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Non-Isothermal Depolymerization Kinetics of Polyethylene Oxide

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Abstract

The depolymerization of low molecular weight poly(ethylene oxide) (PEO) under mild conditions was studied using a linear temperature ramped non-isothermal technique and the results compared with those obtained from a conventional isothermal technique. The analysis of the non-isothermal kinetic (NIK) data was performed using an original computer program incorporating an algorithm that systematically minimizes the sum of the squares of the residuals between the experimental data and the calculated theoretical kinetic profile in order to extract the kinetic parameters. The results revealed that the depolymerization of PEO proceeds in accordance with the Ekenstam model and follows the Arrhenius equation over the temperature range of *ca*. 40 to 130°C. The NIK analysis resulted in a two-dimensional convergence to produce a unique solution set for the kinetic parameters of $E_a = 89.4$ kJ mol^{-1} and $A = 9.6 \times 10^6$ h^{-1}. These data are consistent with the results obtained from the isothermal experiments. It is proposed that NIK analysis is a quick and reliable means of obtaining kinetic parameters relevant to lifetime predictions in polymers whose degradation behaviour can be considered to be close to ideal.

Key words

Non-isothermal kinetics, poly(ethylene oxide), PEO, depolymerization, lifetime prediction

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1. Introduction

1.1 Isothermal and Non-Isothermal Kinetics

In the quest for the accurate prediction of polymer service lifetimes from data obtained in the laboratory under conditions of accelerated testing the need for robust kinetic models that hold over what is often considered to be a wide temperature range has long been recognized [1-3]. There currently exists an extensive body of literature on polymer degradation kinetics wherein the contributions typically describe a series of separate experiments, each conducted isothermally but at a different temperature across a wide range of temperatures, that are then used collectively in order to predict an expected outcome at a temperature typical of service conditions [1, 3-15].

In many cases a series of such "isothermal experiments" have rendered reliable predictions of service lifetimes if the data have been treated appropriately. However, in conducting these experiments and making predictions based on the results one must always be aware of the possible pitfalls in the approach which include: (i) many service applications of polymers involve dynamic, or indeed cyclic, temperature variations and/or fluctuations and so a series of isothermal experiments may not adequately take this into account [3, 5, 16] and (ii) there may or may not be strict adherence to the Arrhenius equation over the temperature range of the study which can significantly affect the expected kinetics and which, in turn, may seriously affect the accuracy of any service lifetime prediction [8, 12, 16, 17].

In an attempt to mimic the dynamic nature of temperature conditions experienced by polymers during their service lifetimes and, at the same time, reduce the experimental times required to produce meaningful lifetime predictions, some workers have adopted "non-isothermal" kinetics (NIK) techniques that usually involve the superposition of a (linear) temperature ramp on the kinetic experiment with a consequent distortion of the observed kinetic profile. In such experiments it can be argued that: (i) the dynamic temperature range will usually include kinetic data that lie within the service life conditions of the material of interest, (ii) the appropriate fitting of the distorted profile is a means by which such data can be accessed and (iii) the successful fit of the profile, in itself, provides some confidence in the reliability of the required data [18-21].

Although the concept of non-isothermal chemical kinetics was originally considered as long ago as the late 19th century [1], the number of such NIK studies pertaining to polymer stability determination reported in the literature is considerably smaller than the "isothermal" studies and non-isothermal studies are mainly confined to thermogravimetric (TG) analyses [22-24]. The non-isothermal pyrolysis and TG analysis of plastic waste material in the search to produce new fuels [25] is one such example appearing in the polymer literature and the non-isothermal decomposition of inorganic salts [26, 27] is representative of fundamental NIK studies that appear elsewhere in the literature. Data derived from non-isothermal pyrolysis techniques such as these, however, can in some cases produce seemingly high values of activation energies compared with other techniques [28]. It has also been suggested that reliable information on the degradation mechanism and kinetic parameters can only be obtained by the use of a set of TG curves recorded at different heating rates [16]. Other examples of NIK studies have included those cited in the chemical education literature [18, 29, 30], the performance of chemiluminescence experiments under imposed temperature ramps [31-35] and NIK studies of the thermal degradation of cellulose [19, 21, 36, 37].

The thermal depolymerization of cellulose can be modeled to a very good approximation by assuming first-order kinetics [38-41] out of which can be derived the familiar Ekenstam [40] equations of which one such version is:

$$\ln(1 - 1/DP) - \ln(1 - 1/DP_0) = k(T)t \tag{1}$$

where DP is the degree of polymerization, DP_0 is the initial DP, and k is the rate constant which is a function of the temperature, T. This model predicts that after prolonged degradation the DP of the polymer will asymptotically approach zero. Unfortunately, this is not what is observed in the case of, say, cellulose which forms stable oligomers after prolonged degradation and the DP tends towards a persistent value of *ca*. 200 corresponding approximately to the crystallite size [19, 42-46].

In order to study in further detail the applicability of NIK techniques where equation (1) can be applied it is necessary to identify a polymer whose behaviour can be described adequately by this equation at all stages in the thermal depolymerization process. To this end, polyethylene oxide (PEO) can be identified as a polymer with a wide range of commercial, scientific and industrial uses including applications in cosmetics and pharmaceuticals [47] whose behaviour during thermal depolymerizartion conforms closely to the Ekenstam model. The structure of PEO, its relatively low degree of thermal stability and its simple mechanism for degradation makes it an ideal candidate to trial. The structure of PEO is simple and a wide range of molecular weights (MW's) can be prepared for various applications. The thermo-oxidative depolymerization of PEO proceeds *via* β_1 and β_2 scissions to produce a range of intermediary products [48].

This paper investigates further the application of the NIK technique described previously [19] to PEO, a polymer that is "well behaved" in terms of its thermal depolymerization kinetics, with a view to drawing conclusions in regard to: (i) the potential savings in experimental time of the NIK technique compared with "isothermal" methods to deliver a result of similar reliability and (ii) whether the computer-based analysis technique used previously [29] delivers a two-dimensional convergence to produce a unique solution of the Arrhenius A-factor and activation energy kinetic parameters from a given set of input data.

1.2 Data Analysis

A previous study on the NIK analysis of the degradation of cellulose [29] described an original computer program that utilized an algorithm based on a variation of equation (1). In the presence of a linear temperature ramp, the first-order rate constant, k(T), varies in accordance with equation (2):

$$k(T) = A \times \exp[-E_a/R(T_0 + \beta t)] \tag{2}$$

where A is the Arrhenius A-factor, E_a is the activation energy, R is the ideal gas constant, T_0 is the initial temperature, β is the heating rate and t is time.

An original computer program was written that iteratively calculates the theoretical DP profile in accordance with equations (1) and (2) over a set range of A and E_a values. During each iteration the program calculates the goodness of fit of the theoretical curve to the input experimental data, expressed in terms of the sum of the squares of the residuals (SSR's) existing between the theoretically calculated data and the experimental data. The SSR values obtained in each iteration were calculated in accordance with equation (3) and were stored for comparative purposes along with the corresponding kinetic parameters:

$$\mathrm{SSR} = \sum_{n=1}^{\mathrm{n}} [\mathrm{F}(t_\mathrm{i}) - DP(t_\mathrm{i})]^2 \qquad (3)$$

where $\mathrm{F}(t_\mathrm{i})$ is the computer-generated non-isothermal DP function, $DP(t_\mathrm{i})$ is the experimental DP at time t_i and n is the number of experimental DP data.

Clearly, the optimum fit of the experimental data is identified by the minimum SSR value where a set range of A and E_a values are systematically scanned in the iterations. These calculations enable the testing of whether or not a two-dimensional convergence of the A and E_a values occurs to render a unique value of the minimum SSR. Such a condition indicates that the analysis produces a unique set (A, E_a) of the kinetic parameters that pertain to the given analysis. The inherent applicability of the derived kinetic parameters over the entire non-isothermal process is evidenced by the goodness of fit of the theoretically calculated kinetic profile to the experimental data. This, in turn, infers a high level of confidence in the applicability of the kinetic parameters, particularly at lower temperatures that are usually of primary interest in service lifetime prediction calculations.

2. Materials and Methods

A sample of PEO powder (MW = 8000 Da, average M_v) was obtained from Sigma Aldrich (Sydney, Australia). Samples were aged in an air-circulating oven (Labec model TWM24/J459) with programmable temperature controller (model 2416). In the case of the isothermal experiments, samples were degraded for up to 40 days at 60, 70, 80 and 90°C. For the non-isothermal experiments, two sets of samples were degraded at different heating rates, namely 0.10°C h^{-1} over the range 52-130°C and 0.04°C h^{-1} over the range 40-100°C. In the case of both the isothermal and non-isothermal experiments, samples were taken periodically and prepared as 5% (w/w) aqueous solutions in 0.1 M phosphate buffer at pH = 7 ready for rheological measurements.

The viscosities of the degraded PEO solutions were measured using an Anton Paar Physica MCR Rheometer (model MCR 301) using a cone and plate accessory (model CP-501). The intrinsic viscosity was calculated and the MW was determined using equation (4), the Mark-Houwink equation [49]:

$$[\eta] = KM^{a} \tag{4}$$

where $[\eta]$ is the intrinsic viscosity, M is the MW and K and a are the Mark-Houwink constants. Samples of PEO (MW = 500 to 20,000 Da, Sigma Aldrich, Sydney, Australia) were used to determine the constants K and a, which were found to be 0.074 mL g^{-1} and 0.71 respectively. These parameters are in agreement with those reported elsewhere which range from 0.5 to 0.82 for the exponent, a, [50-52] and 0.072 mL g^{-1} for the constant, K [51].

3. Results and Discussion

In order to demonstrate the potential efficiencies in experimental times to be realized utilizing the NIK technique over conventional isothermal testing, the NIK computer algorithm was applied to creating a theoretical NIK profile along with an isothermal profile for comparison. These data are shown in Figure 1 for the non-isothermal depolymerization of a theoretical or "ideal" polymer that degrades in accordance with the Ekenstam [40] model (see equations (1) and (2)) and for which DP_0 = 1400, T_0 = 25°C, $A = 7.0 \times 10^9$ h^{-1}, E_a = 90 kJ mol^{-1} and β = 0.5°C h^{-1}. For the comparative isothermal data, no heating ramp was applied and the temperature was set at 25°C. The figure clearly indicates that under isothermal conditions depolymerization takes place very slowly compared with the non-isothermal case as expected and that the DP isothermally decreases by only about 25% in the time it takes for the non-isothermal run to be virtually complete. If it is accepted that a single, non-isothermal run is sufficient to result in the kinetic parameters A and E_a being determined directly then the experimental time advantage of the NIK technique becomes immediately apparent because in order to obtain these parameters isothermally, a whole series of experiments are needed [19].

An indication of the potential efficiency of the NIK method is further considered by comparing experimental times required to obtain 95% degradation under NIK and isothermal conditions for the cellulose/mineral oil system [19] where DP_0 = 1300, $A = 7.5 \times 10^9$ h^{-1} and E_a = 111 kJ mol^{-1}. The experimental time for a single NIK determination from 25°C to 225°C using a heating rate of 1°C h^{-1} is *ca*. 200 h. Under isothermal conditions for 5 runs between 90°C and 170°C, the times are *ca*. 21,300 h for sequential experiments and *ca*. 18,000 h for simultaneous experiments. From the time estimates utilizing the more optimistic timeframe in the isothermal case one can calculate that the NIK technique requires only about 1% of the experimental time required to complete the isothermal experiments.

In order to characterize the depolymerization of the PEO material a series of isothermal degradation experiments were performed and the respective Ekenstam plots were prepared so that the rate constants could be extracted [40, 53, 54]. Shown in Figure 2 are plots of 1000 × $\ln(1 - 1/DP)$ versus time in accordance with equation (1) for the isothermal depolymerization of PEO at temperatures in the range of 60 to 90°C. The high degree of linearity of these plots suggests that the isothermal depolymerization of the PEO sample in the given temperature range proceeds "ideally" in that it obeys the Ekenstam model within this range with an observed increase in the rate of depolymerization with increased temperature as reflected by the gradients of the plots. Indeed, this model has been shown to apply to a range of other polymer materials including polyurethane [55, 56], cellulose as well as various biopolymers [57-59].

Figure 3 is a plot of the natural logarithm of the rate constants extracted from the data shown in Figure 2 as a function of the reciprocal of the absolute temperature. The plot is quite linear suggesting the depolymerization of PEO within the temperature range and conditions used in these experiments can, at least to a very good approximation, be considered to adhere to a single Arrhenius equation. The parameters A and E_a were obtained from the line of best fit and these were 9.85×10^6 h^{-1} and 88.1 kJ mol^{-1} respectively. The value of the latter lies a little outside the range of activation energies reported in the literature for the overall degradation of high MW PEO samples. The lower limit of this range is *ca*. 125 kJ mol^{-1} [22, 60-63]. Such literature values of the Arrhenius parameters have generally been derived from experiments conducted at temperatures much higher than those used in the present study; namely, those typically required in, say, flash pyrolysis [61] and TG analysis [22]. The activation energy calculated in the present study is, however, closer to those activation energies typically reported for the pyrolysis of low MW PEO that is kinetically controlled by desorption and/or evaporation of small, volatile products. In such cases, the overall activation energy is reported to be in the range of *ca*. 40–85 kJ mol^{-1} [62, 63]. Interestingly, the Arrhenius A-factor reported in the present study is close to the upper limit of the range for this parameter reported by Arisawa and Brill [62] for the pyrolysis of low MW poly(ethylene glycol) (PEG, M_w = 2090 Da) for temperatures below *ca*. 460°C. The enormous range in the Arrhenius A-factor reported by Arisawa and Brill [62] in this particular case (i.e. about five orders of magnitude) gives, perhaps, an indication of the experimental variability associated with this kinetic parameter that is to be expected.

In Figure 4, the analysis of the experimentally determined DP during the non-isothermal depolymerization of PEO using two different heating rates is shown. The solid lines in the plots are the computer-generated optimum fit of the experimental data achieved by minimizing the SSR's. This plot highlights the agreement between the computer-generated fit and the experimental DP data and shows that decreasing the heating rate has the expected effect of shifting the DP curve towards longer times. The latter observation is consistent with theoretical studies performed previously using the NIK computer algorithm [19]. The data also suggest that in the case of PEO, the depolymerization proceeds such that the DP asymptotically approaches the time axis after a prolonged period of non-isothermal degradation. This behaviour is in contrast to that of other polymers, such as cellulose, where the DP is observed to approach a non-zero value and persist at that value after a prolonged period of degradation [19, 42-46].

The DP of the PEO used in the current study is relatively low and so its asymptotic approach to the time axis after prolonged degradation under the relatively mild conditions of thermal degradation that have been used can be considered as an almost idealized case. This is in comparison to the thermal degradation of higher MW materials such as PEG at higher temperatures where, for example, non-linearity in the Arrhenius plot over certain temperature ranges has been reported [62]. Indeed, the latter brings into question whether or not the Arrhenius plot shown in Figure 3 can be considered to be linear over the entire experimental temperature range as it could be interpreted as being curved over that range. However, in considering this it is important to keep in mind the major objective of the current work, which is to examine in the first instance the application of NIK analysis to a system that can, for the purposes of the exercise, be considered to behave ideally. It is proposed that: (i) the asymptotic approach of the experimental DP to the time axis in accordance with the prediction made by the theoretical NIK data shown in Figure 1, together with (ii) the acceptable approximation to Arrhenius behaviour revealed by the data in Figure 2 and (iii) the goodness of fit of the experimental data to the NIK model, are collective evidence to propose that under the conditions used in the present study PEO can be considered to behave ideally as required.

Table 1 shows the calculated values of the kinetic parameters A and E_a obtained from the computer-fitting algorithm for PEO at the two different heating rates. For comparison, the values of these parameters obtained from Figure 3 under isothermal conditions are also presented. The data illustrate a high degree of consistency firstly between the non-isothermal data obtained at the different heating rates and secondly between the data derived non-isothermally and isothermally. This inspires some confidence in the NIK technique as being one that is capable of reliably delivering the required kinetic parameters in a relatively short experimental time compared with the traditional isothermal method.

Figure 5 shows a three-dimensional plot of the SSR as a function of each of the values of the kinetic parameters A and E_a that were systematically used in successive iterations of the computer algorithm during the fit of the data presented in Figure 4(a). The SSR surface has a "well" whose minimum coordinates correspond to a unique value of $A = 9.6 \times 10^6$ h^{-1} and a unique value of $E_a = 89.3$ kJ mol^{-1}. This plot validates pictorially that the SSR minimization fitting algorithm used in the analysis of the NIK data obtained in this study produces a two-dimensional convergence leading to a unique solution set of the required kinetic parameters.

To further illustrate the sensitivity of the data to changes in E_a and A values, Figure 6 shows a surface contour plot of the normalized SSR values over a wide range of the kinetic parameters. This plot clearly demonstrates a narrow band of E_a values where the SSR values offer a good fit to the experimental data. In contrast, there appears to be higher variability in the A values with a broader range of values offering adequate fit to the data [62].

Conclusions

The isothermal depolymerization of low MW PEO under mild conditions proceeds almost ideally in accordance with the Ekenstam model for depolymerization and can be assumed to follow the Arrhenius equation over the temperature range of 60 to 90°C. The analysis of results obtained for the non-isothermal depolymerization of this material over the temperature range of *ca*. 40 to 130°C reveals a two-dimensional SSR convergence to produce kinetic parameters that are comparable to those obtained isothermally but in a much shorter experimental time. These observations reflect favourably on the method of NIK analysis that incorporates an SSR minimization algorithm as a reliable method of rapidly determining kinetic parameters in polymer degradation experiments. It is proposed that the NIK analysis described herein is a time-saving tool provided the polymer can be assumed to behave ideally over the experimental temperature range, the kinetics do not change over that range and the method is calibrated against a reference set of isothermal experiments performed over the same or similar temperature range. Clearly, the quality of the data fit across the experimental time-temperature domain of an NIK experiment attests to the validity of these assumptions. The collection of sufficient NIK data at low temperatures should deliver a high degree of confidence in lifetime prediction parameters obtained rapidly from experiments performed closer to "in-service" conditions.

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References

[1] Flynn JH. Degradation kinetics applied to lifetime predictions of polymers. Polym Eng Sci. 1980;20:675-7.

[2] Budrugeac P. Some methodological problems concerning the kinetic analysis of non-isothermal data for thermal and thermo-oxidative degradation of polymers and polymeric materials. Polym Degrad Stab. 2005;89:265-73.

[3] Benes M, Placek V, Matuschek G, Kettrup AA, Gyoeryova K, Emmerich WD, et al. Lifetime simulation and thermal characterization of PVC cable insulation materials. J Therm Anal Calorim. 2005;82:761-8.

[4] Blaese D, Schmachtenberg E. Estimation of lifetime under non-isothermal conditions. ASTM STP 1369. 2000:22-31.

[5] Roy PK, Surekha P, Rajagopal C, Choudhary V. Thermal degradation studies of ldpe containing cobalt stearate as pro-oxidant. eXPRESS Polym Lett. 2007;1:208-16.

[6] Budrugeac P, Segal E. Thermal analysis in the evaluation of the thermal lifetime of solid polymeric materials. Thermochim Acta. 1992;211:131-6.

[7] Flynn JH. A critique of lifetime prediction of polymers by thermal analysis. J Therm Anal Calorim. 1995;44:499-512.

[8] Gillen KT, Clough RL, Wise J. Prediction of elastomer lifetimes from accelerated thermal-aging experiments. Adv Chem Ser. 1996;249:557-75.

[9] Huy ML, Evrard G. Methodologies for lifetime predictions of rubber using Arrhenius and WLF models. Angew Makromol Chem. 1998;261-262:135-42.

[10] Viebke J, Gedde UW. Assessment of lifetime of hot-water polyethylene pipes based on oxidation induction time data. Polym Eng Sci. 1998;38:1244-50.

[11] Heywood RJ, Stevens GC, Ferguson C, Emsley AM. Life assessment of cable paper using slow thermal ramp methods. Thermochim Acta. 1999;332:189-95.

[12] Celina M, Gillen KT, Assink RA. Accelerated aging and lifetime prediction: Review of non-Arrhenius behaviour due to two competing processes. Polym Degrad Stab. 2005;90:395-404.

[13] Wolf C, Macho C, Lederer K. Accelerated ageing experiments with crosslinked and conventional ultra-high molecular weight polyethylene (UHMW-PE) stabilised with α-tocopherol for total joint arthroplasty. J Mater Sci Mater Med. 2006;17:1333-40.

[14] Hoàng EM, Lowe D. Lifetime prediction of a blue PE100 water pipe. Polym Degrad Stab. 2008;93:1496-503.

[15] Käser F, Roduit B. Lifetime prediction of rubber using the chemiluminescence approach and isoconversional kinetics. Chimia. 2008;62:908-12.

[16] Budrugeac P. The evaluation of the non-isothermal kinetic parameters of the thermal and thermo-oxidative degradation of polymers and polymeric materials: Its use and abuse. Polym Degrad Stab. 2000;71:185-7.

[17] Gillen KT, Bernstein R, Celina M. Non-Arrhenius behavior for oxidative degradation of chlorosulfonated polyethylene materials. Polym Degrad Stab. 2005;87:335-46.

[18] Brown ME, Phillpotts CAR. Non-isothermal kinetics. J Chem Ed. 1978;55:556-60.

[19] Bigger SW, Scheirs J, Camino G. An investigation of the kinetics of cellulose degradation under non-isothermal conditions. Polym Degrad Stab. 1998;62:33-40.

[20] Bigger SW, Cran MJ, Scheirs J. The application of non-isothermal kinetics to polymer degradation. 28th Meeting of the Polymer Degradation Discussion Group. Sestri Levante, Italy; September 6-10, 2009.

[21] Dahiya JB, Kumar K, Muller-Hagedorn M, Bockhorn H. Kinetics of isothermal and non-isothermal degradation of cellulose: Model-based and model-free methods. Polym Int. 2008;57:722-9.

[22] Pielichowski K, Flejtuch K. Non-oxidative thermal degradation of poly(ethylene oxide): Kinetic and thermoanalytical study. J Anal Appl Pyrol. 2005;73:131-8.

[23] Sung YK, Kim YJ, Grainger DW, Okano T, Kim SW. Bulk and thermal characteristics of poly(ethylene oxide)-polystyrene multiblock copolymers Korea Polymer Journal. 1993;1:14-20.

[24] Gordon Cameron G, Ingram MD, Younus Qureshi M, Gearing HM, Costa L, Camino G. The thermal degradation of poly(ethylene oxide) and its complex with NaCNS. Eur Polym J. 1989;25:779-84.

[25] Kayacan I, Doğan ÖM. Pyrolysis of low and high density polyethylene. Part I: Non-isothermal pyrolysis kinetics. Energy Sources Part A: Recovery, Utilization & Environmental Effects. 2008;30:385-91.

[26] Maitra S, Bandyopadhyay N, Pal J. Application of non-Arrhenius method for analyzing the decomposition kinetics of $SrCO_3$ and $BaCO_3$. J Am Ceram Soc. 2008;91:337-41.

[27] Chen H, Liu N. Application of non-Arrhenius equations in interpreting calcium carbonate decomposition kinetics: Revisited. J Am Ceram Soc. 2010;93:548-53.

[28] Vijayalakshmi SP, Chakraborty J, Madras G. Thermal and microwave-assisted oxidative degradation of poly(ethylene oxide). J Appl Polym Sci. 2005;96:2090-6.

[29] Salvador F, Gonzalez JL, Tel LM. Non-isothermic chemical kinetics in the

undergraduate laboratory: Arrhenius parameters from experiments with hyperbolic temperature variation. J Chem Ed. 1984;61:921-3.

[30] Hodgson SC, Ngeh LN, Orbell JD, Bigger SW. A student experiment in non-isothermal chemical kinetics. J Chem Ed. 1998;75:1150-3.

[31] Billingham NC, Then ETH, Gijsman PJ. Chemiluminescence from peroxides in polypropylene. Part I: Relation of luminescence to peroxide content. Polym Degrad Stab. 1991;34:263-77.

[32] Celina M, George GA, Lacey DJ, Billingham NC. Chemiluminescence imaging of the oxidation of polypropylene. Polym Degrad Stab. 1995;47:311-7.

[33] Fearon PK, Marshall N, Billingham NC, Bigger SW. Evaluation of the oxidative stability of multiextruded polypropylene as assessed by physicomechanical testing and simultaneous differential scanning calorimetry-chemiluminescence. J Appl Polym Sci. 2001;79:733-41.

[34] George GA, Egglestone GT, Riddell SZ. Chemiluminescence studies of the degradation and stabilization of polymers. Polym Eng Sci. 1983;23:412-8.

[35] Matisov -Rychl L, Rychl L, Clough RL, Billingham NC, Gillen KT. Inherent relations of chemiluminescence and thermooxidation of polymers. Polymer durability. Washington DC: ACS Symposium Series 206, American Chemical Society; 1996. p. 175-93.

[36] Emsley AM. The kinetics and mechanisms of degradation of cellulosic insulation in power transformers. Polym Degrad Stab. 1994;44:343-9.

[37] Emsley AM, Heywood RJ, Ali M, Eley CM. On the kinetics of degradation of cellulose. Cellulose. 1997;4:1-5.

[38] Freudenberg K, Kuhn W, Dürr W, Bolz F, Steinbrunn G. The hydrolysis of the polysaccharides. Eur J Inorg Chem. 1930;63:1510-30.

[39] Kuhn W. On the kinetics of the degradation of high molecular weight chains. Eur J Inorg Chem. 1930;63:1503-9.

[40] Ekenstam Aa. About the behavior of cellulose in mineral acid solutions, Part II.: Kinetic studies of degradation of cellulose in acid solutions. Eur J Inorg Chem. 1936;69:553-9.

[41] Emsley AM, Stevens GC. Kinetics and mechanisms of the low-temperature degradation of cellulose. Cellulose. 1994;1:26-56.

[42] Chang M. Folding chain model and annealing of cellulose. J Polym Sci Polym Symp. 1971;36:343-62.

[43] Chang MMY. Crystallite structure of cellulose. J Polym Sci Polym Chem Ed. 1974;12:1349-74.

[44] Shafizadeh F, Bradbury AGW. Thermal degradation of cellulose in air and nitrogen at low temperatures. J Appl Polym Sci. 1979;23:1431-42.

[45] Shroff DH, Stannett AW. A review of paper aging in power transformers. IEE Proc C. 1985;132:312-9.

[46] Kawamoto H, Saka S. Heterogeneity in cellulose pyrolysis indicated from the pyrolysis in sulfolane. J Anal Appl Pyrol. 2006;76:280-4.

[47] Fuertges F, Abuchowski A. The clinical efficacy of poly(ethylene glycol)-modified proteins. J Control Release. 1990;11:139-48.

[48] Malik P, Castro M, Carrot C. Thermal degradation during melt processing of poly(ethylene oxide), poly(vinylidenefluoride-co-hexafluoropropylene) and their blends in the presence of additives, for conducting applications. Polym Degrad Stab. 2006;91:634-40.

[49] Flory PJ. Determination of molecular weights. Principles of polymer chemistry. Ithaca, NY: Cornell University Press; 1953. p. 266-316.

[50] Brandrup J, Immergut EH, McDowell W editors. Polymer handbook. New York: Wiley; 1975.

[51] Tirtaatmadja V, McKinley GH, Cooper-White JJ. Drop formation and breakup of low viscosity elastic fluids: Effects of molecular weight and concentration. Phys Fluids. 2006;18:043101.

[52] Dinç CÖ, Kibarer G, Güner A. Solubility profiles of poly(ethylene glycol)/solvent systems. II. Comparison of thermodynamic parameters from viscosity measurements. J Appl Polym Sci. 2010;117:1100-19.

[53] Staggs JEJ. Modelling random scission of linear polymers. Polym Degrad Stab. 2002;76:37-44.

[54] Selih VS, Strlic M, Kolar J, Pihlar B. The role of transition metals in oxidative degradation of cellulose. Polym Degrad Stab. 2007;92:1476-81.

[55] Malíková M, Rychlý J, Matisová-Rychlá L, Csomorová K, Janigová I, Wilde H-W. Assessing the progress of degradation in polyurethanes by chemiluminescence. I. Unstabilised polyurethane films. Polym Degrad Stab. 2010;95:2367-75.

[56] Rychlý J, Lattuati-Derieux A, Lavédrine B, Matisová-Rychlá L, Malíková M, Csomorová K, et al. Assessing the progress of degradation in polyurethanes by chemiluminescence and thermal analysis. II. Flexible polyether- and polyester-type

polyurethane foams. Polym Degrad Stab. 2011;In Press, Corrected Proof.

[57] Strlic M, Kolar J, Pihlar B, Rychlý J, Matisová-Rychlá L. Initial degradation processes of cellulose at elevated temperatures revisited -- chemiluminescence evidence. Polym Degrad Stab. 2001;72:157-62.

[58] Rychlý J, Matisová-Rychlá L, Lazár M, Slovák K, Strlic M, Kocar D, et al. Thermal oxidation of cellulose investigated by chemiluminescence. The effect of water at temperatures above 100 °c. Carbohyd Polym. 2004;58:301-9.

[59] Pleteníková M, Matisová-Rychlá L, Rychlý J, Lacík I. Chemiluminescence related to degradation of thermally oxidized pullulans. Comparison with cellulose and dextran. Carbohyd Polym. 2007;69:50-64.

[60] Madorsicy SL, Straus S. Thermal degradation of polyethylene oxide and polypropylene oxide. J Polym Sci. 1959;36:183-94.

[61] Calahorra E, Cortazar M, Guzmán GM. Thermal decomposition of poly(ethylene oxide), poly(methyl methacrylate), and their mixtures by thermogravimetric method. J Polym Sci Polym Lett. 1985;23:257-60.

[62] Arisawa H, Brill TB. Flash pyrolysis of polyethyleneglycol II: Kinetics determined by T-jump/FTIR spectroscopy. Combust Flame. 1997;109:105-12.

[63] de Sainte Claire P. Degradation of PEO in the solid state: A theoretical kinetic model. Macromolecules. 2009;42:3469-82.

Table 1. Arrhenius A-factors and Activation energies obtained from isothermal and non-isothermal depolymerization of PEO.

Kinetics	$A/10^6 h^{-1}$	E_a/kJ mol^{-1}
Isothermal	9.9	88 ± 2
NIK (β = 0.10°C h^{-1})	9.6	89 ± 2
NIK (β = 0.04°C h^{-1})	9.1	88 ± 2

Figure Captions

Figure 1. Theoretical plots generated from the computer algorithm described elsewhere [19] for the depolymerization of an ideal polymer for which $DP_0 = 1400$, $T_0 = 25°C$, $A = 7.0 \times 10^9$ h^{-1}, and $E_a = 90$ kJ mol^{-1}: (a) isothermal depolymerization at $T = 25°C$ and (b) non-isothermal depolymerization using a heating rate of $\beta = 0.5°C$ h^{-1}.

Figure 2. Plot of $1000 \times \ln(1 - 1/DP)$ versus time for the isothermal depolymerization of PEO for which $DP_0 = 1400$ at: (a) $T = 60°C$ (○), (b) $T = 70°C$ (●), (c) $T = 80°C$ (☐) and (d) $T = 90°C$ (■).

Figure 3. Arrhenius plot of data obtained from the isothermal depolymerization of PEO for which $DP_0 = 1400$. The rate constants were obtained from the gradients of the isothermal depolymerization plots shown in Figure 2.

Figure 4. Analysis of the non-isothermal depolymerzation of PEO for which $DP_0 = 8000$ and the heating conditions are: (a) $T_0 = 52°C$, $\beta = 0.10°C$ h^{-1} (●) and (b) $T_0 = 40°C$, $\beta = 0.04°C$ h^{-1} (○). The solid curves through the points are the computer-generated fits to the experimental data.

Figure 5. Plot of the SSR values obtained from the computer fitting algorithm applied to the data shown in Figure 4(a) as a function of the A and E_a kinetic parameters. The surface exhibits a minimum corresponding to a unique solution for these parameters.

Figure 6. Contour plot of the normalized SSR values obtained from the computer fitting algorithm applied to the data shown in Figure 4(a) as a function of the A and E_a kinetic parameters.

Figure 1.

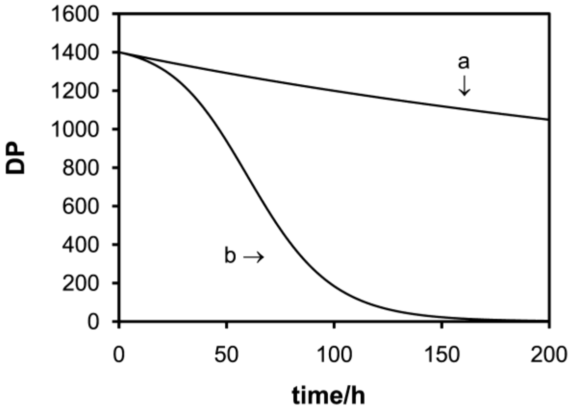

1600
1400
1200
1000
800
600
400
200
0
DP
0
50
100
150
200
time/h
a ↓
b →

Figure 2.

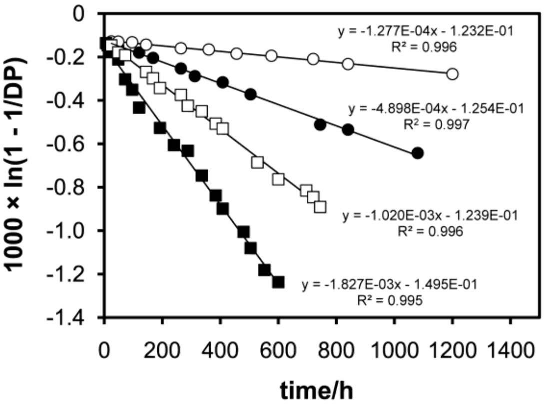

y = -1.277E-04x - 1.232E-01
R² = 0.996
y = -4.898E-04x - 1.254E-01
R² = 0.997
y = -1.020E-03x - 1.239E-01
R² = 0.996
y = -1.827E-03x - 1.495E-01
R² = 0.995
1000 × ln(1 - 1/DP)
0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
0
200
400
600
800
1000
1200
1400
time/h

Figure 3.

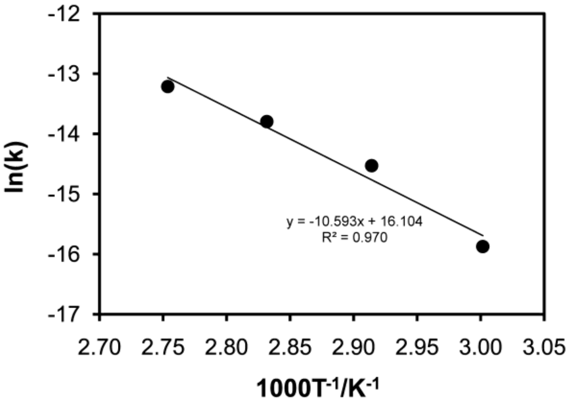

-12
-13
-14
-15
-16
-17
ln(k)
y = -10.593x + 16.104
R² = 0.970
2.70
2.75
2.80
2.85
2.90
2.95
3.00
3.05
1000T-1/K-1

Figure 4.

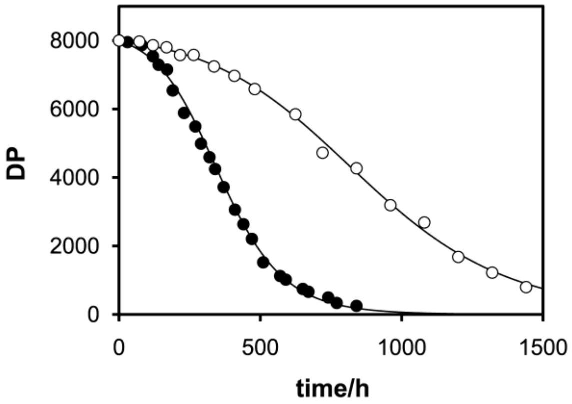


Figure 5.

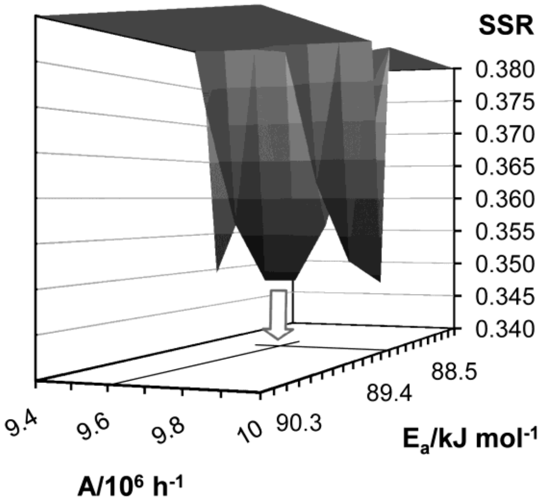
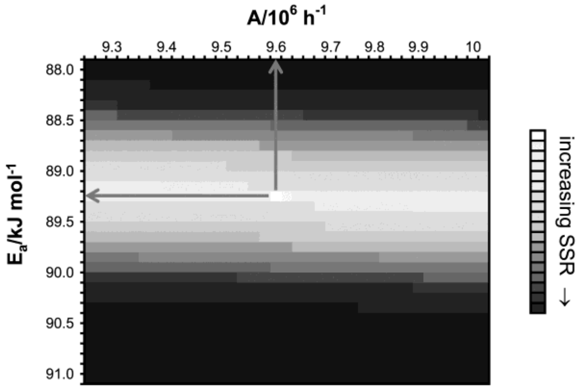

SSR
0.380
0.375
0.370
0.365
0.360
0.355
0.350
0.345
0.340
88.5
89.4
90.3
E_a/kJ mol^{-1}
9.4
9.6
9.8
10
A/10^6 h^{-1}

Figure 6.


$A/10^6\ h^{-1}$
9.3
9.4
9.5
9.6
9.7
9.8
9.9
10
E_a/kJ mol^{-1}
88.0
88.5
89.0
89.5
90.0
90.5
91.0
increasing SSR →