Determination of kinetic parameters for isothermal decomposition of azo initiators of polymerization by differential scanning calorimetry

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Summary: A new method for the determination of kinetic parameters for thermal decomposition of initiators of polymerisation by isothermal Differential Scanning Calorymetry (DSC) is described. This method is mainly applied to the azo initiators which exhibit a phase transition in their decomposition range. First the procedure for AIBN, taken as model, is described. Then this method is applied to two synthesized initiators: a $\alpha,\omega-$ dihydroxy azo and an $\alpha,\omega-$azo disubstitued by fluorinated groups.

Introduction

The main characteristic of aliphatic azo compound concerns their easy thermal decomposition. This produced radical is able to initiate many polymerization reactions olefin. In order to control the kinetics of this polymerization, it is required to know both the decomposition rate constant of the initiator (k_d) and its activation energy (E_a). The determination of these parameters can be performed according six methods:

The oldest and the most employed technique is volumetry (1-6). The rate constant of decomposition were determined by mesuring the nitrogen produced versus time for an azo compound at different temperatures. This shows that "k_d" is independent of the nature of the solvent and that the reaction is not complicated by induced decomposition.

Talat-Erben and Bywater (7) monitored the change in optical density in the near ultraviolet of an AIBN solution, from 70 to 105°C. Aliphatic azo compound have a symmetrical absorption band in the region of near ultraviolet with a peak at 345 mµ.

Ukida (8) studied the decomposition of the azo compound by polarography. The results are in good agreement with the other techniques but a deviation from Arrhenius plot is observed when dioxane was used as the solvent.

The fourth method is calorimetry; the principle is to determine the radicals production rate as a fonction of time, using 2,2'-diphenyl-1-picrylhydrazyl (DPPH) as reagent. However, Bevington (9) has shown that DPPH reacts with only 70% of produced radicals.
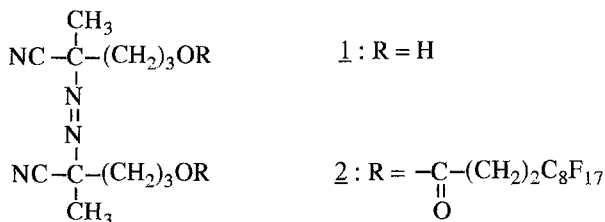
Furthermore, Bevington (10) determined the amount of incorporated radioelements in a polystyrene synthesized from a labeled AIBN (C^{14}).

Finally the most recent technique is "temperature variant" or "dynamic" DSC (11-13) described by Barrett (14). However, this method cannot be applied to certain initators which present simultaneously both a thermal decomposition and a phase transition such as the

melting (azo compounds) (15). For this reason, mathematical exploitation of exotherm of decompositon is imposible. Then, we have modified the DSC classical experimental procedure by performing for each reaction kinetical analyses of azo decomposition at constant temperatures different from the melting point. A new DSC method for measuring kinetical constants of thermic initiator decomposition at constant temperature was developped. First, this isothermal technique was investigated for AIBN, taken as reference in the "dynamic" classical method. The isothermal or "static" technique was used for two other kinds of azo initiators
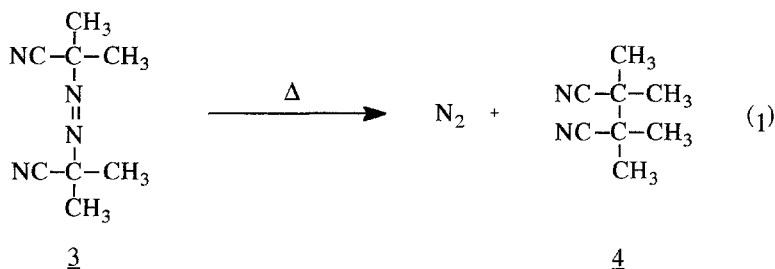
Results and discussion

The 4,4' azobis-(4-cyanopentanol) or ACP $\underline{1}$ has been studied. This compound exhibits a melting point concomitant with its decomposition For this compound classical technique of DSC in "dynamic mode" is not applicable: the exotherm of decomposition is cutted down by the melting endotherm (Figure 1). In these conditions , it is imposible to determine the heat of decomposition (ΔH), the rate constants (k_d) and the energy of activation (E_a). This fact explains that the kinetic parameters of ACP were determined so far by volumetry only.(16) A similar physical problem occured with a synthesized fluorinated compound $\underline{2}$ (17).

$$\begin{array}{l} \text{NC} - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\underset{\underset{\displaystyle CH_3}{|}}{\overset{\displaystyle |}{C}}}{\overset{\displaystyle N}{\underset{\displaystyle N}{\|}}}}{C}} - (CH_2)_3 OR \end{array} \qquad \underline{1} : R = H$$

$$\text{NC} - C - (CH_2)_3 OR \qquad \underline{2} : R = -\overset{\|}{\underset{O}{C}} - (CH_2)_2 C_8 F_{17}$$

That is the reason why the experimental procedure of "dynamic" DSC technique has been modified. In dynamic DSC, a standard aluminium sample pans containing AIBN (5-10% by weight of initiator) and di-n-butylphtalate as solvent (18-20), were heated from 50°C up to 200°C; the heating rate was 4°C/min (21-23). In order to be independant of the melting phenomenon, the isothermal decomposition of the initiator has been studied at five temperatures imposed by the "dynamic" thermogram. Five decomposition exotherms similar to that represented in Figure 2 were obtained. For each isothermal thermogram, the heat of decomposition (ΔH) and the rate constant of decomposition (k_d) where calculated (Table 1).

The heat of decomposition (ΔH) is directely determined from the ratio of the thermogram area to the quantity of used sample. It mainly corresponds to the reaction (1) since it was checked that the heating of AIBN $\underline{3}$ in toluene yields tetramethylsuccinonitrile (TMSN) $\underline{4}$ with a yield higher than 95%.

$$\text{NC} - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\underset{\underset{\displaystyle CH_3}{|}}{\overset{\displaystyle |}{C}}}{\overset{\displaystyle N}{\underset{\displaystyle N}{\|}}}}{C}} - CH_3 \xrightarrow{\ \Delta\ } N_2 \ + \ \begin{array}{l} \text{NC} - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_3 \\ \text{NC} - \underset{\underset{\displaystyle CH_3}{|}}{C} - CH_3 \end{array} \qquad (1)$$

$$\underline{3} \qquad\qquad\qquad\qquad \underline{4}$$
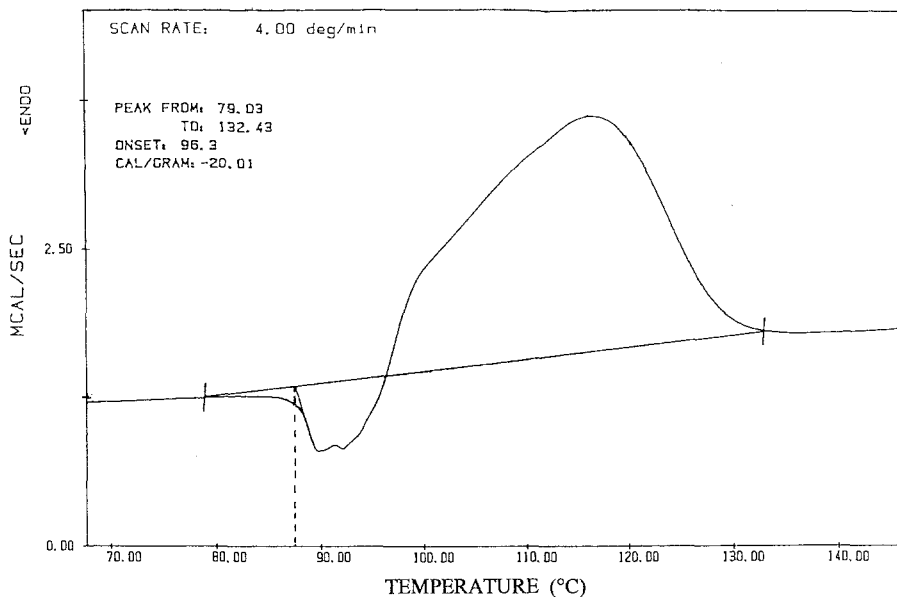
Figure 1: Differential enthalpic curve obtained for the decomposition of ACP in "dynamic" mode.

The value obtained for AIBN <u>3</u> (ΔH= - 230 kJ/mol) is in a good agreement with that obtained in "dynamic" mode (ΔH= - 213 kJ/mol). Each isothermal rate constants $(k_d)_T$ is deduced from the area under the slope during a certain time. Each calculation is characterized by a correlation rate higher than 0.995. The value of decomposition rate constants obtained for AIBN are very close to those of the litterature (24) (Table 1). This experimental mode does not point out any difference from the classical method. From Arrhenius plot, drawn from the five $(k_d)_T$ values, an activation energy (E_a=128kJ/mol) close to the dynamic one (E_a=134kJ/mol) is observed.
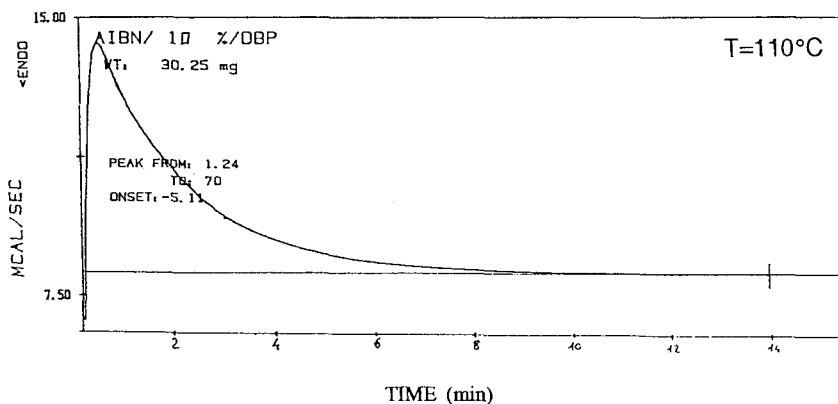

Figure 2: Differential enthalpic curve obtained for the decomposition of AIBN in "isotherm" mode.

	k_d (s-1)			
	"Dynamic" mode	"Isotherm" mode		
T	AIBN	AIBN	ACP	Flurinated Azo
(°C)	(ref 24)	3	1	2
80	$2.64 \ 10^{-4}$	$2.22 \ 10^{-4}$	$2.55 \ 10^{-4}$	---
90	$6.47 \ 10^{-4}$	$4.23 \ 10^{-4}$	$7.99 \ 10^{-4}$	$9.86 \ 10^{-4}$
100	$1.78 \ 10^{-3}$	$1.99 \ 10^{-3}$	$2.81 \ 10^{-3}$	$2.11 \ 10^{-3}$
110	$4.88 \ 10^{-3}$	$5.3 \ 10^{-3}$	$8.99 \ 10^{-3}$	$4.4 \ 10^{-3}$
120	$1.43 \ 10^{-2}$	$1.48 \ 10^{-2}$	$2.6 \ 10^{-2}$	$1.1 \ 10^{-2}$
130	---	---	$5.2 \ 10^{-2}$	$1.42 \ 10^{-2}$
ΔH(kJ/mol)	---	- 230	- 209	- 242
E_a(kJ/mol)	122	127	130	88

Table 1: Kinetic and thermodynamic parameters of azo initiators

Afterwards, this method was applied to ACP. Its thermogram in "dynamic" mode gives the melting temperature at 87.5°C and the decomposition temperature between 80 and 140°C. With this, one can choose the working temperature in isothermal mode: 80, 90, 100, 110, 120 and 130°C. From the corresponding thermogram, the average heat of decomposition of the reaction (ΔH= - 209kJ/mol) and isothermal rate constants (Table 1) have been calculated; from Arrhenius plot, the activation energy of the system (E_a=130kJ/mol) is obtained. It is noted that k_d and E_a are close to the volumetric values.

The application of our method to fluorinated disubstitued azo 2 has finally been developped; melting point occurs at 78.5°C with a pertinant phase transition from solid to liquid state. After setting the decomposition temperature range (80-140°C) from "dynamic" thermogram five working temperature values in "isothermal mode" were chosen: 90, 100, 110, 120 and 130°C. Kinetic and thermodynamic parameters of this compound are summarized in Table 1. The low activation energy value of compound 2 (E_a=88kJ/mol) is certainly due to the steric interactions of fluorinated substituents which produce a scission binding CN more easily.

Conclusion

Isothermal DSC can be applied to the other groups of thermal initiators; its advantage is to complete the dynamic DSC in the numerous cases of initiators showing a phase transition in the decomposition temperature range. However, our method takes in the time than the classical one at varying temperature ("dynamic" mode). For this reason, the second method has been developed for measuring kinetic constants of chemical reactions in spite of their inaccuracies described by Prime (25,26). Isothermal DSC methodology displays for all that, a wider application range leading to more accurate (14,23) and precise results.

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