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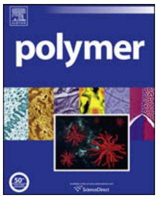

A kinetic model for thermal degradation in polymers with specific application to proteins

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ABSTRACT

We present a novel method for calculating degradation kinetics in polymers. Our calculations directly use the dissociation energy of chemical bonds in a polymer chain to predict weight loss as a function of time and temperature in an Arrhenius-type activation function. The novelty lies in quantifying the thermal energy term for skeletal bonds in the chain backbone in the activation function that initiates the bond fission process and that also quantifies the pre-exponential rate term. Our method allows prediction of TGA experiments with any time–temperature profile directly from the polymer structure using tools such as quantum mechanics simulations for bond dissociation energy. The model is demonstrated by application to a number of synthetic polymers with different temperature ramp rates. Application of the model to protein polymers shows significant differences from synthetic example polymers, since the synthetics use a single average dissociation energy, whereas proteins seem to degrade sequentially with the individual skeletal bond energies.

1. Introduction

The reduction in mechanical properties with time at elevated temperatures is a key limiting factor in the use of polymers in engineering applications. This reduction in properties is attributed to the breaking of chemical bonds in the polymer chain backbone macromolecules as the amplitude and energy of atomic vibrations increase with increasing temperature. Properties such as stiffness and strength are critically dependent upon the molecular weight of a polymer, and tend to reduce rapidly as the average molecular weight reduces.

As a general rule, polymer properties can degrade significantly without much observable change such as loss of mass. However, the exponential form of decomposition kinetics at high temperatures tends to give degradation over a limited temperature range, such that the use of quite coarse measures of thermal degradation is often adequate for practical purposes. Degradation can be monitored by changes in the polymer mass and analysed quantitatively by measuring enthalpy changes and detecting the reaction products [1–4]. The most important tool in the quantification of thermal degradation is thermogravimetric analysis (TGA), where the mass of a polymer sample is measured as a function of temperature and time, usually with a constant rate of temperature increase of about 5–20 degrees per minute under an inert atmosphere.

The likely upper temperature limits of polymer applicability can often be calculated quite effectively using simple empirical structure–property models (such as group additivity [5] or connectivity indices [6]) if group contribution values are not available for novel polymers. The increased tendency to char formation is shown by the high temperature polymers as a high residual weight at high temperatures and is associated, for example, with substituted rings that have very high dissociation energies due to resonance stabilisation [5] and groups that rebond after dissociation to form carbon network structures.

Due to its practical importance, a considerable body of experimental work has been published on the subject of thermal degradation and a number of useful reviews are listed here for reference [1–4]. Much of this body of work is focused on specific polymer types or problems, and the chemistry of degradation products and processes is well documented for many common polymers. Indeed, TGA measurement of thermal degradation in polymers is so routine that it is probably fair to say that experimental data is available for most polymer types, or can be obtained very quickly.

While the above discussion on thermal degradation sounds very positive, a number of important basic problems remain, which are

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the motivation for the work reported here. Most generally, we find that it is impossible to predict (rather than empirically fit) degradation kinetics for polymers directly from their chemical composition and structure in order to estimate useful lifetimes at elevated temperatures. More specifically, we find that predictions for the thermal degradation of proteins (i.e. an important class of natural polymers) are inconsistent with comparable synthetic polymers (such as polyamides). This is true for both the kinetics of the degradation process and the much higher levels of char than the zero predicted value for the constituent hydrocarbon and amide groups [5]. On a more applied level, proteins such as silks and soy protein isolate, SPI, are considered as environmentally friendly and sustainable polymers with potentially excellent mechanical properties [7]. However, they are exposed to high heat loading during their preparation and thermal stability could play a large part in their exploitation [8].

2. Experimental and modelling procedures

Thermal degradation was analysed in a Pyris 1 thermogravimetric analyser (Perkin Elmer Co., Ltd) under nitrogen (40 mL/min). Non-isothermal experiments were performed in the temperature range 20–700 °C. Unless specified, the heating rate was 10 degrees per minute, except for the soy protein isolate, where rates of 2, 5, 10, and 20 degrees per minute were used. Before heating, the soy protein isolate sample was held for 3.0 min at 20 °C to remove the surface water under the nitrogen atmosphere. All data reported in the text were the means and standard deviations for at least three separate runs.

Poly(ethylene) and poly(styrene) samples were prepared as standards from commercially available granules.

Soybean protein isolate powder was dissolved in 6 mol/L CH_5N_3HCl aqueous solution and then stirred at room temperature for 3 h while adding 0.01 mol/L 2-mercaptoethanol (2-ME). After dialysis against NaOH aqueous solution ($pH = 11.5$) for two days and deionized water for another day at room temperature, the solution was centrifuged at a speed of 9000 rpm for 10 min to obtain a clear supernatant. The concentration of soybean protein solution was about 1.6% (w/w) analysed by gravity method. To prepare films, the solution was first diluted to 0.8% (w/w). Then, 0.8 mL of this soybean protein solution was transferred to a 3×3 cm polystyrene weighing boat and allowed to dry overnight at ~ 25 °C and 50% relative humidity. All of the films were dried under vacuum for two days. The thickness of the soybean protein films was about 6 μm.

As a compromise between speed of calculation, accuracy, and establishing a 'fundamental' basis for the bond dissociation energy, we used semi-empirical quantum mechanics simulations based upon MOPAC with the PM3 UHF method, as implemented in the HYPERCHEM suite of modelling software [9]. Models were isolated chains in a minimum energy configuration and covalent bond dissociation energy was calculated by constructing a potential well and using the difference between the well minimum energy and the plateau value of energy at distances greater than the minimum energy bond length, usually at a length of about 0.35 nm.

3. Kinetics model

Conventional kinetic models are usually based upon an activated process with an Arrhenius form in terms of an activation energy, E_a, and a pre-exponential rate constant, A

$$\frac{d\alpha}{dt} = (1-\alpha)A\exp\left(-\frac{E_a}{RT}\right) \tag{1}$$

where α is the extent of the dissociation reaction, R is the gas constant, and T is temperature. Modelling usually reduces to finding the best combination of E_a and A values, often with multiple relaxation components, to fit experimental data [10,11].

Unfortunately, empirical values of E_a from experimental observations are not usually equivalent to the conventional bond dissociation energy and A has no direct relation to dynamic events at a molecular level [10,12]. However, direct relations between degradation rate and bond energy are reflected in the very simple empirical relation of van Krevelen for mainly aliphatic chains [5]

$$T_{1/2} = 1.6E_{dis} + 140 \tag{2}$$

where $T_{1/2}$, is defined as the isothermal temperature at which half the volatile polymer mass is lost in 30 min under vacuum and E_{dis} in kJ/mol is the dissociation energy of the *weakest* bond in the polymer chain. Interestingly, this in itself is inconsistent with the group contribution implication i.e. that average bond energy is the dominant factor in the overall degradation kinetics [5].

While accepting that the general mathematical form of the degradation kinetics equation (1) is a useful starting point, we suggest here that an inappropriate quantitative relation for the energy that drives the degradation process (RT in equation (1)) is the root cause of the difficulties in predicting degradation kinetics. Our proposal is that, by quantifying this causal energy term, the activation energy and rate parameter, A, can be predicted directly from the chemical and morphological structure of a polymer. Once the role of bond dissociation has been quantified at a structural level, we can then investigate why dissociation in apparently similar polymers might be different.

Taking equation (1) as our mathematical relation to describe degradation kinetics, the objective here is to replace the thermal energy term RT by a more appropriate relation that can be expressed in a straightforward way in terms of parameters derived from the chemical structure of a polymer. Wunderlich has established a large body of experimental data for thermal properties of polymers, from which parameters for a one-dimensional Debye model for the contribution of skeletal mode vibrations to heat capacity can be deduced [13,14]. These skeletal modes control the temperature dependence of mechanical properties in polymers via their effect on intermolecular bonding energy [15].

It is important to use the thermal energy per group of atoms in the chain backbone, rather than a simple Arrhenius term RT, since the bonds in question are part of the skeletal backbone of the polymer chains and their thermal energy is given by a one-dimensional Debye function with a reference temperature for skeletal mode vibrations, θ_1, and N degrees of freedom per characteristic structural group. A more complete discussion of this thermal energy function in terms of structure–property relations has been published elsewhere [15], but to a good first approximation of the computationally complex Debye functions, the thermal energy per group of atoms, H_T, is calculated using

$$H_T \approx NR\left(T - \frac{\theta_1}{6.7}\tan^{-1}\left(\frac{6.7T}{\theta_1}\right)\right) \approx NR(T - 0.22\theta_1) \quad \text{for } T > \theta_1 \tag{3}$$

where the simplified approximation is used at higher temperatures characteristic of polymer melting or degradation and $R \approx 8.3$ J/mol/K is the gas constant. For most aromatic polymers and a simple poly(ethylene) aliphatic chain in an all-*trans* conformation $\theta_1 \approx 550$ K, and for branched chains θ_1 is simply proportional to $1/\sqrt{M}$, where M is the molecular weight of the characteristic group of atoms in a chain.

The pre-exponential rate parameter A can be estimated as the skeletal mode vibrational frequency associated with the Debye temperature, and takes a value of

$$A = \frac{k}{h}\theta_1 = 2.3\times10^{10}\theta_1 \tag{4}$$

where k is Boltzmann's constant and h is Planck's constant and for a typical value of $\theta_1 = 550$ K, $A \approx 1.3\times10^{13}$ Hz. The logic of the identity is that the vibrating bonds are essentially sampled every cycle for their probability of breaking, which is quantified by the thermal energy, H_T, relative to the bond dissociation energy, E_d, which we assume can be predicted *ab initio* using quantum mechanics simulations of bond energy [16]. Thus, we can rewrite the kinetics equation (1) and integrate over time to give an expression for the weight fraction remaining after exposure to a given thermal history, $W(t)$ expressed as $H_T(t)$; for example, a linear temperature ramp.

$$W(t) = \exp\left(-2.3\times10^{10}\theta_1\cdot\int_0^t \exp\left(\frac{-E_d}{H_T(t)}\right)\mathrm{d}t\right) \tag{5}$$

Taking isothermal conditions and a time of 30 min for the loss of half the weight in a sample from the definition of $T_{1/2}$, equations (3) and (5) can be combined to give

$$T_{1/2} = 1.57E_d + 120 \tag{6}$$

which is very similar to the empirical equation (2) of van Krevelen, and gives a rough indication that the confusion between E_a and E_{dis} is resolved in the model.

The next problem is to determine if E_d is specific to each potentially broken chain bond as suggested by equation (2), or is it a cooperative average value, as suggested by group contribution methods. We evaluate this aspect by looking at practical examples, which also serve to validate the model and probe the problem of protein degradation.

4. Results

Experimental results for standard TGA analyses of poly(ethylene), PE, are shown in Fig. 1 for HDPE and LDPE samples run under nitrogen with a temperature ramp rate of 10 degrees per minute, such that $T(t) = 300 + 10t$, where t is in minutes. The accepted value of $T_{1/2}$ for poly(ethylene) is 680 K (407 °C) [5], which corresponds to the start of mass loss in the curves shown in Fig. 1. The maximum rate of mass loss usually occurs at about 50 degrees above $T_{1/2}$ under these conditions. Fig. 1 suggests that crystalline degradation occurs at a slightly higher temperature than in the amorphous form.

For the parameter, E_d, tables of bond dissociation energies are available for many organic molecules and polymers [5]. To emphasise the predictive nature of this model, we chose to calculate E_d by means of readily available semi-empirical quantum mechanics tools, as outlined in the procedures section. The calculated value of $E_d = 364$ kJ/mol for the–CH_2–CH_2– bond compares with a tabulated value of 345 kJ/mol [5]. The Debye temperature $\theta_1 = 550$ K and $N = 2$ for each main chain carbon atom for poly(ethylene) in equation (5) give a model relation, which is also plotted in Fig. 1

$$W = \exp\left(-1.3\times10^{13}\cdot\int_0^t \exp\left(\frac{-21{,}927}{T(t)-120}\right)\mathrm{d}t\right) \tag{7}$$

Experimental and model plots for PE in Fig. 1 are in reasonable agreement, since PE has only one characteristic skeletal bond. The next example is poly(styrene), PS, where the three key skeletal bonds are two directly in the chain backbone with $E_d = 334$ kJ/mol and the side chain CH_2–C_6H_5 bond with $E_d = 374$ kJ/mol as predicted values. The experimental plot in Fig. 1 for PS is modelled best by using an arithmetic average of these three values of E_d in equation (5) with parameter values of $\theta_1 = 285$ K and $N = 2$ for each bonded atom or group, also shown for comparison in Fig. 1. Calculations on the activation energy for poly(propylene) give an average $E_a = 352$ kJ/mol similar to PS, such that it is also predicted to degrade at about 50 degrees lower temperature than PE due to the change in bond energies around the branch point.

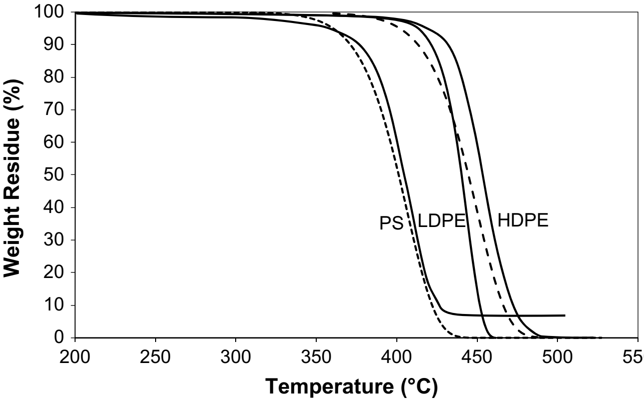

Fig. 1. Comparison of TGA experimental data (solid lines) and model predictions (dashed lines) for poly(ethylene) and poly(styrene).

The next step for the model is to look at the amide group contribution to E_d and the predictions for different thermal histories by looking at the degradation of polyamide 6, PA6. Experimental data for PA6 is taken from literature [17,18], and Fig. 2 shows TGA measurements under nitrogen at a rate of 10 degrees per minute. This data is best modelled again by an average value of $E_d = 342$ kJ/mol, which is composed of $4\times CH_2$–CH_2 each with 364 kJ/mol, CH_2–CO with 321 kJ/mol, N–CH_2 with 330 kJ/mol, and the lowest CO–N bond with 282 kJ/mol. Also shown in Fig. 2 are model plots with four different temperature ramp rates of 1, 5, 10, and 20 degrees per minute with $\theta_1 = 512$ K and $N = 2$ per atom group to demonstrate the ability of the model to predict kinetics in a realistic way, which agrees well with the observed rate dependence [18].

For reference, predicted and measured [19,20] TGA plots for Kevlar are shown in Fig. 2 at a temperature ramp rate of 10 degrees per minute to show how to include aromatic chain groups into the model. Again an average $E_d = 332$ kJ/mol is used, composed of Ph–CO = 348, CO–N = 276, and N–Ph = 371 kJ/mol. The structural parameters are $\theta_1 = 550$ K and $N = 1.5$. The value of N is an average

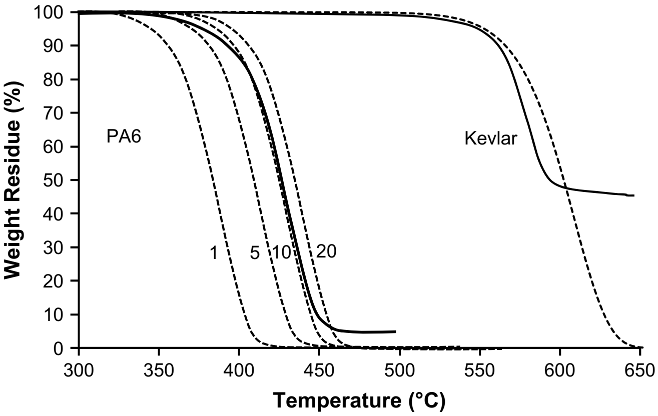

Fig. 2. Comparison of TGA experimental data at a heating rate of 10 degrees per minute (solid lines) and model predictions (dashed lines) for polyamide 6 [17,18] and Kevlar [19,20]. Model heating rates for PA6 as marked.

of $N = 2$ for the –CO– and –NH– groups as previous, but the two bonded phenyl carbons have only $N = 1$ due to normal mode restrictions imposed by the ring bonding. Thus, a lower average value of thermal energy via N increases the degradation temperature over an aliphatic PA6, in spite of a lower E_d value.

Fig. 3 shows experimental TGA plots at a temperature ramp rate of 10 degrees per minute for a number of different protein materials, taken from literature and measured in house as labelled. The most notable features of these protein plots compared with the PA6 plots in Fig. 2 are the onset of degradation at lower temperatures (ignoring the water release), the broader distribution of degradation temperatures, and the residual char of about 30–40% by weight.

For comparison, Fig. 3 also shows model predictions for a simple poly(glycine) protein using the same approach as that for PA6 in Fig. 2. The model parameters are $\theta_1 = 472$ K and $N = 2$ per chain atom, with an average dissociation energy $E_d = 313$ kJ/mol calculated from the three components: –CO–NH– = 285, –CH$_2$–CO– = 318, and –NH–CH$_2$– = 337 kJ/mol. The model assumes zero char residue using the group contribution values of zero for all the component groups [5].

The simplest model alternative to using an average value for E_d is to calculate the separate dissociation probabilities for each of the skeletal bonds as a function of temperature and time. As a first attempt, we assign equal weight to each of the three skeletal bonds. Clearly, this raises many issues about how the model parameters change after the first dissociation events develop, but it is an obvious alternative strategy to test here. The char residue is assumed in the first instance to be 30% by weight, and is discussed below. Fig. 4 compares such a model with a shaded envelope that encloses the experimental TGA data from Fig. 3. The model using separate dissociation values for E_d shows a good general agreement with the observed range of TGA data. In reality, dissociation energy and thermal energy have a distribution of values due to the distribution of chain conformers, such that the model curve would be expected broaden and lose the distinct bends due to the individual activation steps, but it is interesting here to show these individual processes and consider the broadening in future work.

Fig. 5 compares model predictions for a protein with specific experimental data for SPI at 4 different ramp rates of 2, 5, 10, and 20 degrees per minute. The predicted overall degradation profile and rate dependence are in excellent agreement with observation, given the assumed char residue. Note the SPI data is normalised to 100% weight at $T = 373$ K (100 °C).

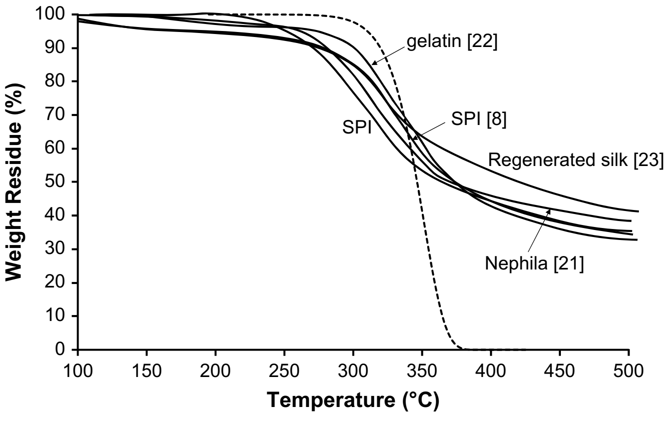

Fig. 3. Solid lines show TGA experimental plots for a number of proteins as marked to show a general range of observed properties [8,21–23]. Dashed line is model prediction using a single average value of E_a.

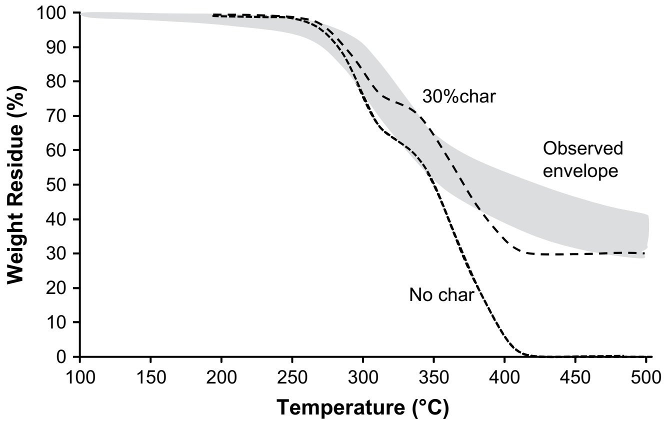

Fig. 4. Model predictions for TGA degradation of SPI with two values of char (dashed lines) compared with experimental data from Fig. 3 (shaded area).

5. Discussion

Since the subject of thermal stability in polymers is so full of discussions on the detailed degradation processes in specific polymers, we restrict ourselves here a specific case: why do (some) proteins behave in an unexpected way relative to apparently similar synthetic polymers such as polyamides?

Work on predictive structure–property relations in proteins such as silks led us to suggest that intermolecular interactions in proteins can be divided into ordered and disordered states, which correspond very roughly with crystal and amorphous states that have one or two hydrogen bonds per amide segment respectively [24]. The key point for many proteins is that the skeletal amide and hydrocarbon side chains tend to interact with their own kind, due to the great difference in their polarities. This means that adjacent macromolecular chains have strong hydrogen bonded morphologies, where many of the hydrogen bonds in the ordered states are stable at temperatures well above the degradation temperatures. This is not the case in polymers such as simple polyamides shown in Fig. 2, where the global glass transition and melting of the polymer occur well below the degradation temperature, thereby completely removing the specific hydrogen bond interactions.

We suggest that this strong hydrogen bonded segregated morphology has two consequences. First, that the skeletal bonds have strong individual identities as conformer states with a restricted range of bond energies, such that each bond responds

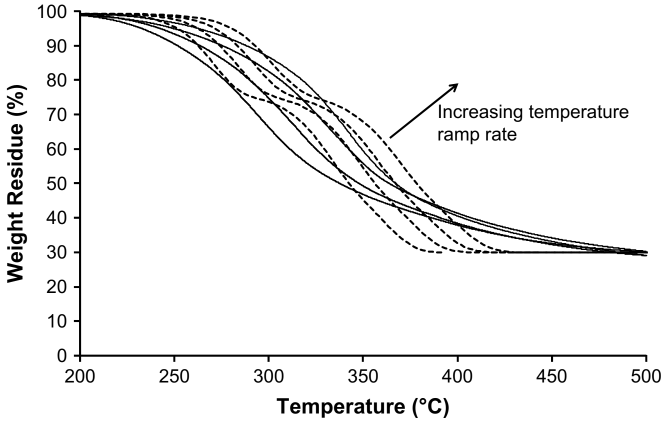

Fig. 5. Rate model SPI (dashed lines) compared with experimental observation (solid lines) at heating rates of 2, 5, 10, and 20 degrees per minute.

individually to the thermal energy of the skeletal bond vibrations, rather than having a shared identity with an average bond energy that is characteristic of a broad range of isomeric states. Second, that the strongly hydrogen bonded amide groups can reconfigure around dissociated bonds to form new branched network structures. According to the thermal energy model, these network structures have reduced thermal degrees of freedom, *N*, due to loss of normal mode vibrations, just like crosslinked thermoset resins that lose 3 degrees of freedom per branch site [25]. This means that the degradation temperature for the same bond dissociation energy in the residue is increased considerably to remain as a tar or char up to high degradation temperatures. In future work, we will explore these suggestions using molecular modelling. Given that many proteins that we considered in this thermal degradation study had intrinsic fractions of about 50% strongly bonded ordered states, the assumed char residue value of 30% used in the model application to proteins is a reasonable value to choose.

6. Conclusions

The prediction of degradation kinetics in a polymer is fraught with difficulties at a fundamental level [6], and the parameters used in activation functions to empirically extrapolate degradation at elevated temperatures bear little relation to properties such as bond strength and vibrational frequency. A method for calculating degradation kinetics is suggested here, which directly uses the dissociation energy of chemical bonds in a polymer chain to predict weight loss as a function of time and temperature in an Arrhenius-type activation function.

The novelty here is to quantify the thermal energy term for skeletal bonds in the chain backbone in the activation function that initiates the bond fission process, which also quantifies the pre-exponential rate term as a frequency in the one-dimensional Debye model for thermal energy. The method allows prediction of TGA experiments with any time–temperature profile directly from the polymer structure at a relatively fundamental level using tools such as quantum mechanics simulations for bond dissociation energy.

The model is demonstrated by application to a number of synthetic polymers with different temperature ramp rates. These examples show that the effective bond dissociation energy takes an average value of all the covalent bonds in the chain backbone, which is in general agreement with the averaging process in group contribution methods for degradation conditions. However, application of the model to proteins shows significant differences over the synthetic examples, since proteins seem to degrade sequentially with the individual skeletal bond energies, with the lowest energy –CO–NH– bond determining the lower temperature initiation point for degradation. We suggest that this difference is due to the strong segregation of the hydrogen bonded amide–amide interactions in proteins, which emphasizes the individual characteristic of each bond and also promote char formation.

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