

AROMATIC POLYAMIDES

VIII. Kinetic analysis of the thermal- and thermo-oxidative degradation *

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Kinetics of the initial degradation of poly(1,3-phenylene isophthalamide) and of poly(chloro-2,4-phenylene isophthalamide) has been studied by TG in inert as well as oxidative atmospheres. The information derived from the kinetic data is in agreement with our earlier reported studies on the degradation mechanism of these polyamides. The difference-differential method of Freeman–Carroll is shown to have problems when applied to high-char forming polymeric materials. The isoconversion method of Ozawa involving simple computations based on a particular reaction extent, is considered suitable for studying the complex degradation behavior of high-temperature and high-char forming polymer systems. Using this procedure, an activation energy of 215–230 kJ/mole is obtained for the initial degradation of the studied aromatic polyamides in inert and oxidative environments.

Recently we have reported on the thermal degradation mechanism of poly(1,3-phenylene isophthalamide) and poly(chloro-2,4-phenylene isophthalamide) [1] based on the pyrolysis studies using gas chromatography (GC), Fourier transform infrared spectroscopy (FT-IR), mass spectroscopy (MS), combined GC/FT-IR, GC/MS, and thermogravimetric analysis (TG). We proposed that the two polymers had similar degradation mechanisms since they involved breaking of all the chemical bonds (except the benzene ring), formation of water, and subsequent hydrolytic reactions. In order to substantiate the similarity of the degradation mechanism of these polyamides, it was desirable to study the kinetic aspects of the thermal- and thermo-oxidative decompositions.

There is numerous literature on the kinetic investigations by TG of polymers, especially the addition polymers. However, there are hardly any reports on the kinetics of thermal decomposition of high-temperature and high-char forming polymeric materials such as aromatic polyamides, polyamide-imides, and phenolics. High-char yield, typically 50–80% at 700°, and the nature of weight loss pattern in these materials can present difficulties in evaluating the degradation kinetics.

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In this article we describe some of the useful information that could be derived from the kinetic data from TG technique regarding the degradation mechanisms of poly(1,3-phenylene isophthalamide) and poly(chloro-2,4-phenylene isophthalamide). A critical evaluation of the kinetic data by two commonly used procedures is also presented for these speciality polymers.

Experimental

The two polyamides were analyzed using TG at several constant heating rates (1 to 50 degree/min) in argon as well as in oxygen media. The experiments were performed with a Perkin Elmer TGS-2 instrument using about 5.2 mg of sample.

Evaluation of kinetics

There is numerous literature on the evaluation of kinetic parameters of polymer degradation reactions by TG. The majority of the methods are derived from the formal kinetic equation:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

where $f(\alpha)$ depends on the reaction mechanism and is often assumed to be of the form $(1 - \alpha)^n$; α is the degree of conversion, t the time, k the rate constant, and n the order of reaction.

The temperature dependence of the rate constant is obtained by the application of Arrhenius equation:

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where A is the frequency factor or pre-exponential factor, E the activation energy and T the temperature in Kelvin. Substituting (2) in (1), equation (3) is obtained

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)(1 - \alpha)^n \quad (3)$$

The expression (3) can be integrated or differentiated to give equations describing the TG curve. Derivations by Ozawa [2] and Coats and Redfern [3] are popular examples of the integral method where weight-time curves are evaluated directly. Method of Freeman and Carroll [4] is one of the most popular differential methods that utilize the rate of weight loss.

The difference-logarithmic form of Eq. (3) is used in the Freeman–Carroll method.

$$\Delta \ln \left(\frac{d\alpha}{dt}\right) = n\Delta \ln (1 - \alpha) - \left(\frac{E}{R}\right)\Delta \frac{1}{T} \quad (4)$$

Thus from the TG data at a constant heating rate, " n " and " E " can be obtained from the slope and intercept of a plot of $\Delta \ln \left(\frac{d\alpha}{dt} \right)$ vs. $\Delta \ln (1 - \alpha)$ at constant $\Delta \left(\frac{1}{T} \right)$. Knowing these parameters, the value of " A " can be obtained from Eq. (3). For the determination of kinetic data, the method of Freeman and Carroll [4] is most frequently used although uncertain or meaningless values could be obtained due to a number of reasons such as the invalidity of $f(\alpha)$ as $(1 - \alpha)^n$, dependence of the weight loss pattern on heating rate and other experimental factors, and the difficulties encountered in computing the three difference functions.

Critical assessment and comparison of the different methods have been carried out by various workers [5-9]. Thus, Flynn and Wall [5] conclude that integral and differential methods involving a single TG curve appear to be applicable only to those systems in which the isothermal order is known and the materials volatilize by the same simple kinetic process. Moreover, it was suggested that only those methods involving different heating rates, such as that derived by Ozawa [9] can give the "correct value" of activation energy in the cases of "varying order" and to some extent, resolve cases of "varying activation energy" in which several competing reactions occur.

At a constant rate of heating $\beta \left(= \frac{dT}{dt} \right)$, Eq. (3) can be written as:

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta} \right) \exp \left(- \frac{E}{RT} \right) (1 - \alpha)^n \quad (5)$$

Eq. (5) upon integration could be represented in the following form:

$$\ln [(1 - \alpha)^n] \cong \ln \left(\frac{AE}{R} \right) - \ln \beta - 5.33 - 1.05 \left(\frac{E}{RT} \right)$$

The above expression for several heating rates at constant α becomes

$$\ln \beta \cong \text{constant} + 1.05 \left(\frac{E}{R} \right) \left(\frac{1}{T} \right) \quad (6)$$

Therefore, a plot of $\ln \beta$ vs. $\frac{1}{T}$ has a slope of $1.05 \frac{E}{R}$.

Thus, by plotting logarithmic heating rate vs. reciprocal temperature, at a fixed fractional degradation, the energy of activation can be calculated. This method is simple and widely used for determining activation energies from TG investigations of polymer degradation reactions. However, this involves the assumption that $f(\alpha)$ is independent of thermal history.

Results and discussion

(A) Freeman-Carroll procedure

Figure 1 shows the TG curves of poly(1,3-phenylene isophthalamide), PPI, and poly(chloro-2,4-phenylene isophthalamide), PCI, at a heating rate of 10 degree/min in an argon atmosphere. The weight loss due to degradation of these materials begins in

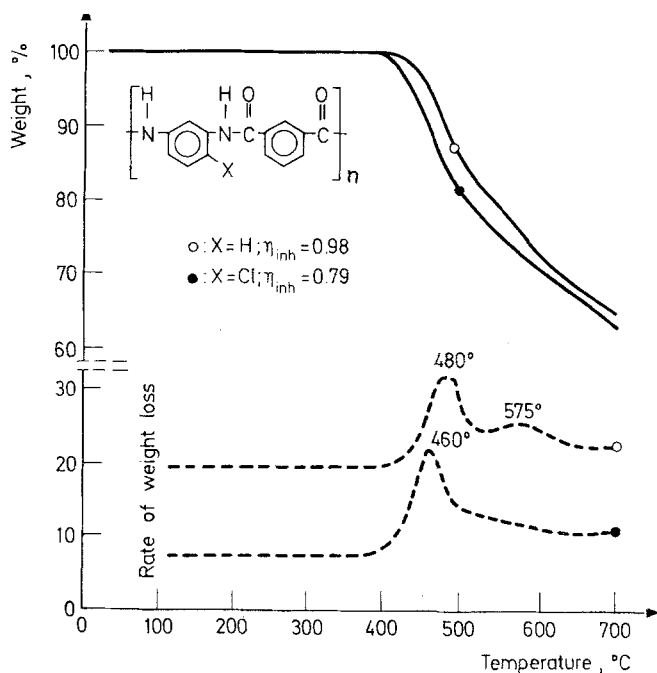


Fig. 1 TG and DTG of poly(1,3-phenylene isophthalamide) and poly(chloro-2,4-phenylene isophthalamide) in an argon atmosphere at a heating rate of $10^\circ/\text{minute}$

the vicinity of 400° and reaches its maximum rate at about 15% conversion. Beyond this region the rate of weight loss decreases continuously due to the complex char forming mechanisms. As a result of this it was realized that the kinetics be evaluated only in the $\alpha = 0$ to 15% range which predominantly represents the thermal breakdown of the linear polyamide.

Figure 2 shows the Freeman-Carroll plots for the initial degradation ($\alpha = 0$ to 15%) of PPI and PCI in an argon atmosphere. The data points are found to be scattered significantly. As a check on the validity of the procedure, the method was applied to the thermal degradation of polystyrene (NBS Standard 706); a material well studied by several investigators. As shown in Figure 3, the straight line is obtained only in the 25 to 85% conversion range, below this the points do not fall on the straight line and at higher conversions, the data points deviate from the line. In the $\alpha = 25$ to 85% range, an activation energy, E , of 224 kJ/mole is obtained which is within the wide range of values of E (164–252 kJ/mole) reported for polystyrene [10]. [It is to be noted that our purpose of determining the activation energy for polystyrene is simply to show the limitations of Freeman-Carroll method. We do not necessarily imply that this E value of 224 kJ/mole for polystyrene is the most appropriate; it will depend upon the precision of computation, the range of used, and the experimental variables. Most of the published data reveal $E = 155$ –200 kJ/mole

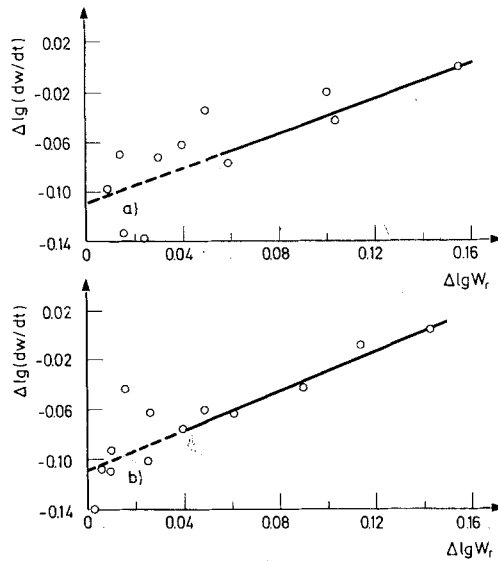


Fig. 2 Freeman-Carroll plot at constant $\Delta(1/T)$ for the initial (0–15%) degradation of the two polyamides in argon, at a heating rate of $10^\circ/\text{minute}$

- a) poly(1,3-phenylene isophthalamide) $n = 0.80$, $E = 89$ kJ/mole, $A = 2.6 \times 10^{13} \text{ min}^{-1}$
 b) poly(chloro-2,4-phenylene isophthalamide) $n = 0.81$, $E = 82$ kJ/mole,
 $A = 1.9 \times 10^{13} \text{ min}^{-1}$

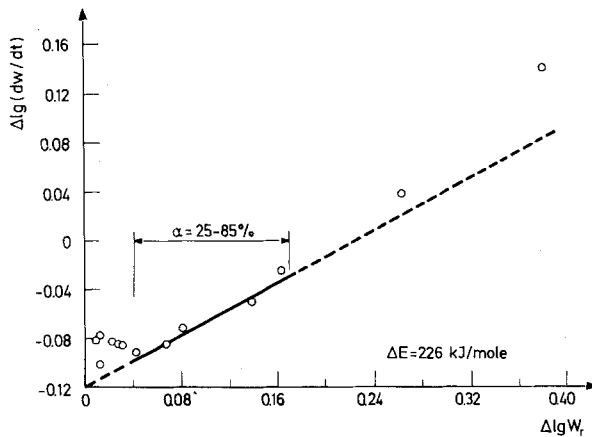


Fig. 3 Freeman-Carroll plot for the thermal degradation of polystyrene (NBS 706) in argon, at a heating rate of $10^\circ/\text{minute}$. $\Delta E = 226$ kJ/mole

for the polystyrene degradation. Using the isoconversion method (to be described in Section B) we obtain $E = 175(\pm 8)$ kJ/mole for the thermal degradation of polystyrene and this value can be considered quite reliable.] Interestingly enough, Anderson and Freeman [11] have also reported that the Freeman–Carroll plot for polystyrene and polyethylene shows linearity only in the $\alpha = 15$ to 95% and $\alpha = 35$ to 95% range, respectively. Based on these facts and our experience with other polymers, it appears that generally the data points that fall on the straight line of Freeman–Carroll plot originate from the conversion range where the rate of weight loss increases linearly with temperature (Fig. 4). This range could represent somewhere

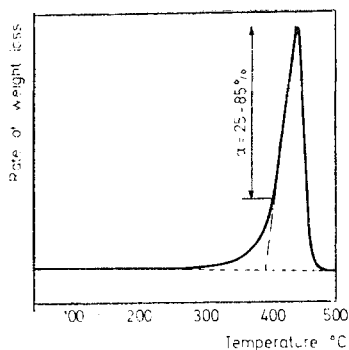


Fig. 4 Differential thermogravimetric analysis curve of polystyrene (NBS 706) in argon, at a heating rate of $10^\circ/\text{minute}$

between 15 to 95% weight loss in the case of non-char forming polymers. Using the above described criterion for PPI and PCI, only about 5% of the weight loss region would be expected to fit into a Freeman–Carroll plot. It not only explains the scatter observed in Fig. 2 but also indicates that the kinetic parameters evaluated from such a narrow conversion range (i.e., about 5%) are questionable.

Due to the heterogeneous nature of the polymer degradation [12] and the complexities of the char forming reactions, one has to be cautious in attaching any theoretical significance to the kinetic parameters for the decomposition of these polyamides. Nevertheless, the similarity of the kinetic data for PPI and PCI, i.e., reaction order (n) $\cong 0.8$, activation energy (E) $\cong 84$ kJ/mole, and pre-exponential factor (A) $\cong 2 \times 10^{13} \text{ min}^{-1}$, strongly suggests that the two polymers undergo similar degradation mechanisms. Therefore, regardless of the reliability of the kinetic parameters for the thermal breakdown of poly(1,3-phenylene isophthalamide) and poly(chloro-2,4-phenylene isophthalamide) by the Freeman–Carroll procedure, we conclude that the two materials involve closely related mechanisms.

(B) Ozawa's procedure

In accordance with the isoconversion method of Ozawa [9], Fig. 5 shows a plot of logarithmic heating rate vs. reciprocal temperature for PPI and PCI in the $\alpha = 0$ to 15% range. The nearly parallel straight lines for the initial 15% degradation indicates that the degradation mechanism of each polyamide does not change in that range and that the two polyamides degrade basically by similar mechanisms [13]. Activation energies of 215(\pm 8) and 230(\pm 8) kJ/mole are calculated (linear regression analysis) for the initial degradation of PPI and PCI, respectively. Mechanistic studies on the thermal degradation of these two aromatic polyamides reported earlier by us [1] suggested random scission of the chain by homolytic and hydrolytic cleavages. According to the

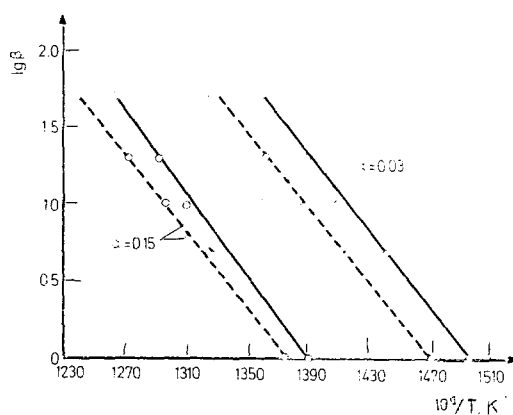


Fig. 5 Logarithmic heating rate vs. reciprocal absolute temperature for the two polyamides in argon

- poly(1,3-phenylene isophthalamide) $\Delta E = 215(\pm 8)$ kJ/mole
- poly(chloro-2,4-phenylene isophthalamide) $\Delta E = 230(\pm 8)$ kJ/mole

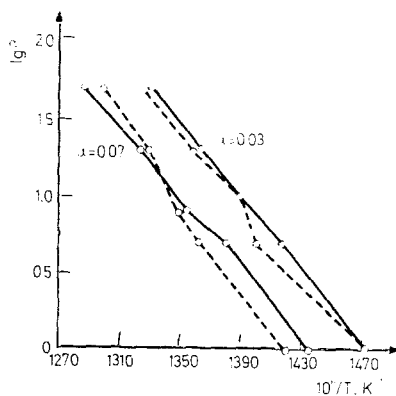


Fig. 6 Logarithmic heating rate vs. reciprocal absolute temperature for poly(1,3-phenylene isophthalamide) in argon (—) and oxygen (---)

critical analysis of methods for kinetics evaluation by Ozawa [9], the values of E obtained by the present procedure should be closer to the true activation energies for these two polyamides which involve two competing degradation mechanisms.

Now regarding the effect of oxygen on the degradation behavior of these materials, it appears that oxygen does not influence the initial degradation significantly. The

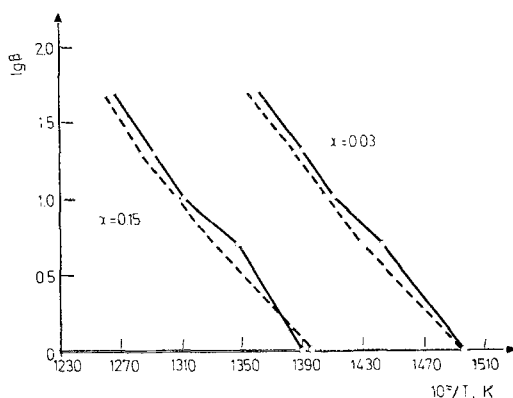


Fig. 7 Logarithmic heating rate vs. reciprocal absolute temperature for poly(chloro-2,4-phenylene isophthalamide) in argon (—) and oxygen (---)

plots of $\log \beta$ vs. $\frac{1}{T}$ for poly(1,3-phenylene isophthalamide) are quite similar in argon and oxygen up to about 10% conversion after which the polymer char burns in oxygen (Fig. 6). Poly(chloro-2,4-phenylene isophthalamide), possesses much higher thermo-oxidative resistance and, as shown by the Fig. 7, its initial degradation mechanism is virtually unaffected by the presence of oxygen.

Conclusions

Kinetic studies on the initial degradation of poly(1,3-phenylene isophthalamide) and poly(chloro-2,4-phenylene isophthalamide) by TG, have suggested that the two materials undergo closely related degradation mechanisms that are not affected by oxygen to any significant extent. This information agrees with our earlier studies on the degradation of these polyamides. Regarding the evaluation of kinetics by TG for high-char forming polymeric materials, it appears that the Freeman-Carroll procedure is not only difficult to apply but also could provide false data. The iso-conversion method of Ozawa is simple and reliable and is especially advantageous for studying the high-char forming polymers.

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Zusammenfassung — Die Kinetik der Anfangsphase des Abbaus von Poly(1,3-phenylen-isophthalamid) und Poly(chlor-2,4-phenylen-isophthalamid) wurde in inerter und oxydierender Atmosphäre thermogravimetrisch untersucht. Die aus den kinetischen Daten erhaltenen Informationen stimmen mit unseren früher veröffentlichten Untersuchungen über den Abbaumechanismus dieser Polyamide überein. Es wird gezeigt, dass die Anwendung der Methode von Freeman—Carroll auf stark teerbildende polymere Substanzen problematisch ist. Die einfache, auf einem bestimmten Reaktionsgrad sich beziehende Berechnungen in sich einschliessende Inversionsmethode nach Ozawa wird als zur Untersuchung des komplexen Abbauverhaltens von stark teerbildenden und Hochtemperatur-Polymersystemen geeignet angesehen. Bei Anwendung dieses Verfahrens wird für die Anfangsphase des Abbaus der untersuchten aromatischen Polyamide in inerter und oxydierender Atmosphäre eine Aktivierungsenergie von 215–230 kJ/mol erhalten.

Резюме — Кинетика реакции начального разложения поли-1,3-фениленизофталамида и поли-2,4-фениленизофталамида была изучена методом ТГ в инертной и окислительной атмосферах. Полученная при этом информация согласуется с ранее проведенными авторами исследованиями механизма разложения этих полиамидов. Показано, что применение дифференциального метода Фримена-Кэрролла к высокообугливающимся полимерным веществам является неоправданным. Изоконверсионный метод Озава, включающий простое вычисление на основе особой степени реакции, считается приемлемым для изучения сложного разложения высокотемпературных и высокообугливающих полимерных систем. Используя этот метод было получено значение энергии активации равное 215–230 кдж/моль для реакции начального разложения исследованных ароматических полиамидов в инертной и окислительной атмосферах.