Journal of Thermal Analysis and Calorimetry, Vol. 58 (1999) 201-214

THE USE OF ADIABATIC CALORIMETRY FOR THE PROCESS ANALYSIS AND SAFETY EVALUATION IN FREE RADICAL POLYMERIZATION

G. Maschio[1*], *J. A. Feliu*[2], *J. Ligthart*[2], *I. Ferrara*[1] *and C. Bassani*[2]

[1]Dipartimento di Chimica Industriale, Universitŕ di Messina, Salita Sperone 31
98166 Sant'Agata di Messina (ME), Italy
[2]Safety Technology Institute, Joint Research Center of the European Commission, T.P. 680
21020 Ispra (VA), Italy

Abstract

Adiabatic calorimetry is a technique that has been introduced as an important approach to hazard evaluation of exothermically reactive systems. In this paper the free radical polymerization of methyl methacrylate (MMA) has been studied. One of the most important aspects of MMA polymerization is its exothermicity and autoaccelerating behaviour, these characteristics can generate the occurrence of a runaway reaction.

In a runaway situation the reacting system is close to adiabatic behaviour because it is unable to eliminate the heat that is being generated. An even worse situation can be reproduced in the laboratory with the Phi-Tec pseudo-adiabatic calorimeter. Process design parameters that are usually calculated from thermodynamic data or using semiempirical rules, such as adiabatic temperature rise or maximum attainable pressure, can be directly determined.

The existence of the ceiling temperature has been experimentally demonstrated.

Keywords: adiabatic calorimetry, hazard evaluation, polymerization, runway reaction, safety

Introduction

Potential hazards associated with the thermal behaviour of chemical processes require that an accurate stability analysis should be carried out to assure safe processing, handling and storage of reagents and products. One essential aspect of a thermal-stability hazard evaluation is the development of a methodology of thermal analysis using different calorimetric techniques.

An uncontrolled process of self-heating in the operation of the chemical reactor can generate the occurrence of a 'runaway reaction' or 'thermal explosion'. In general, the majority of accidents involving runaway reactions are associated either with human error or with the failure of controls and safe-guards. However in many cases accidents are generated because of inadequate provision for heat removal when increasing plant size from laboratory scale to production scale. It has been remarked

---

[*] Author for correspondence: e-mail: maschiog@.unime.it

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

that a reaction may not be recognised as particularly exothermic when conducted on a laboratory scale.

Bowes [1] judged that 20 per cent of explosions or uncontrolled releases in batch processes were associated with apparent ignorance of the self-heating hazard. Moreover, it is known that polymerization reactions are characterised by strong exothermicity, which is often accompanied by autoaccelerating kinetics that can lead the system to uncontrollable situations. Acrylate and methacrylate monomers are, in general, highly reactive and release considerable heat that can generate a significant pressure increase during uncontrolled polymerization reactions (runaway reaction). Therefore, runaway polymerizations have the potential to inflict considerable damage if appropriate emergency measures are not in place.

In the past, some accidents caused by runaway have occurred in polymerization plants [2]. From an analysis of case histories, the development of incidents, in many cases, is found to be due to a lack of understanding of the process chemistry and thermodynamics and poor reactor design.

Adiabatic calorimetry is a technique that has been introduced as an important approach to the hazard evaluation of exothermic reactive chemicals. It can be used to simulate and to study self-heating phenomena that can initiate thermal runaway reactions. A key feature in the design of the device is that it maintains the sample in a near-perfect adiabatic environment. A single adiabatic experiment can provide much thermokinetic data which are applicable to the design of batch reactors, safe processing, storage and transportation of chemicals and mixtures [3].

Adiabatic calorimetry provides information such as the rate of temperature and pressure increase and the overall reaction rate. Additional information obtained from adiabatic runs permits the calculation of the relief capacity needed to prevent damage following a runaway. Some commercial adiabatic calorimeters are available. The accelerating rate calorimeter ARC^{TM} [4] represents one of the most commonly used apparatus; with the ARC it is possible to follow a runaway reaction under adiabatic conditions. However, one of its major disadvantages is the relatively high heat capacity of the sample bomb. PHITEC II (H.E.L.) [5, 6] and RSST [7, 8] represent two pseudoadiabatic calorimeters characterised by a low heat capacity sample cell. The use of an apparatus with a low thermal inertia presents some advantages and is recommended by the AIChE's Design Institute for Emergency Relief Systems (DIERS) [9].

In the evaluation of the adiabatic temperature rise the thermal inertia of the sample cell play an important role. The cell acts as a heat sink, absorbing part of the heat from the sample. A commonly calculated quantity is the so-called Φ-factor which is defined as:

$$\Phi = \frac{m_s c_{ps} + m_c c_{pc}}{m_s c_{ps}} = 1 + \frac{m_c c_{pc}}{m_s c_{ps}} = \frac{(\Delta T_{ad})_{theor}}{(\Delta T_{ad})_{obs}} \quad (1)$$

where m_s and m_c are the masses of the sample and the cell respectively. The Φ-factor is a direct measure of the fraction of the heat released by the reaction converted into sensible heat of the sample cell. In an adiabatic calorimeter with a high value of the Φ-factor the observed adiabatic temperature rise is lower than the theoretical value.

In this paper the free radical polymerization of methyl methacrylate (MMA) has been studied. One of the most important aspects of MMA polymerization is its exothermicity and autoaccelerating behaviour [10–12]. During the reaction, large quantities of heat are released which must be either removed by a coolant or dissipated to the surroundings in order to avoid a thermal excursion that could accelerate the process and initiate an uncontrollable runaway event. In a runaway situation the reacting system is close to adiabatic behaviour because it is unable to eliminate all the heat that is being generated. An even worse situation, almost completely adiabatic conditions, can be reproduced in the laboratory with the Phi-Tec pseudo-adiabatic calorimeter based on the compensation of heat loss. Process design parameters that are usually calculated from thermodynamic data or using semiempirical rules, such as adiabatic temperature rise or maximum attainable pressure, can be directly determined.

Laboratory tests were designed in order to determine experimentally the limitation in the adiabatic temperature rise due to the ceiling temperature effect [13, 14].

Complimentary results obtained using different calorimetric techniques such as DSC and TGA are presented in this paper.

Experimental

Purification of materials

The initiators used in this study, (AIBN: 2,2'-azo-bis-isobutyronitrile, BPO: Benzoyl peroxide (Fluka, Switzerland), PKD26: Perkadox 26, PKDBC: Perkadox BC, TGNB: Trigonox B and TBNK80: Trigonox K-80 (AKZO, Holland)) were recrystallized from ethanol.

Methylmethacrylate (MMA) stabilised with 0.0025% hydroquinone (Fluka, Italy) was washed twice with 5%(w/v) aqueous sodium hydroxide solution and later three times with distilled water. After drying over anhydrous sodium sulphate and filtering through a silicone filter paper, the monomer was degassed with nitrogen and used immediately.

Reacting solutions were prepared at an initiator concentration of 0.05 M by weighing the initiator and dissolving it in the monomer. Solutions were degassed again and used immediately.

Differential scanning calorimetry

The bulk isothermal polymerization of MMA was investigated using a differential scanning calorimeter (Perkin Elmer Model DSC-7). Samples of solutions were weighed (35–50 mg) into DSC sample pans and sealed. In order to find any mass loss, sample pans were weighed before and after each experiment. Indium was used as the calibrant for enthalpy and temperature measurements.

All kinetic data were obtained in isothermal experimental runs. The samples were heated from a temperature of 303 K to the desired isothermal polymerization temperature at a rate of 40 K min^{-1}. In order to take the reaction to complete conversion, it was necessary to carry out a temperature scan up to 453 K once the isothermal run was finished. The enthalpies of polymerization were calculated by integrating the area between the DSC curves and the baseline established by extrapolation from the trace produced after complete (equilibrium) polymerization.

Thermogravimetric analysis

The depolymerization of poly-methylmethacrylate (PMMA) was investigated using a Thermogravimetric Analyser TGA 2950 (T.A. Instruments). In particular, the High Resolution TGA (HR-TGA) technique was used to improve the transition resolution and then to determinate the ceiling temperature. In the Hi-Res TGA technique the system varies the heating/cooling rate of the furnace in response to changes in the rate of decomposition of the sample in such a way as to maintain a pre-selected constant mass loss rate (% min^{-1}). As this rate increases the heating rate is decreased and vice versa. This allows the precise determination of temperature of the onset of the transition.

A sample of poly-methylmethacrylate (20 mg) (MMW PMMA - Sigma Aldrich) was placed in a platinum pan and was loaded into the TG furnace. A flow of 100 $\mathrm{cm}^3\ \mathrm{min}^{-1}$ of an inert gas (N_2) was used to control the sample atmosphere during TG experiment. The purge gas was distributed separately to two parts of TG: 60 percent to the furnace and 40 percent to the balance chamber. The sample was heated to 373 K and kept at this temperature for 5 min to dry it and then was heated to 773 K using a maximum rate of 10 K min^{-1} and a resolution of 5 K.

Adiabatic calorimetry

A Phi-Tec calorimeter HEL, UK) was used to carry out the pseudo-adiabatic measurements of the bulk polymerization of MMA. Samples of around $6\cdot10^{-5}$ m^3 were weighed and then introduced into the previously evacuated reactor which consisted of a stainless steel stirred vessel ($V\mathrm{r}=10^{-4}$ m^3). A small impeller was placed inside the cell and driven by an electric motor. In our experimental runs a typical value of the Φ-factor is 1.08–1.12. This value is acceptably low, therefore the experimental data can be expected to mimic results expected from a plant scale runaway without the need for extrapolation. Figure 1 shows the Phi-Tec experimental apparatus. Samples were heated to the desired initial temperature and then allowed to react until no increase in temperature was detected. During the course of an experiment the temperature and pressure inside the vessel were measured, the system was maintained in pseudo-adiabatic conditions using a sophisticated control system based on the compensation of the heat losses. The rates of change of temperature and of pressure were also monitored and stored. This data, after appropriate processing, can be used to execute a further analysis. In particular the heat rate generated by the reactions, the reaction rate, the conversion and a pseudo-first order rate constant can be determined.

At the end of each experiment, final conversions were determined gravimetrically. The reactor was opened, polymer and unreacted monomer were dissolved in acetone and polymer was reprecipitated with methyl alcohol. After solvent evaporation and solid drying, mass difference gave the percent of monomer reacted.

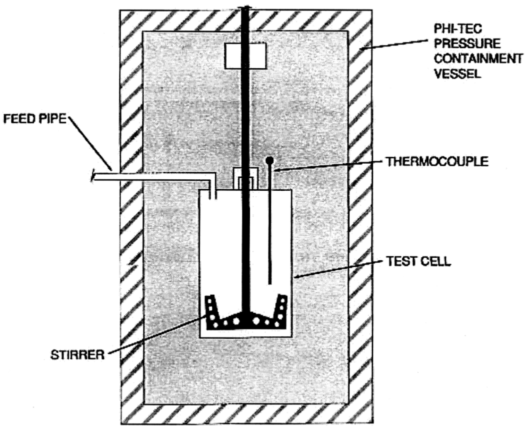

Fig. 1 Phi-Tec experimental apparatus

Experimental results

Differential scanning calorimetry

In a previous work [15], an extensive kinetic study of the polymerization of MMA has been carried out using a differential scanning calorimeter operating under isothermal conditions, in this way some characteristic parameters of the bulk polymerization of MMA initiated by AIBN were determined. In the absence of diffusion limitations, the apparent first order constant was estimated for temperatures ranging from 338 to 368 K.

The main results can be summarised by averaging the values obtained for the heat of reaction and calculating the temperature dependence of the apparent first order constant:

$$\Delta H_p = -57.2 \pm 0.6 \text{ kJ mol}^{-1}\text{MMA}$$

$$k_{app} = 4.1 \cdot 10^9 \exp\left(\frac{-10^4}{T}\right)\frac{l^{1/2}}{\text{mol}^{1/2}\ \text{s}}$$

Conversions were always higher than 90% for all the temperatures tested.

Adiabatic calorimetry

Later studies, focused on hazard evaluations, permitted the use of adiabatic calorimetry to determine the temperature rise due to the consumption of all of the reactants. The adiabatic temperature rise, ΔT_{ad}, can be calculated from thermodynamic data:

$$T_{\mathrm{ad}} = T_0 + \frac{m(-\Delta H_{\mathrm{p}})}{MC_{\mathrm{p}}} \tag{2}$$

where T_{ad} is the adiabatic temperature, T_0 is the initial temperature, ΔH_{p} is the heat of polymerization, m the initial amount of monomer, and M and C_{p} the mass and the heat capacity of the reacting system.

A maximum temperature rise of 260 K is possible for the bulk MMA polymerization [14]. In the Phi-Tec calorimeter the reacting mass was kept under pseudo-adiabatic conditions to allow it to react completely without heat limitations. Nevertheless, it is known that at very high temperatures polymethylmethacrylate begins to decompose into shorter fragments. Dainton and Ivin (1958) [13] have defined the ceiling temperature (T_{c}) as the temperature at which the rate of depolymerization equals the rate of chain propagation. Under conditions of equilibrium propagation-depolymerization, the ceiling temperature may be expressed as:

$$T_{\mathrm{c}} = \frac{\Delta H_{\mathrm{p}}}{(\Delta S_{\mathrm{p}}^0 + R\ln(M))} \tag{3}$$

where ΔS_{p}^0 is the entropy of the reaction, R is the gas constant and $[M]$ is the concentration of monomer.

In an adiabatic experiment, with no heat exchange with the surroundings, and assuming first order kinetics, the temperature increases linearly with conversion. Due to this increase of temperature, the free volume of the system also increases and the critical values at which the diffusive control of polymerization starts are reached later, and higher conversions can be achieved without diffusion problems arising. So the kinetic data obtained are not affected by diffusion control.

As mentioned in the experimental section, the temperature and pressure of the reacting mass were continuously monitored during the experiments. Their rate of change with time were also stored. Typical plots of the raw data obtained during the course of an experiment is showed in Fig. 2. An initial experiment was performed using AIBN as initiator and starting at 308 K and with an initial initiator concentration of 0.05 M. The maximum temperature reached by the system during an experimental run was 477±1 K. This value is far from the theoretical value of the maximum adiabatic temperature (308+260=568 K) predicted on the basis of the thermodynamic data. This temperature increase corresponds to a MMA conversion of about 65%.

The effect of the initial AIBN concentration on the reaction development was also checked. Three different initial concentrations were tested, 0.02, 0.05 and 0.075 M. In all cases, the temperature increase is lower than the theoretical thermodynamic value, this fact indicates that the conversion of the polymerization it is incomplete. This is due to kinetic and thermodynamic factors that indicate the existence of a ceiling temperature as discussed below.

Further experimental investigations will be carried out in order to determine the relationship between the maximum temperature increase and the ceiling tempera-

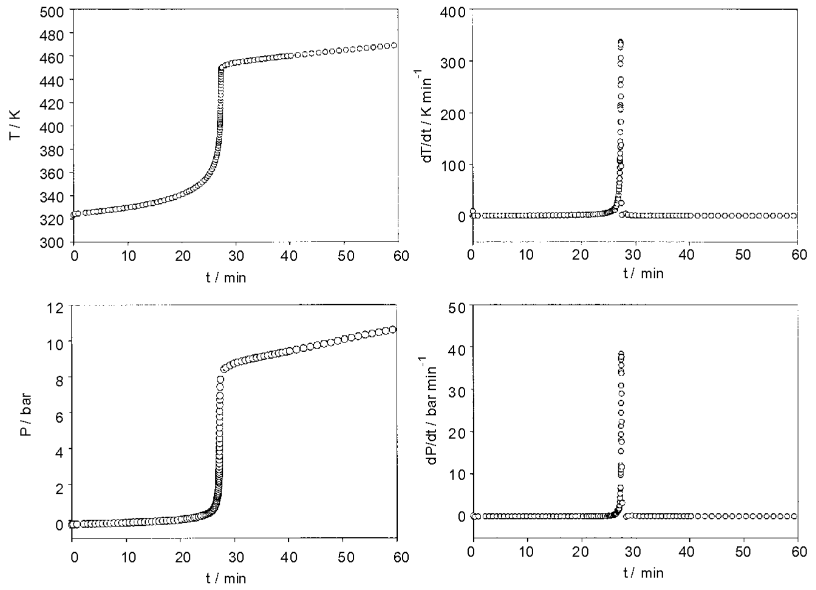

Fig. 2 Plot of the raw data obtained during the course of a Phi-Tec experiment. Initiator AIBN 0.05 M

ture. Lab tests were designed in order to determine experimentally the limitation in the adiabatic temperature rise due to the ceiling temperature effect. Different initiators have been used. They have been chosen with different half life times and different maximum temperature of operation in order to cover a broad range of possible situations.

The temperature and pressure evolution of the reacting systems depends on the kind of initiator used as shown in Figs 3a and 3b respectively. The rate of temperature increase or self-heating rate, proportional to the heat fluxes were also monitored by the calorimeter and are presented, *vs.* temperature, in Fig. 4. Due to the time response of the controller, and its self-adapting behaviour, the heat flux curves show more noise than the temperature curves. The heating rate initially increases linearly with conversion, but as higher temperatures are reached the contribution of the depolymerization becomes more and more important until the equilibrium limit represented by the ceiling temperature is reached.

Two different initial temperatures were used for the six initiators tested depending on the initiator decomposition temperature. The shape of the curve shows that MMA had already begun to react at 323 K when initiated with PKD26. The initiator PKD26 decomposes faster than the other initiators, and was completely consumed, before the ceiling temperature was reached. Nevertheless, very high rates of temperature increase (that can be considered as equivalent to reaction rate, as later will be demonstrated) were measured and the reaction went to completion with no other limitation than PKD26 consumption. AIBN and BPO, having higher decomposition

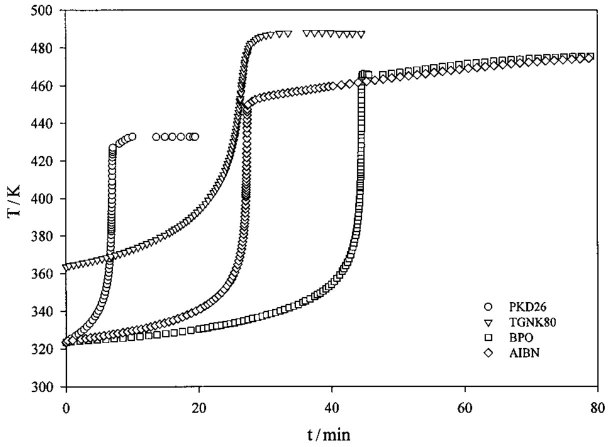

Fig. 3a Temperature *vs.* time for some initiators tested

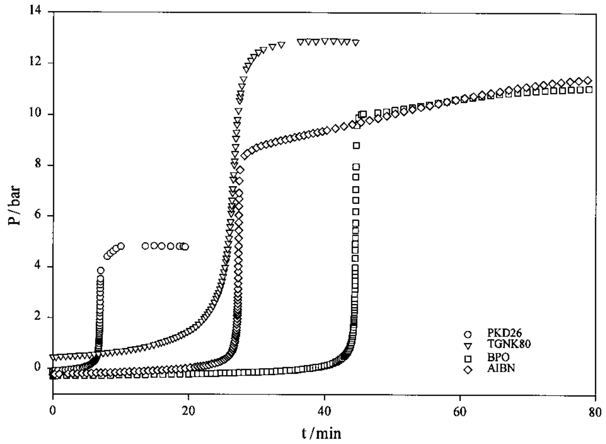

Fig. 3b Pressure *vs.* time for some initiators tested

temperatures, began to react later, reached reaction rates close to that of PKD26 and both stopped at about the same temperature and reached approximately the same maximum reaction rate. When a set of initiators with longer half lives was used (PKDBC, TGNB, TGNK80), a different kind of limitation was detected. Slightly higher temperatures were reached by the reacting masses, but the rates of temperature increase were one order of magnitude lower showing that the system was limited by something other than initiator consumption. The data obtained serves as a starting point for further analysis.

Temperature and heat flux data can be transformed into conversion and reaction rate applying the following transformations:

$$X=\frac{T-T_0}{\Delta T_{\mathrm{ad}}} \tag{4}$$

$$r_p = \frac{dX}{dt} = \frac{1}{\Delta T_{ad}} \frac{dT}{dt} \tag{5}$$

where X is conversion and r_p reaction rate. A first period with a linear increase of the reaction rate is detected, and a pseudo-first order kinetic constant can be determined and its temperature dependence calculated using the Arrhenius equation. The values of final conversion calculated from the previous equation are very close to the experimental values determined gravimetrically.

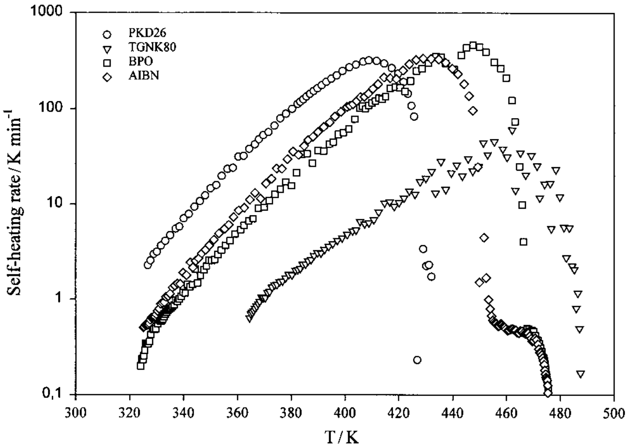

Fig. 4 Logarithmic plot of heat rate *vs.* temperature for some initiators tested

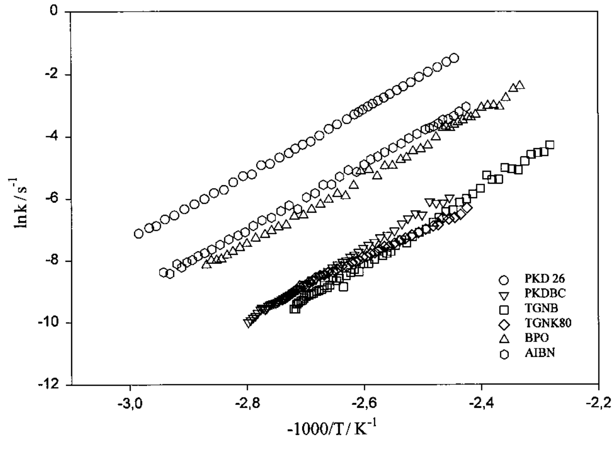

Fig. 5 Arrhenius plot obtained for each initiator

The local rate of temperature rise and overall temperature increase may be used to determine a pseudo-first order rate constant, k, calculated by the equation:

$$k = \frac{\mathrm{d}T/\mathrm{d}t}{(T_{\mathrm{max}} - T)} \tag{6}$$

where T_{max} is the maximum recorded temperature. The evaluation of Arrhenius constants for the polymerization reaction has been carried out in the range of temperature where the heat rate increases linearly with temperature using a first order linear regression of ln*k* *vs.* $-1000/T$ plot. In this range of temperature the contribution of depolymerization reaction can be neglected and the calculated rate constant is the polymerization rate constant. Figure 5 shows the Arrhenius plot obtained for each initiator. Table 1 shows the experimental values of the overall kinetic constant and the results obtained when fitting the Arrhenius' equation parameters.

Table 1 Arrhenius' equation parameters and final conversions obtained for the initiators used

Initiator	Pseudo-first order rate constant k		Initiator decomposition rate constant k_d^a		Final conv.
	$\ln A$	E_aR^{-1}/K	$\ln A$	E_aR^{-1}/K	
AIBN	22.4	10520	29.7	13506	0.65
Benzol peroxide (BPO)	22.6	10740	28.7	13618	0.60
Perkadox 26 (PKD26)	24.3	10560	38.8	15862	0.49
Perkadox BC (PKDBC)	23.3	11880	27.5	14446	0.64
Trigonox B (TGNB)	22.9	11940	29.8	15725	N.D.[b]
Trigonox K-80 (TGNK80)	15.6	9040	N.D.[b]	N.D.[b]	0.59

[a] AKZO-Product Catalog

[b] N.D.: not determined

Thermogravimetric analysis

A final measurement, in order to confirm the ceiling temperature, was performed on a TG apparatus. A sample of PMMA was tested for its thermal decomposition. Figure 6 shows the results of a thermogravimetric experiment where at 476 K an endothermic process begins that can only be related to the decomposition of PMMA into monomer molecules. The value of the temperature of the onset of this thermal decomposition is very close to the ceiling temperature determined in the pseudo-adiabatic runs carried out in the Phi-Tec.

The similarity of the decomposition and ceiling temperatures is a possible explanation of why PMMA is one of the polymers that can be recovered in near 90% of monomer by thermal decomposition.

Discussion

Figure 7 shows the curves of $\ln r_p$ *vs.* $1/T$ obtained in adiabatic runs using different initiators. At lower temperatures the overall Gibbs free energy change (ΔG) is

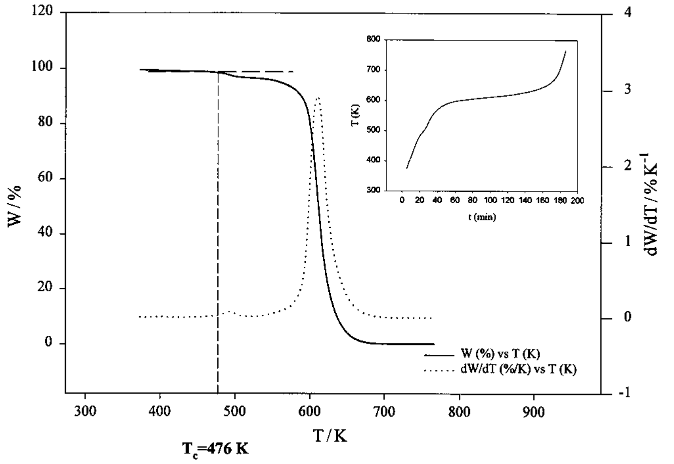

Fig. 6 Thermal decomposition of PMMA

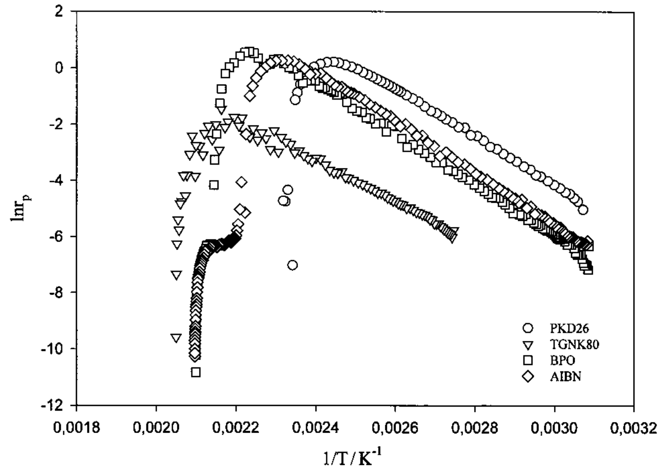

Fig. 7 Logarithmic plot of the overall reaction rate *vs.* $1/T$ obtained in pseudo-adiabatic runs using different initiators

negative and the polymerization is thermodynamically feasible. These conditions favour the formation of polymer and the polymerization rate increases as temperature increases. In this temperature range $\ln r_p$ increases about linearly with $1/T$ following the Arrhenius low. At higher temperature the depolymerization reaction becomes more important and the ΔG becomes less negative. The overall polymerization rate reach a maximum and then decreases. When the overall polymerization rate is zero the ceiling temperature is reached.

From the analysis of adiabatic runs the existence of a ceiling temperature of about 220°C is confirmed. If both the propagation and depropagation reactions are treated as radical reactions the overall rate expression depends on the kinetic rate constants of propagation (k_p) and depropagation (k_{dp}) and on the concentration of monomer $[M]$ and free radical $[P^o]$:

$$r_p = k_p[P^o][M] - k_{dp}[P^o] \tag{7}$$

at the ceiling temperature, r_p=0 and so:

$$\frac{k_p}{k_{dp}} = \frac{1}{[M]_c} \tag{8}$$

where $[M]_c$ is the equilibrium monomer concentration. The ceiling temperature can be described as the intersection of the propagation and depropagation rate curves. The dependence of the overall rate of free radical formation shows that a certain dependence of the value of the ceiling temperature on the type of initiator can be assumed.

During the pseudo-adiabatic runs carried out in the Phi-Tec calorimeter a strong increase in the pressure has been observed, when the temperature approaches the ceiling temperature the rate of increase in pressure is reduced. The ceiling temperature is about 100 K lower than the theoretical maximum adiabatic temperature predicted on the basis of thermodynamic data, also the maximum value of pressure reached during the adiabatic run is lower than expected. As a consequence the presence of a ceiling temperature in the polymerization of MMA determines an intrinsic limitation on the consequences of thermal runaway in this process.

Conclusions

Laboratory tests were designed in order to determine experimentally the limitation in the adiabatic temperature rise due to the ceiling temperature effect. The existence of the ceiling temperature has been demonstrated experimentally. The fact that an intrinsic limitation to the increase of temperature and pressure, due to the ceiling temperature, exists, should permit the design of equipment with less restrictive safety specifications. In conclusion the use of adiabatic calorimetry represents a very efficient tool for obtaining a deeper knowledge of the polymerization processes finalised to a safety analysis of the process.

The experimental data, such as rate of temperature rise and rate of pressure rise, obtained using the Phi-Tec apparatus can be used in the DIERS vent sizing methodology to provide realistic equations for the design of large scale apparatus. The results obtained in this study can be also used in the building of a model, including the depolymerization process, that will be used for a parametric sensitivity analysis of the process and to execute an efficient scaling from the laboratory to an industrial reactor and to determine the onset of self-heating conditions in order to determine intrinsically safe operating conditions.

Nomenclature

c_p	heat capacity of the reacting system	$J\ kg^{-1}\ K^{-1}$
E_a	activation energy	J
k_{app}	overall polymerization rate constant	$m^{3/2}\ kmol^{-1/2}\ s^{-1}$
k_p	propagation rate constant	$m^{3/2}\ kmol^{-1/2}\ s^{-1}$
k_d	initiator decomposition rate constant	$m^{3/2}\ kmol^{-1/2}\ s^{-1}$
m	initial amount of monomer	kmol
M	mass of the reacting system	kg
r_p	rate of polymerization reaction	$kmol\ m^{-3}\ s^{-1}$
R	gas constant	$Pam^3\ mol^{-1}\ K^{-1}$
t	time	s
T_{ad}	adiabatic temperature	K
T_0	initial temperature	K
T_c	ceiling temperature	K
T_{max}	maximum recorded temperature	K
V	volume	m^3
V_r	volume of reacting system	m^3
X	conversion	dimensionless
$[P^o]$	free radical concentration	$kmol\ m^{-3}$
$[M]$	monomer concentration	$kmol\ m^{-3}$
ΔH_p	heat of polymerization	$kJ\ mol^{-1}$
ΔS_p^o	entropy of polymerization	$kJ\ K^{-1}\ mol^{-1}$
ΔT_{ad}	adiabatic temperature rise	K

* * *

The financial support of the Regione Siciliana and of the Commission of European Community (Progetto POP Sicilia) and of Italian MURST (Progetto ex 40%) is gratefully acknowledged.

References

1 B. C. Bowes, in Self-heating: evaluating and controlling the hazards, Elsevier Science Publishing Co,. New York 1984.
2 J. A. Barton and P. F. Nolan, J. Hazard. Mat., 14 (1987) 233.
3 M. Duch, K. Marcali, M. D. Gordon, C. J. Hensler and G. J. O'Brien, Plant/Operations Progress, 1 (1982) 19.
4 D. I. Townsend and J. C. Ton, Thermochim. Acta, 37 (1980) 1.
5 J. Singh, Int. Symposium on Runaway Reaction, Cambridge, MA AIChE, New York 1989, p. 313.
6 J. Singh, Thermochim. Acta, 226 (1993) 211.

7 J. C. Leung and H. K. Fauske, Thermochim. Acta, 104 (1986) 13.
8 H. K. Fauske, Proc. Safety Progress, 17 (1998) 190.
9 H. G. Fisher, Chem. Eng. Prog., 81 (1985) 33.
10 S. T. Balke and A. E. Hamielec, J. Appl. Polym. Sci., 17 (1973).
11 S. K. Soh and S. C. Sundberg, J. Pol. Sci. Chem. Ed., 20 (1982) 1299.
12 G. Maschio and C. Moutier, J. Appl. Pol. Sci., 37 (1989) 825.
13 F. S. Dainton and K. J. Ivin, Quarterly reviews, 12 (1958) 61.
14 B. M. Louie, G. M. Carrat and D. S. Soong, J. Appl. Polym. Sci., 30 (1985) 3985.
15 J. A. Feliu, C. Sottile, C. Bassani, J. Ligthart and G. Maschio, Chem. Eng. Sci., 51 (1996) 2793.