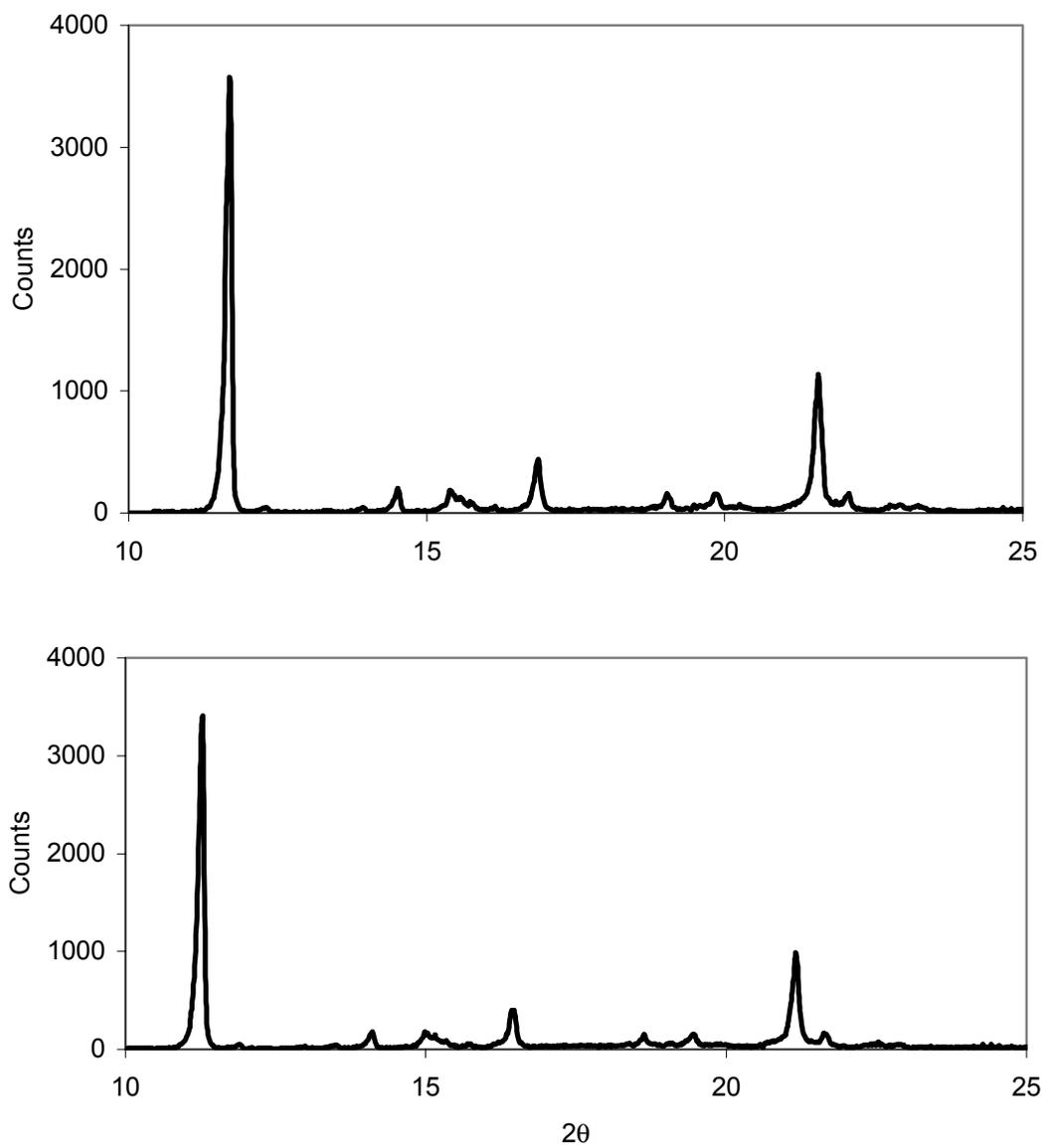**Figure 7:** TGA trace of *N,N*-1,6-hexanediyl(2-ureido-6-methyl-4-pyrimidone **3**

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	Peak Melting Temperature (ºC)	Weight Loss by TGA (%)	Temperature Range (ºC)
p-Methoxybenzoic acid	182-185	98	133 – 244
1,2-Di(4-pyridyl)ethylene	148-152	99	154 – 279
Tetraethyleneglycoxy bis(4-benzoic acid)	187	71	235 - 460
Model Complex **1**	171	98.5	150 – 250
Polymer Complex **2**	178	72	163 - 450

Table 1: Themal events of complexes **1** and **2** and their components

Hold Temperature (ºC/K)	Rate Constant, k (Ms^{-1})	Half Life, t½ (s)
141 / 414	3 x 10^{-5}	2.3 x 10^4
146 / 419	4 x 10^{-5}	1.7 x 10^4
150 / 423	5 x 10^{-5}	1.4 x 10^4
156 / 429	1 x 10^{-4}	6.9 x 10^3
167 / 440	2 x 10^{-4}	3.5 x 10^3
174 / 447	4 x 10^{-4}	1.7 x 10^3
183 / 456	1.3 x 10^{-3}	5.3 x 10^2
193 / 466	2.2 x 10^{-3}	3.1 x 10^2
205 / 478	3.8 x 10^{-3}	1.8 x 10^2
216 / 489	6.5 x 10^{-3}	1.0 x 10^2
220 / 493	8.7 x 10^{-3}	7.9 x 10^1
241 / 514	2.3 x 10^{-2}	3.0 x 10^1

Table 2: Kinetic data for model complex **1**