Short Communication

Scission kinetic model for the prediction of polymer pyrolysis curves from chain structure

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Abstract

There is a significant interest in correlating polymer structure with thermal degradation behavior. Thus, polymer pyrolysis curves could be predicted from the chemical structure of the polymer. Recent proposals correlate the kinetic temperature function directly with the chemical structure of the polymer by means of the dissociation energy while assuming a semiempirical first order model for the reaction fraction function. However, first order model lacks physical meaning and it produces significant deviations of the predicted curves, mostly under isothermal conditions. Thus, in this work an upgrade of the method is proposed by using a new random scission kinetic model. The newly proposed kinetic equation has been checked by fitting the experimental data reported by different authors for the thermal pyrolysis of polystyrene. It has been demonstrated that it accounts for the experimental data of polymer degradation under different heating schedule with considerably higher precision than the previously assumed first order kinetics.

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1. Introduction

Predictions of polymer properties, such as thermal stability could be assessed from quantitative structure-property relationships. Van Krevelen [1] in a pioneering work, proposed the Additive Molar Thermal Decomposition Function, based on the assumption that the thermal decomposition of a polymer is determined by a sum of contributions made by the different groups in the molecule. Biceranto approach considered additive contributions of atoms and bonds, while the environment of each atom and bond is taken into account [2, 3]. Very recently, Porter et al proposed an interesting approach to predict the mass loss curve as a function of time (and temperature) by the use of two functions:[4] an energy function, directly related to the dissociation energy of the chain backbone, and other a reaction fraction, defined for the sake of simplicity, by a first order, F1, kinetic model. The use of F1 models for polymer degradation studies is widely extended in literature since pioneering works by Van Krevelen et al. [5], Reich [6, 7], Broido [8] and others used such model. The simplicity of F1 (and in general of "n order") model and the lack of alternative proposals would explain its extensive use, despite the importance of using proper models in kinetic studies. [9-14] In this communication, deviations in Porter et al prediction curves due to first order model assumption are discussed, while the use of a new model based on the polymeric chain scission and volatilization of the subunits is proposed. Prediction reliability of the method is tested with experimental curves under both linear heating and isothermal conditions.

2. Experimental

Atactic polystyrene (Goodfellow 261595) was used. Thermogravimetric experiments were performed in nitrogen flow (100mL min^{-1}) using small mass samples (~10 mg) under either linear heating or isothermal conditions using a Q5000 TGA (TA Instruments).

3. Results and discussion

For polymer pyrolysis, the general kinetic equation correlates reaction rate, $d\alpha/dt$, with temperature, T, and reaction fraction, α, by means of a function of temperature, $k(T)$, and a function of reaction fraction, $f(\alpha)$:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

Usually, the $k(T)$ is approached by an Arrhenius equation defined in terms of the apparent activation energy and the Arrhenius preexponential factor, while $f(\alpha)$ is the mathematical expression of an ideal kinetic model. Thus, $k(T)$ and $f(\alpha)$ are determined from the kinetic analysis of a series of experimental curves [15-19]. Once the temperature and reaction functions are determined, the thermal behavior could be modeled under any heating conditions. A different approach is that proposed by Porter that relates chemical structure with thermal behavior, in such a way that mass loss curves could be directly predicted from the knowledge of parameters such as dissociation energy [4]. In Porter's approach, $k(T)$ is defined in terms of the polymer chemical structure, by means of the following equation:

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$$k(T) = 2.3 \ 10^{10} \theta_1 e^{-\frac{E_d}{H_T}} \tag{2},$$

where θ_1 is the Debye reference temperature, E_d is the dissociation energy and H_T is the thermal energy per group of atoms. H_T, can be approximated by [4]

$$H_T \approx NR(T - 0.22\theta_1) \tag{3},$$

being N the number of degrees of freedom for characteristic structural group. Eq. (3) is valid for temperatures, T, higher than θ_1 [20, 21].

For the reaction fraction function, $f(\alpha)$, Porter's approach assumes a simple first order kinetic model.

$$f(\alpha) = (1 - \alpha) \tag{4}$$

From eqs (2), (3) and (4), the general kinetic equation (eq. (1)) can be written as follows:

$$\frac{d\alpha}{dt} = 2.3 \ 10^{10} \theta_1 e^{-\frac{E_d}{NR(T-0.22\theta_1)}} (1 - \alpha) \tag{5}$$

This equation is a general differential expression valid for any heating schedule. For different heating conditions, eq (5) can be integrated as follows [22]:

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)} = 2.3 \ 10^{10} \theta_1 \int_0^t e^{-\frac{E_d}{NR(T-0.22\theta_1)}} dt \tag{6},$$

The first order kinetic model in Porter's method is used as a *semiempirical* fitting function without any physical meaning. For its simplicity, this model is extensively used in polymer pyrolysis studies, but its application has been recently criticized as they provide significant deviations for experimental curves. Other physically sound approach is that based on the scission of the polymeric chain and volatilization of the subunits, such as Simha and Wall model that describes the reaction fraction in terms of the fraction of bonds broken, the initial degree of polymerization and the minimum length of the polymer that is not volatile [23]. This model is complex and require determining a number of parameters that are difficult to quantify experimentally. Therefore, its application to real systems is very scarce. Very recently, the model of Simha and Wall has been reformulated in terms of the reactions fraction, which could be determined from thermal analysis measurements [24, 25]. Thus, using the new functions, the reaction rate of the thermal degradation of polymers that go through a random scission mechanism could be directly related to the reacted fraction of the process.

For a polymer that degrades by cleavage of chemical bonds following first order kinetics, all breakable bonds within the polymer have the same probabilities to be broken [23]. Thus, the rate of bond breakage can be written as follows:

$$\frac{dx}{dt} = k_T(1 - x) \tag{6},$$

where x *is* the fraction of bonds broken and K_T the rate constant of bond breakage. Moreover, x and α are related by the following approximated expression:

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$$\alpha \approx 1 - (1-x)^{L-1}\left[1 + x(L-1)\right]$$ (7)

Being L the minimum length of not volatile polymer subunit. This equation (eq. (7)) relates α (as for example mass loss) with the fraction of broken bonds. Nevertheless, as x cannot be measured by conventional techniques, and L is very difficult to determine experimentally, the application of eq. (7) is limited. Nevertheless, by differentiating eq. (7), and incorporating eq. (6), the value of the conversion function $f(\alpha)$ can be determined [24, 25]:

$$f(\alpha) = L(L-1)x(1-x)^{L-1}$$ (10)

For L=2, a symbolic solution can be obtained:

$$f(\alpha) = 2\left(\alpha^{1/2} - \alpha\right)$$ (11)

For other values of L, the $f(\alpha)$ conversion functions can be easily determined numerically [24, 25]:

Porter et al approach for the kinetic analysis of polymer degradation can be easily upgraded by considering a random scission kinetic model, L2, as the one described above, which has a physical significance, instead of the empirical F1 model. Thus, the general differential kinetic equation will take the following form:

$$\frac{d\alpha}{dt} = 2.3 \; 10^{10} \theta_1 e^{-\frac{E_d}{H_T}} 2(\alpha^{1/2} - \alpha)$$ (12)

This equation, eq. (12), is a general expression that is valid for predicting the thermal behavior under any heating schedule. Moreover, the shapes of $f(\alpha)$ obtained for L in the range 2-8 are very similar[25] and, therefore, eq (12) could be consider as a general equation for any value of L.

Fig. 1 shows a comparison of the thermogravimetric experimental data (dots) for polystyrene (PS) at 10 K min^{-1}, as digitalized from Porter et al paper [4], and predictions using the same kinetic parameters as in Porter et al (E_d = 344 kJ mol^{-1}, θ_1= 285 K and N = 2) but assuming either F1 (dashed-line), as in Porter et al or the newly proposed L2 (solid-line) models. Whereas F1 provides a rough fitting of the experimental curve, L2 provides a much better fitting.

Fig. 2 shows three thermogravimetric curves corresponding to the thermal pyrolysis of polystyrene sample recorded at three heating rates, i.e. 1, 2 and 5 K min^{-1}. The comparison of the experimental curves (dots) and model predictions using the same kinetic parameters as in Fig. 1 and assuming F1 (dashed line) or L2 (solid line) kinetic models are also included in Fig. 2. For all three curves, as it happened with Porter et al experimental data shown above, the fitting is also much better for L2 than for F1.

It is well known that experimental thermogravimetric curves obtained under linear heating rate conditions present sigmoidal shapes independently of the kinetic parameters, including the kinetic model, that describe the process. Thus, it has been shown that a single curve obtained under linear heating rate conditions could be perfectly fitted by any of the kinetic models proposed in literature by properly selecting the other kinetic parameters, i.e. kinetic

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energy and preexponential parameter [26]. Nevertheless, curves obtained under other heating schedules, such as isothermal or sample-controlled conditions, present a shape that is characteristic of the kinetic model that describes the process [9, 27, 28]. Curves corresponding to the pyrolysis of PS under isothermal conditions at different temperatures, i.e. 325ºC and 330ºC, are included in Fig. 3. This figure (Fig. 3) also shows the curves simulated with the same values of E_d, θ_1 and N as those used in Figs. 1 and 2 but for F1 (dashed-line) and L2 (solid-line). It is even clearer that the L2 model provides a much better fitting of the experimental curves. Thus, pyrolysis curves under isothermal conditions for the PS present sigmoidal shape with a characteristic small induction period that is nicely fitted by the random scission model in the entire range, while the first order one shows quite a different shape and both experimental and simulated curves are far away. Thus, for the first order model at α=0.5, the deviations observed are larger than 80 and 110 minutes for the isothermal curves at 330 and 325ºC, respectively.

4. Conclusions

In conclusion, the novel method for predicting polymer pyrolysis curves under any heating schedule, recently proposed by Porter et al [4], has been modified by considering a kinetic model that describes the polymer chain breakage and evaporation of the subunits as a function of the reaction fraction. The proposed method is a simple approach that does not take into consideration all the complex processes that takes place during pyrolysis, but provides a simple tool for predicting the pyrolysis curves of polymers directly from the chain structure. The proposed method has been tested with the thermal pyrolysis of polystyrene. It has been observed that it provides a better modeling of the experimental curves, mostly for isothermal conditions where the shapes of the curves are quite dependent on the kinetic model followed by the process.

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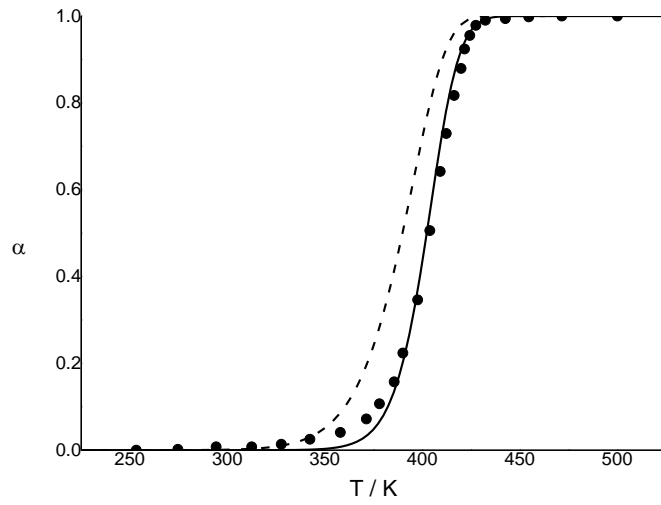52
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Figure Captions

Fig. 1. *Comparison of the thermogravimetric experimental data (dots) for polystyrene (PS) at 10 K min^{-1}, as digitalized from Porter et al paper, and model predictions employing the same kinetic parameters used by Porter et al (E_d = 344 kJ mol^{-1} that corresponds to the average dissociation energy of the three key skeletal bonds, θ_1 = 285 K and N = 2) and assuming either first order (dashed line), as in Porter et al proposal, or random scission (solid line) kinetic model.*

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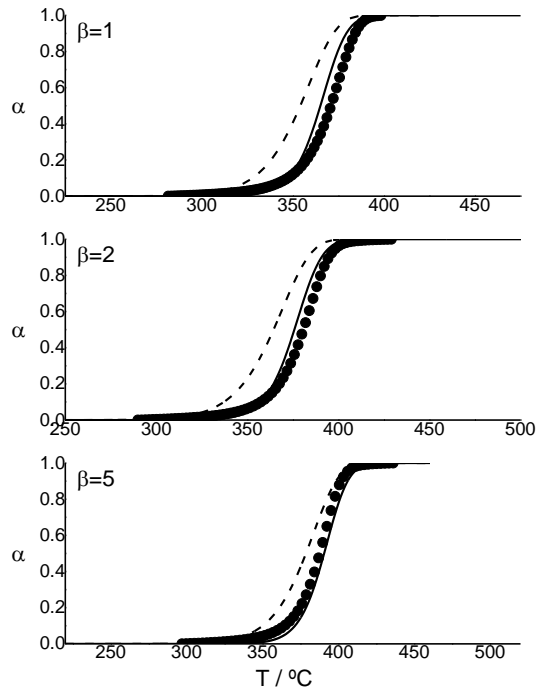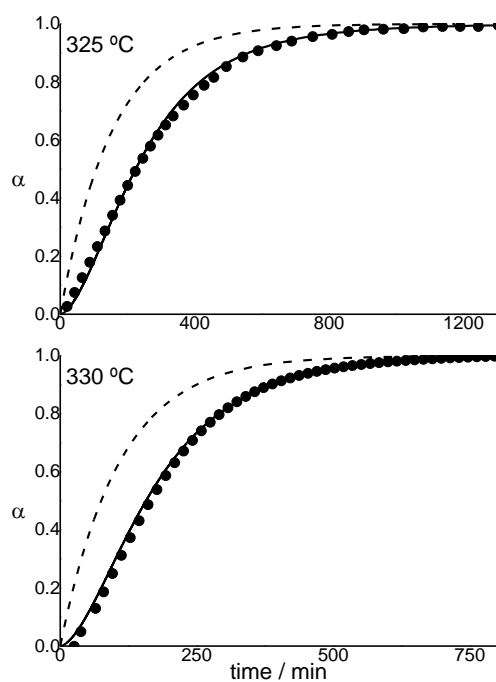
Fig. 3. *Comparison of curves corresponding to the thermal pyrolysis of PS under isothermal conditions at 325ºC and 330ºC and curves simulated using the same values of E_d, θ_1 and N as those used in Figs. 1 and 2 but different kinetic model, i.e. first order (dashed line) and random scission (solid line).*

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