ELSEVIER

Thermochimica Acta 388 (2002) 275–281

thermochimica
acta

www.elsevier.com/locate/tca

The utility of variable temperature techniques in the determination of kinetic parameters

Bob A. Howell[*]

Center for Applications in Polymer Science, Central Michigan University, Mt. Pleasant, MI 48859, USA

Received 10 July 2001; received in revised form 3 December 2001; accepted 10 December 2001

Abstract

Thermogravimetry is a useful, convenient method for the study of polymer degradation. Several approaches have been developed for the extraction of kinetic parameters from thermogravimetric data. Various variable temperature techniques permit a rapid, almost effortless, estimation of the activation energy of any well-defined process. However, the values generated are subject to greater uncertainty than those obtained using an isothermal method in which rate constants at several temperatures are determined and used to construct a temperature dependence plot from which the activation energy may be extracted. Although the isothermal method is the more time-consuming it provides more reliable results than can be obtained using dynamic methods. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: TG kinetic parameters; Activation energy; Reliability; Isothermal versus dynamic methods

1. Introduction

Under appropriately forcing conditions many polymeric materials undergo thermal decomposition [1]. In some cases this may occur by a single, well-understood process. The unzipping, by reformation of monomer, of poly(methyl methacrylate) or the degradative dehydrochlorination of vinylidene chloride copolymers provide examples of this kind of decomposition. However, most polymers undergo decomposition by processes that are much more complex and may involve several degradation processes occurring simultaneously. Polymer degradation is often studied by thermogravimetry (TG/TGA) or TG coupled with some method for determining the structure/identity of evolved gaseous products [2]. Popular methods include TG/mass spectrometry (TG/MS), TG/gas chromatography/MS (TG/GC/MS), and TG/Fourier transform infrared spectroscopy (TG/FTIR). While these are powerful techniques and often are capable of providing considerable insight they are seldom sufficient to permit complete characterization of the degradation processes occurring as the polymer decomposes. Such understanding is sought to permit the projection of more suitable production/processing conditions, predictions of structural modifications which may extend use range, predictions of suitable flame retardant methodology, meaningful estimations of expected lifetime under a variety of conditions, etc.

Kinetic parameters obtained from thermogravimetric measurements are often used for lifetime projections. These may include rate constants at several temperatures. More commonly they include an estimation of the enthalpy of activation, $\Delta H^{\ddagger}$ or even more commonly the Arrhenius activation energy, E_a. These

---

[*] Tel.: +1-517-774-3582; fax: +1-517-774-3883.
E-mail address: bob.a.howell@cmich.edu (B.A. Howell).

PII: S0040-6031(02)00018-7

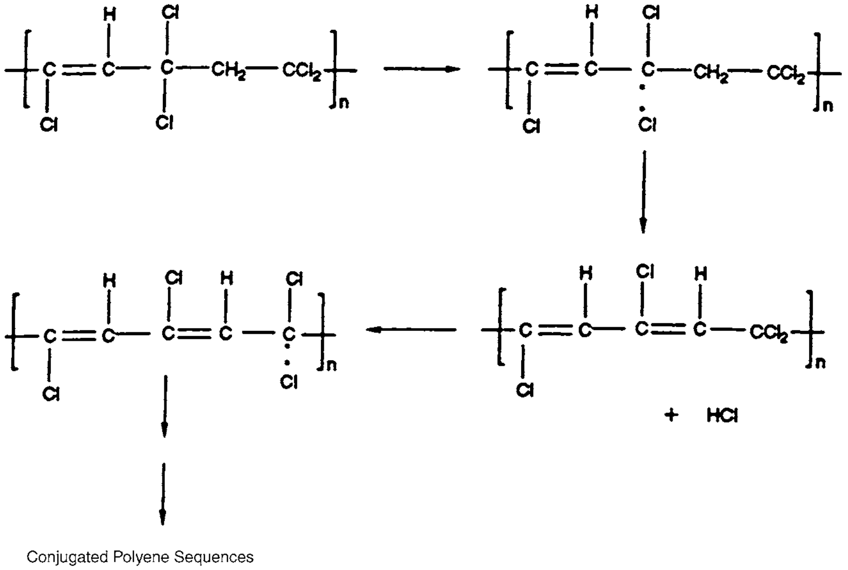
may have some sound basis when a single, well-defined process is being characterized. However, values for such parameters are often generated and reported for complex decompositions involving several degradation reactions each of which occurs with a unique activation enthalpy. Such values may have some limited utility in lifetime prediction but, in the main, are of little value. Most reliably, the enthalpy of activation for any single process may be obtained from the slope of a plot of $\ln(k/T)$ versus $1/T$, where k is the rate constant at a particular Kelvin temperature, T. The slope of this plot is $-\Delta H^{\ddagger}/R$, where R is the gas constant, 1.9872 cal/mol° or equivalent. This procedure requires that rate constants be obtained at several temperatures. Because this is tedious and time-consuming, a number of variable temperature techniques for determining activation energies have been developed [3–13]. While these methods afford convenience and speed in generating activation values, the reliability and utility of the values obtained are often less than satisfactory.

2. Results and discussion

Many solid phase reactions including polymer degradation occur with the formation of volatile fragments. As a consequence TG represents a convenient and popular method for studying these processes [2]. A limitation, of course, is that the sample mass-loss profile must adequately reflect degradation by a unique, well-understood process. When this is not the case, it is impossible to obtain values for kinetic parameters which have any fundamental meaning.

Because of their importance in the barrier plastic packaging industry the degradation of vinylidene chloride polymers has been extensively studied [14–17]. The commercial prominence of these polymers is a consequence of low permeability of oxygen and flavor/aroma constituents such that food quality is maintained in packaging prepared from these materials [18–20]. These polymers are generally free of the defect sites characteristic of similar vinyl polymers, i.e. they are regular head-to-tail, unbranched and highly crystalline polymers [21]. However, when subjected to thermal stress, these polymers undergo degradative dehydrochlorination. This thermal dehydrochlorination is a typical radical chain process with distinct initiation, propagation and termination phases [2,21].

Initiation of degradation is promoted by the presence of any of a variety of agents capable of introducing random double bonds into the polymer mainchain [21]. Unsaturation in these polymers appears to be a



Scheme 1. Mode of degradation of vinylidene chloride polymers.

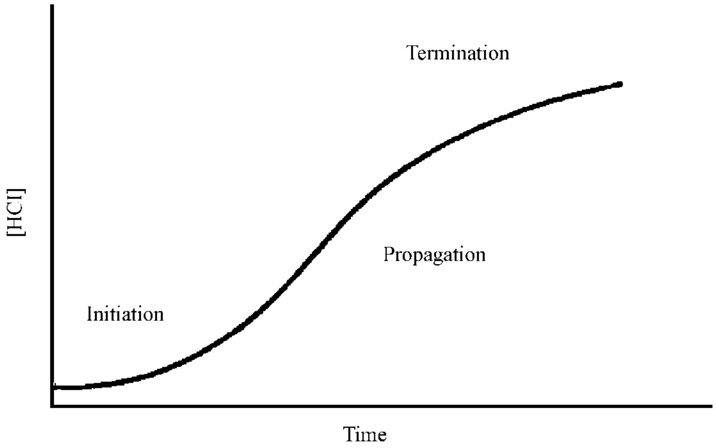


Fig. 1. Hydrogen chloride evolution for the thermal degradation of a typical vinylidene chloride polymer.

principal defect structure (allylic dichloromethylene units) responsible for degradation [21,22]. Thermal homolysis of an allylic carbon–chlorine bond generates a tight carbon chlorine radical pair. The chlorine atom most generally abstracts an adjacent hydrogen atom to extend the unsaturation by one unit, to regenerate an allylic dichloromethylene group, and to propagate the dehydrochlorination reaction. This is outlined

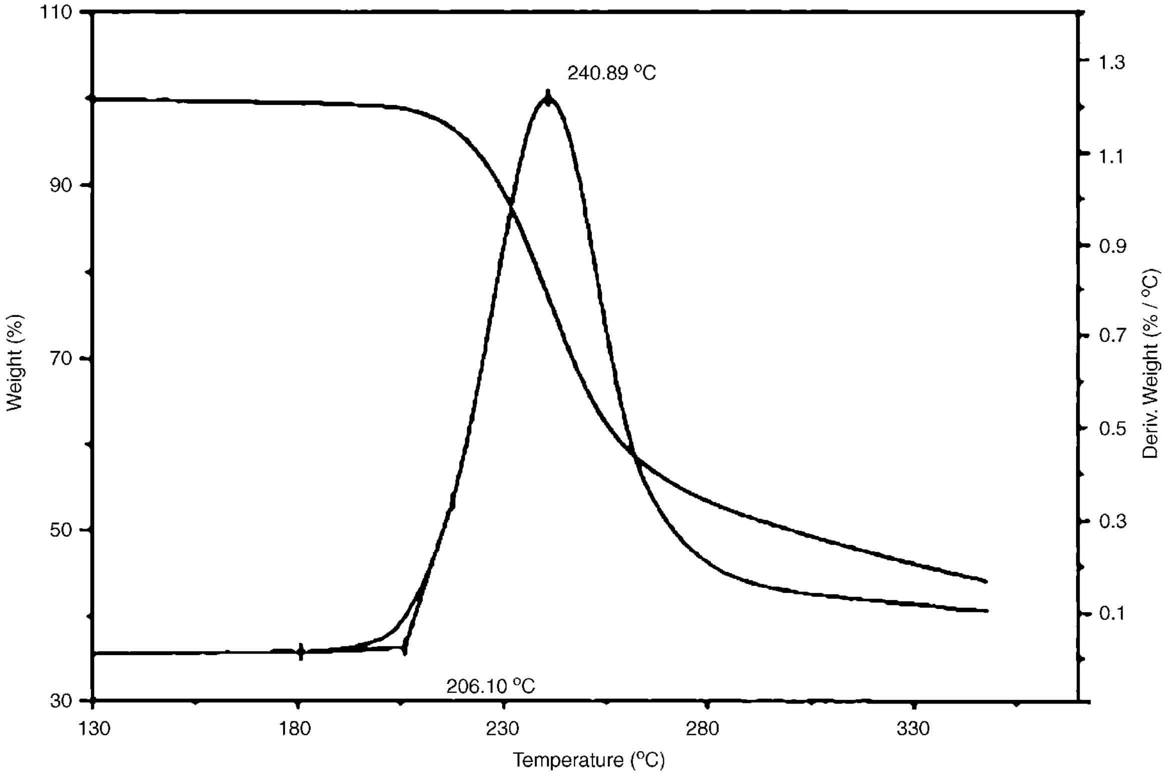


Fig. 2. Thermogram for the degradation of a typical vinylidene chloride polymer.

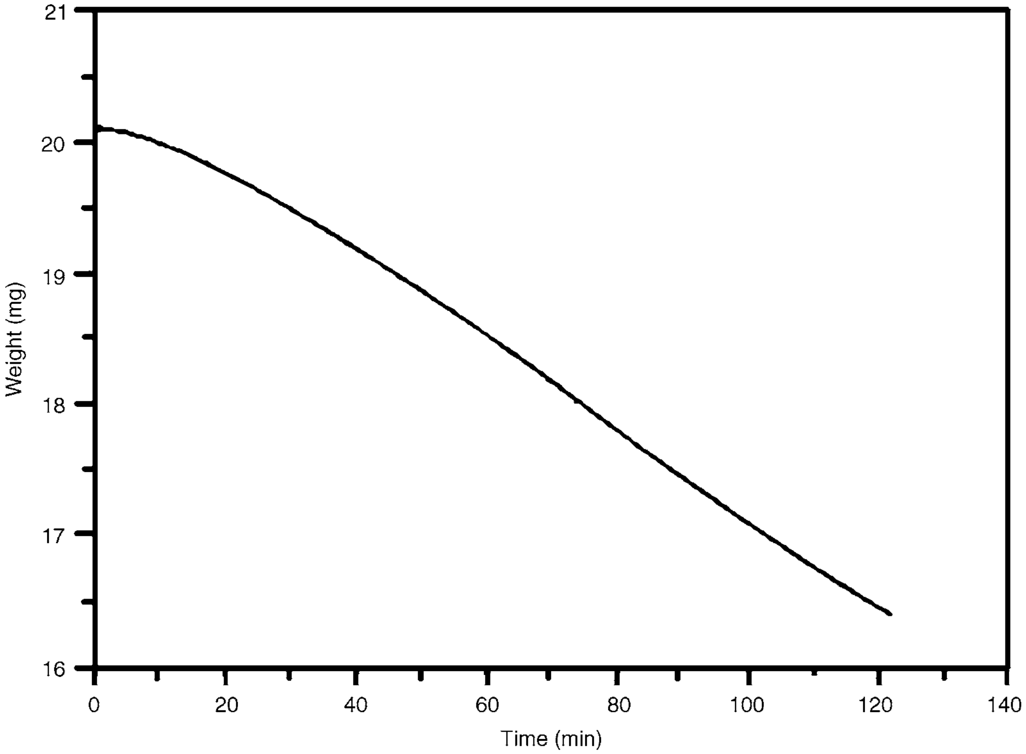


Fig. 3. Degradation of a typical vinylidene chloride polymer at 180 °C.

in Scheme 1. The consequence of sequential dehydrochlorination is the formation of conjugated polyene sequences of sufficient size to absorb in the visible portion of the electromagnetic spectrum. This leads to the development of color which may be aesthetically unpleasing in an item of packaging. For this reason degradation during processing must be controlled. Effective stabilization strategies depend on a detailed understanding of the degradation mechanism.

A profile for the evolution of hydrogen chloride accompanying the degradation of a typical vinylidene chloride polymer is displayed in Fig. 1. This reaction is ideally suited for study by TG since the only process occurring at modest temperatures (120–200 °C) is the loss of hydrogen chloride, i.e. no other volatile products are formed at these temperatures [2]. Therefore, the rate of change of sample mass accurately reflects the rate of degradation. A thermogram for degradation of a typical vinylidene chloride polymer as a function of temperature is shown in Fig. 2. As can be seen degradation becomes prominent as the temperature approaches 200 °C and occurs smoothly to reflect the loss of hydrogen chloride from each vinylidene chloride mer unit in the polymer. The thermogram for isothermal degradation of the same polymer at 180 °C is displayed in Fig. 3. Both the initiation and propagation phases of the degradation are apparent in this plot. These regions are even more obvious in a plot of $\ln((w_\infty - w_0)/(w_\infty - w_t))$ versus time, where w_∞ is the weight of the sample at infinite time (t_∞) taken as that weight that remains after 37.62% of the initial vinylidene chloride component weight (corresponding to the complete loss of 1 mol of hydrogen chloride per vinylidene chloride unit in the polymer) has been lost; w_0 the weight at time zero (t_0), i.e. the time at which the first data point was recorded and w_t is the weight at any time t, during the run. This is illustrated in Fig. 4. Rate constants for both initiation (k_i) and propagation (k_p) may be obtained from the appropriate linear portions of this plot. This is illustrated in Figs. 5 and 6 in which portions of the data presented in Fig. 4 are replotted. It might be noted that an excellent

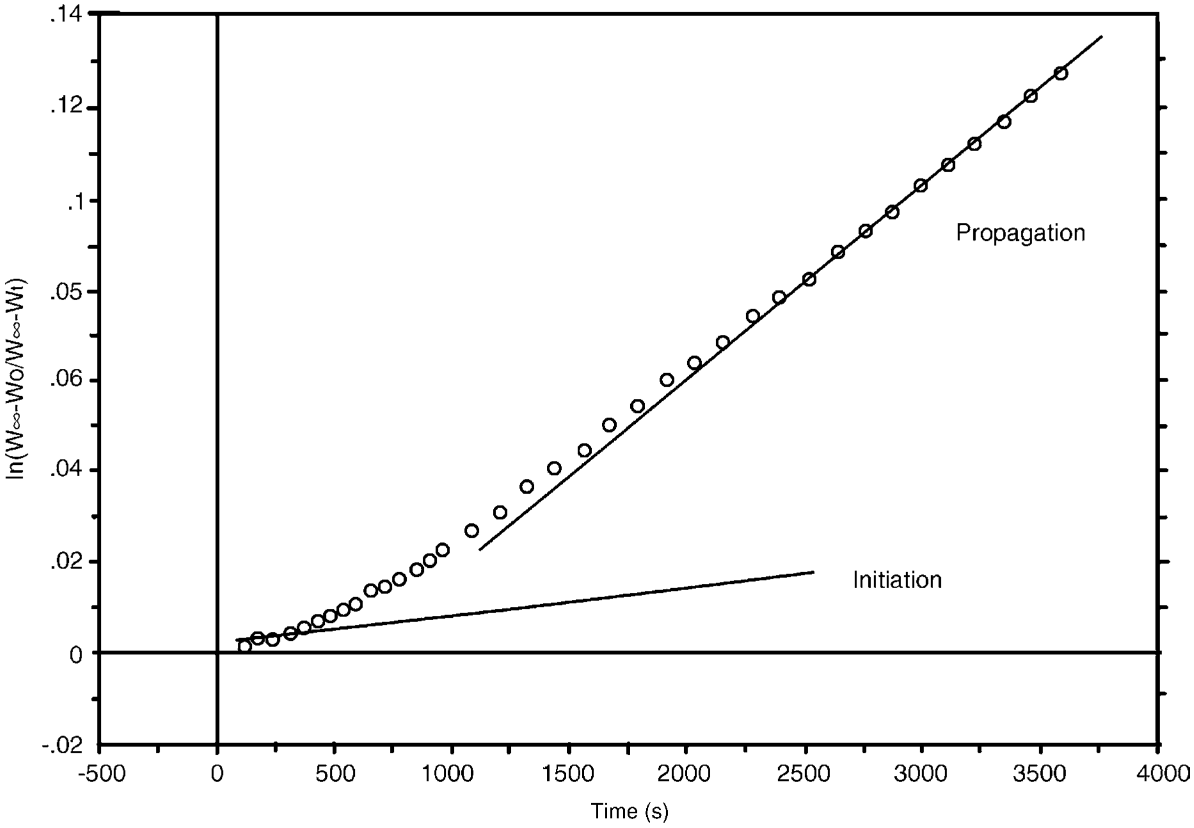


Fig. 4. Thermal degradation of a typical vinylene chloride polymer at 180 °C.

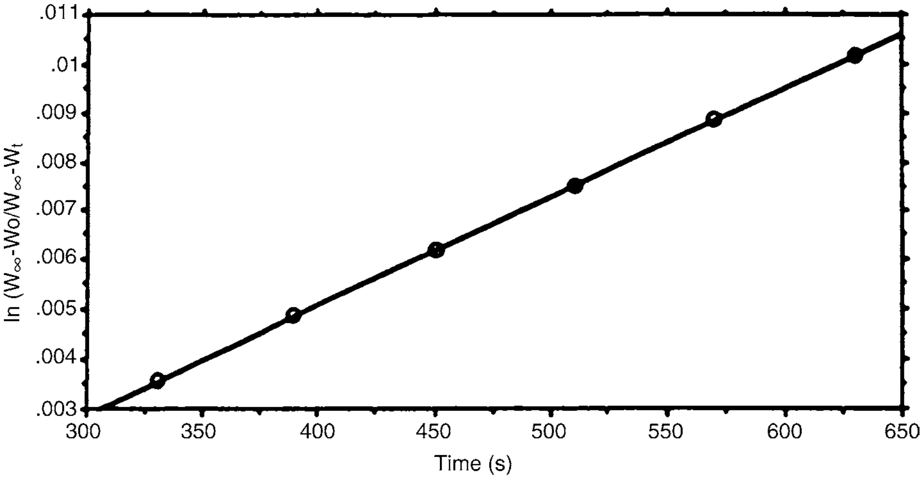


Fig. 5. Initiation rate constant (k_i) for the thermal degradation of typical vinylidene chloride polymer at 180 °C.

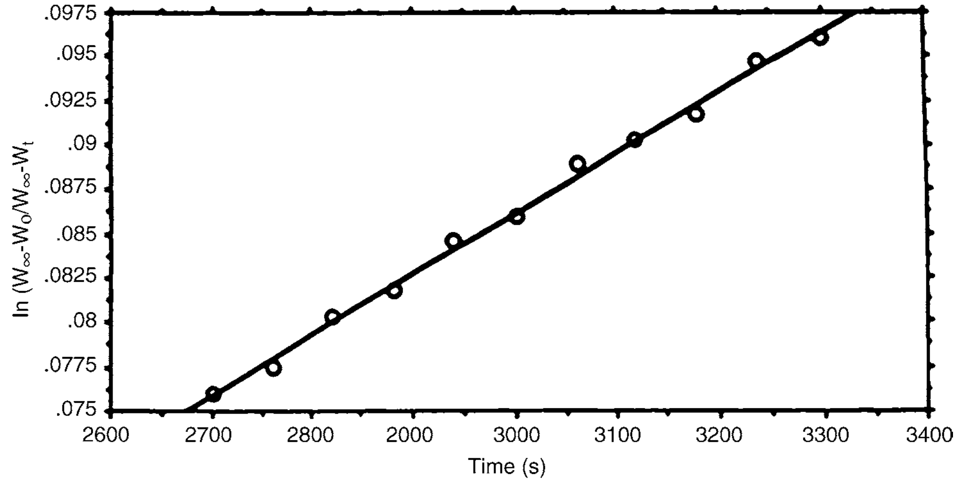


Fig. 6. Propagation rate constant (k_p) for the thermal degradation of a typical vinylidene chloride polymer at 180 °C.

least squares fit is obtained in both cases. In practice, data for multiple runs are plotted and the average reported as the rate constant [2,14–16,21,22]. This permits a ready assessment of the uncertainty in the value for the rate constant. Reproducibility is typically excellent. Determination of rate constants at several temperatures (e.g. 170, 180, 190 and 200 °C) provides the data needed for the construction of a plot of $\ln(k/T)$ versus $1/T$ (where k is the rate constant and T is the corresponding Kelvin temperature) and the extraction of the enthalpy of activation ($\Delta H^{\ddagger}$) [16]. Values for an activation energy may also be obtained by a variety of variable temperature techniques [13]. For this particular reaction which is well-defined, uncomplicated by competing processes and for which reaction variables can be carefully controlled, the variable temperature approaches yield good approximations of the value obtained as described above. However, even for this very well-defined process the values obtained using the variable temperature procedures are never as reflective of the true activation energy as those obtained from isothermal determinations of rate constants at several temperatures. These observations have recently been directly confirmed [23]. The stability of a vinylidene chloride copolymer used for coating poly(propylene) was assessed using both dynamic and isothermal thermogravimetric techniques.

In particular, activation energy values for propagation of the degradation reaction obtained from the two approaches were compared. Using the isothermal method rate constants (k_p) were obtained at 190, 200, 210 and 220 °C and used to construct the corresponding temperature dependence plot from which an activation energy of 28.2 kcal/mol was extracted. Variable temperature techniques provided an average value for the activation energy of approximately 29.6 kcal/mol. The value obtained using variable temperature methods was 1.5 kcal/mol larger than that obtained using the isothermal method and contained much larger uncertainty. It was concluded that, “the isothermal method resulted in data plots showing significantly less scatter than those produced from dynamic data and although it is the more time-consuming technique it represents the more reliable approach”.

3. Conclusions

The degradation of vinylidene chloride polymers represents an ideal reaction for study using thermogravimetric techniques. Degradation corresponds to a single, well-defined process—the elimination of hydrogen chloride—such that mass loss as a function of time provides a direct reflection of the rate of degradation. Because this process is so well-behaved, it provides a good vehicle for an evaluation of the relative merits of various approaches to the extraction of kinetic parameters from thermogravimetric data.

It has been demonstrated that the isothermal method which involves the determination of rate constants at several temperatures and the construction of a plot of ln(*k*/*T*) versus 1/*T* for the extraction of the activation energy is clearly superior to any of several variable temperature approaches for obtaining the same quantity.

Acknowledgements

Funding from the Michigan Research Excellence Fund for the establishment of the Center for Applications in Polymer Science is gratefully acknowledged.

References

[1] W. Schnabel, Polymer Degradation: Principals and Practical Applications, Hanser International, Munich, GDR, 1981.
[2] B.A. Howell, Thermochim. Acta 148 (1989) 375.
[3] J.H. Flynn, L.A. Wall, Polym. Lett. 4 (1966) 323.
[4] T. Ozawa, Bull. Chem. Soc. Jpn. 38 (1965) 1881.
[5] J. Rouquerol, Bull. Soc. Chim. (1964) 31.
[6] F. Paulik, J. Paulik, Anal. Chim. Acta 56 (1971) 328.
[7] R.N. Mukherjee, V.S. Vijaya, P.K. Gogoi, Thermochim. Acta 57 (1982) 387.
[8] J.D. Cooney, M. Day, D.M. Wiles, J. Appl. Polym. Sci. 28 (1983) 2887.
[9] J.H. Flynn, J. Therm. Anal. 34 (1988) 367.
[10] P.S. Gill, S.R. Sauerbrunn, B.S. Crowe, J. Therm. Anal. 38 (1992) 255.
[11] I.M. Salin, J.C. Seferis, J. Appl. Polym. Sci. 47 (1993) 847.
[12] S. Sauerbrunn, P. Gill, Am. Lab. 26 (1) (1994) 29.
[13] B.A. Howell, B.B.S. Sastry, Thermochim. Acta 340 (1999) 311.
[14] B.A. Howell, Z. Ahmed, S.I. Ahmed, Thermochim. Acta 357 (2000) 103 and previous papers in the series.
[15] B.A. Howell, B.S. Warner, C.V. Rajaram, S.I. Ahmed, Z. Ahmed, Polym. Adv. Technol. 5 (1994) 485.
[16] B.A. Howell, C.V. Rajaram, J. Therm. Anal. 40 (1993) 575.
[17] S. Collins, K. Yoda, N. Anazawa, C. Birkinshaw, Polym. Degrad. Stability 66 (1999) 87.
[18] G. Strandburg, P.T. Delassus, B.A. Howell, in: S.J. Risch, J.H. Hotckiss (Eds.), Food and Packaging Interactions II, American Chemical Society, Symposium Series No. 473, Washington, DC, 1991 (Chapter 12).
[19] P.T. Delassus, W.E. Brown, B.A. Howell, in: A.L. Brody, K.S. Marsh (Eds.), Encyclopedia of Packaging Technology, 2nd Edition, Wiley, New York, 1997, pp. 958–961.
[20] P.T. Delassus, G. Strandburg, B.A. Howell, Tappi J. 71 (1988) 177.
[21] B.A. Howell, J. Polym. Sci., Polym. Chem. Ed. 25 (1987) 1681.
[22] B.A. Howell, P.T. Delassus, J. Polym. Sci., Polym. Chem. Ed. 25 (1987) 1697.
[23] M.D. Wright, G.C. Lees, S.J. Hurst, Thermochim. Acta 263 (1995) 51.