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Kinetics of initiation in reactive processing: Nonisothermal decomposition of initiators

Béla Turcsányi

Central Research Institute for Chemistry of the Hungarian Academy of Sciences, P.O. Box 17, H-1525 Budapest, Hungary

Abstract

For the complex radical reaction systems of reactive processing the kinetics of the rate determining initiator decomposition is of preeminent importance. Thermal decomposition of initiators takes place here in nonisothermal regime. Simplified kinetic treatment shows how the important characteristics - e.g. the temperature at which the initiation rate has maximum value - relate to the Arrhenius parameters of initiator decomposition and rate of temperature increase. The results give orientation for optimization of conditions in reactive processing.

Introduction

Reactive processing, in other words, modification of polymers by chemical reactions generally in the melt phase, using polymer processing devices (e.g. extruders) as continuous reactors has rapidly growing importance [1], [2]. In some cases the reactions taking place during this processing are relatively simple. Such simple reaction is the chain scission of polypropylene, widely used in the production of "controlled rheology" grades of PP from polymerizates having high MW and broad MW distribution [3]. More complex is the chemistry of the graft modification of various polymers where the mechanism consists of polymer radical formation and grafting steps and may contain propagation and chain transfer steps too. Examples are the alkoxysilane modification of polyethylene for hydrolytically crosslinkable products [4] and the graft modification of polyolefines with unsaturated acids or acid anhydrides [5].

The above mentioned processes are radical reactions and this has important consequences. Radicals terminate pairwise by disproportionation (transfer reaction) or combination, the latter resulting in bond formation and crosslinking. Thus, the grafting process is always accompanied by bond formation and crosslinking on the one side and often by chain scission and molecular size reduction on the other [2]. The importance of these processes relative to the grafting process depends on the structure of the polymer and the modifier (monomer) as depends on the radical concentration - a function of the initiation rate - too. The consequence of this is that the whole course of the reactive processing depends sensitively on the control of the initiation process. Examples are known for graft reactions with not very well defined initiation (mechanochemical or oxidative radical production), the above mentioned control can be, however, accomplished only by suitable radical initiators under appropriate reaction conditions.

The two main types of thermally decomposing organic initiators are the azo and the peroxy compounds. As initiators of the polymerization of vinyl monomers the two types are about equally important, for the reactive processing, however, nearly exclusively peroxides are used. The commercially available peroxides have an excessive structural diversity and similarly the radicals formed from the various peroxides vary with respect to their reactivity. Strongly depends on the structure the sensitivity of the peroxides to radical attack (induced decomposition) and, of course, also the characteristic parameters of the thermal decomposition are dependent on the structure [6]. The thermal sensitivity of the peroxide is often expressed as the temperature where the half-life of the compound is equal to 10 hours. In case of the normally conducted vinyl polymerization this gives sufficient orientation, but has no informative value for the reactive processing with residence times (and total reaction times) of some minutes. For this latter, the temperature values corresponding to half-lives of one minute, or to the 1 min^{-1} value of the first-order decomposition rate constant would be much more suitable.

The reaction steps which are following the initiation step (monomer addition, chain transfer) are very rapid, thus, even in the case of long reaction chains the rate of the whole reaction will be determined essentially by the initiation i. e. the thermal decomposition process of the initiator.

Typical radical polymerizations are often conducted relatively slowly (some hours of total reaction time) in isothermal regime with nearly constant rate of initiation. The conditions during the melt processing are vastly different from this. First of all, an isothermal reaction is not realizable because of the short residence times and the relative high polymer melting and reaction temperatures occurring in the practice. But the isothermal reaction would be even impractical. With respect to the stability of the product, residues of the peroxide initiator are clearly detrimental. At constant temperature relative long times are needed for the nearly complete decomposition of the initiator resulting in excessive heat load of the polymer. The nonisothermal regime, corresponding to the real conditions, is much better even in this respect. With increasing temperature the decomposition process accelerates at first in consequence of the increase of the rate constant and, after passing a maximum, decreases and goes to zero rapidly as the initiator is exhausted. For the initiated melt processing reactions the main characteristics of this nonisothermal decomposition (temperature at the maximum decomposition rate, range of decomposition) and the dependence of these on the thermal parameters of initiator decomposition and on processing conditions have the real importance.

Experimental

Decomposition of dicumyl peroxide in polyethylene melt was studied by DSC using various initial peroxide concentrations and heating rates.

The peroxide-containing polyethylene samples were prepared in a Brabender mixing chamber at 50 rpm, 140 °C set temperature. Unstabilized LDPE polymer (product of TVK, Hungary) and synthesis grade dicumyl peroxide (Merck) were used. After 4 min mixing the melt temperature was 146-7 °C. Peroxide loss during these operations was considered negligible.

The DSC measurements were made using a Mettler TA 3000 thermoanalytical system with a DSC 30 cell. Sample sizes were in the 10 mg range, corresponding to rather low, 0.2-0.5 mg amounts of peroxide per sample. For the calculation of Arrhenius parameters and reaction order the multiple linear regression routine KINETIC of the TC 10 A processor was used. No corrections were made.

Discussion

The processes of transport, mixing, changes of temperature and pressure during the extrusion of a polymer are exceedingly complex. Essentially, the working extruder is a continuous tubular reactor, but a realistic modelling of the conditions in this reactor would need huge computing efforts. There is both a radial and an axial mixing and, as a consequence of this, the residence times can be given in form of a distribution. The conditions of heat exchange, heating and cooling change along the extruder. The conversion of mechanical work to heat is a very important, locally changing contribution to the heat balance. Even in the steady state regime it is difficult - both theoretically and experimentally - to determine the temperature profile along the device and describe the time/temperature profile of some small part of the reaction mixture. Thus, not knowing the exact form of this latter function, we have to determine only the most general characteristics of the nonisothermal initiator decomposition.

In the ideal case, the initiator decomposition is a first-order process described by the differential equation (1):

$$- d[I]/dt = k_d [I] \tag{1}$$

where k_d is the decomposition rate constans of the dimension time^{-1}, [I] can be given in any unit of concentration, total or relative amount. Depending on the chemical structure of the initiator the radical induced decomposition may be important, but will not be considered here.

Decomposition and initiation rates differ by the factor 2f, as one decomposed peroxy group produces two radicals, but only the fraction f escapes termination in the cage and can react with the reaction partners. The temperature dependence of this factor will not be reckoned with in the following.

If we assume some time function for the temperature of the reaction mixture, the temperature dependent rate constant $k_d(T)$ can be expressed as time-dependent function $k_d(t)$ and substituted into (1). The temperature dependence is given by the Arrhenius formula (2):

$$k_d(T) = A \exp(- B/T) \tag{2}$$

where the preexponential factor A has the same unit as k_d and $B \equiv E_a/R$ contains the energy of activation.

The treatment is most simple if the temperature dependence is hyperbolic [7] albeit the solution of the D.E. for the linear temperature increase is known too [8]. The hyperbolic dependence can be given as follows:

$$1/T = 1/T_r - C\ t \tag{3}$$

where T_r is some reference temperature and C is the rate of reciprocal temperature change (K^{-1} min^{-1}). Using this, the time-dependent rate constant becomes

$$k_d(t) = k_r \exp(B\ C\ t) \tag{4}$$

where k_r is the rate constant at the reference temperature ($T = T_r$ and $t = 0$) and the solution of the D.E. is as follows:

$$[I] = [I]_r \exp \{k_r(1 - \exp[BCt])/BC\} \tag{5}$$

where $[I]_r$ is the concentration of initiator at the reference temperature ($t = 0$).

For other time-temperature dependencies the solution will, of course, be different. But we are interested for a relatively narrow temperature interval including the locus of maximum decomposition rate where the various smooth temperature changes can be approximated by the hyperbolic one. The locus of maximum rate is easily found from

$$BC = k_r \exp(BCt) \tag{6}$$

(corresponding to $d^2[I]/dt^2 = 0$) and is as follows:

$$t^* = [\log(BC/k_r)]/BC \tag{7}$$

"log" denoting here and in the following natural logarithms. Remark that t^* is the <u>time</u> corresponding to the maximum rate and the <u>temperature</u> T^* can be calculated by (3), resulting in:

$$1/T^* = 1/T_r - [\log(BC/k_r)]/B \tag{8}$$

Now, if the reference temperature corresponds to the maximum decomposition rate $T_r = T^*$ (we have the liberty to make this choice) then $k_r = k^* = BC$ and, expressing k^* by the Arrhenius expression

$$A \exp(-B/T^*) = BC \tag{9}$$

the temperature at the maximum decomposition rate can be given in function of the Arrhenius parameters and the C heatig rate:

$$T^* = B/(\log A - \log B - \log C) \tag{10}$$

With this point of reference the time dependence of the initiator concentration becomes

$$[I] = [I]^* \exp(1 - \exp[BCt]) \tag{11}$$

the zero point of the time scale being at the maximum decomposition rate. It is easy to see, that for $t \to -\infty$ i.e. $T \to 0$ the amount of initiator must be $[I]_0 = e[I]^*$. In other words, the amount of initiator at the maximum decomposition rate is 36.8 % of the initial, at low temperatures practically stable amount.

Generally, the undecomposed fraction of the initiator, φ, is equal to

$$\varphi = [I]/[I]_0 = e^{-1} \exp(1 - \exp[BCt]) \tag{12}$$

and the time (with $t = 0$ at the maximum rate) in function of φ is

$$t(\varphi) = \log(-\log \varphi)/BC \tag{13}$$

The temperature, $T(\varphi)$ is given then by the following expression:

$$1/T(\varphi) = 1/T^* - \log(-\log \varphi)/B \tag{14}$$

showing clearly, that the length of the interval on the reciprocal temperature scale corresponding to the decomposition of a given fraction depends only on the energy of activation, but independent from the heating rate.

Example: dicumyl peroxide decomposition

Dicumyl peroxide (DCP, di(2-phenylisopropenyl)peroxide) is one of the most important thermal initiators. As a high-temperature initiator, it has special importance in the reactive processing of polyolefines (e.g. grafting of polyethylene, molecular size reduction of polypropylene, etc.).

The isothermal decomposition kinetics of DCP is well studied. It was investigated between 128 and 158 °C in dodecane solution by Kharasch [9]. For the energy of activation in this solvent 33.5 kcal mol^{-1} (140.3 kJ mol^{-1}) was published. We recalculated the Arrhenius parameters of the decomposition process using the $t_{1/2}$ values published by Kharasch and determined for the energy of activation 147.06 kJ mol^{-1}, a somewhat higher value. For the Arrhenius parameters we obtained $B = E_a/R = 1.768.10^4$, $\log B = 9.78$ and $\log A = 38.72$. The temperature at which the rate constant has the valued $k_d = 1$ min^{-1} is 183.5 °C calculated with these parameters. Similar values were found in cumene solvent between 111 and 150 °C ($E_a = 144.5$ kJ mol^{-1}, $\log A = 37.79$) by Bailey and Godin [10].

We used the above given recalculated values in our calculations, the results of which are given in Table 1.

Table 1: Dicumyl peroxide decomposition: characteristic temperatures calculated with the Arrhenius parameters $\log A = 38.72$ and $\log B = 9.78$

heating rate		$T_{0.95}$	$T_{0.5}$	T^*	$T_{0.05}$	$t_{0.95} - t_{0.05}$
dT/dt at T^* (K min^{-1})	10^4 C (K^{-1} min^{-1})		(K)			(min)
0.1	0.00599	382.4	405.2	408.6	419.3	384
1	0.05396	401.5	426.7	430.5	442.3	42.6
10	0.48353	422.5	450.5	454.8	468.0	4.76
35	1.59029	434.9	464.6	469.1	483.2	1.45
50	2.23118	438.5	468.8	473.4	487.7	1.03
70	3.07048	442.0	472.8	477.5	492.1	0.75
100	4.30660	445.8	477.1	481.9	496.7	0.53

The temperature values characterizing the course of decomposition were calculated for various heating rates. With respect to the reactive processing, the heating rates greater than 10 K min^{-1} are important, but for comparison the table contains low values of heating rates, too. The temperature values T_φ were calculated with the aid of (14) i.e. for the hyperbolic temperature change. C and the temperature of maximum decomposition rate T^* were determined by simple iteration. At the temperature T^* the linear and reciprocal temperature change rates are connected by (15):

$$C = (1/T^*)^2 \, dT/dt \tag{15}$$

thus, starting with the guess T_1^* a C_1 value was calculated by (15), then T_2^* computed according to (10) and these steps were repeated. The iteration converged rapidly and stable results were obtained in five cycles. Table 1. contains also the time needed for the decomposition of 90 % of the initiator, Δt. These values show clearly that for the practice heating rates exceeding 10 K min^{-1} have real importance. On the other side, these values, connected with the residence times, determine the temperature domain of initiation and of the whole reaction for the given initiator.

Table 2. shows the results of DSC measurements on the decomposition of DCP in polyethylene melt. Two concentrations of DCP (2 and 5 % w/w) were studied with linear heating programs at 5-30 K min^{-1} heating rates. The temperature values corresponding to the 50 % decomposition and to the maximum decomposition rate are nearly the same as the comparable calculated values. The values calculated for the parameters of the decomposition process (reaction order, energy of activation and preexponential factor) need some comment, however. The reaction order is, with one exception, close to 1. The energy of activation found for the 2 % DCP containing samples is significantly higher, for the 5 % samples lower than the value determined the usual way. The corresponding values of log A show clearly the compensation effect. We conclude that Arrhenius parameters calculated directly from DSC data, using the enthalpy change rate values, must be treated with caution.

Table 2: Dicumyl peroxide decomposition: results of DSC measurements on DCP containing polyethylene samples

DCP content (w%)	heating rate (K min^{-1})	$T_{0.5}$ (K)	T_{peak}	reaction order	E_a (kJ mol^{-1})	log A (k in min^{-1})
2.0	5	446.1	448.2	1.06±0.13	154.9±12.8	40.80±3.56
2.0	10	454.4	458.9	1.02±0.06	158.4±5.7	41.60±1.56
5.0	10	451.9	456.9	0.79±0.13	120.1±10.8	31.22±2.97
5.0	20	464.5	467.8	0.95±0.12	127.4±9.8	33.15±2.64
5.0	30	470.0	471.0	1.06±0.09	124.1±7.3	32.27±1.94

Conclusions

Radical reactions realized in polymer processing devices (extruders) as continuous reactors take place under exceedingly complex conditions. Even in this case, the most simpe nonisothermal modelling the kinetic analysis of the rate-determining initiation process under gives important and useful information. The temperature interval needed for the decomposition of a given fraction of the radical initiator is determined by the energy of activation. The temperature corresponding to the maximum initiation rate increases with increasing heating rate and the heating rate determines also what kind of time is needed for the nearly total decomposition of initiator. This time interval must be in accord with the mean residence time of the reacting materials between the appropriate lower and higher temperature loci of the processing device. The results presented here give important orientation for the approximation of optimal conditions in reactive processing.

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