THE QUANTITATIVE EVALUATION OF TG-CURVES OF POLYMERS

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ABSTRACT

It is shown that any attempt of kinetic interpretation of TG-data of polymer degradation has to consider all peculiarities of polymer destruction processes. Besides the heterogeneous character of this process, mainly its radical chain reaction nature, the presence of weak bonds and possible scission in chain fragments of different length will prevent stationary state of reaction. Therefore rather a variation of activation energy during non-isothermal degradation of polymers will be the consequence. Supplementary larger polymer chain fragments must not be volatile at temperature of formation.

GENERAL

As everybody knows thermogravimetry (TG) is a method of analysis of mass changes in sample supposed to a well defined temperature programme. The corresponding weight change of the sample will be represented against the temperature and gives the respective TG-curve. The first derivative of this TG-curve is the belonging DTG-curve.

Thermal degradation in condensed phase accompanied by the evolution of volatile reaction products will be a heterogeneous process and will show weight loss during temperature increase. Thermal degradation, however, may occure in several succesive degradation steps.

Taking into account the heterogeneous character of this process the chemical transformation can be exprimed either by the procentual weight change, $(w_T/w_\infty) \times 100$, or more convenient by the conversion degree, $\alpha = w_T/w_\infty$. w_∞ is the weight loss at the end of the respective degradation step and w_T at a given instant at the reaction temperature T.

The degradation process itself my be characterized by the respective temperature range, delimited by the initial, T_i, and final temperature, T_f, of degradation. Sometimes also the temperature of

maximum reaction rate, T_M, is specified. The temperature range of degradation will be shifted to as higher temperatures as higher the heating rate.

Due to the heterogeneous character of the process, diffusion and heat transfer will influence and therefore both the size and the shape of the sample, as well as the surrounding atmosphere and pressure are determinant. Consequently any qualitative comparison of TG-data supposes constant reaction conditions and apparative disposition as well as constant heating rate.
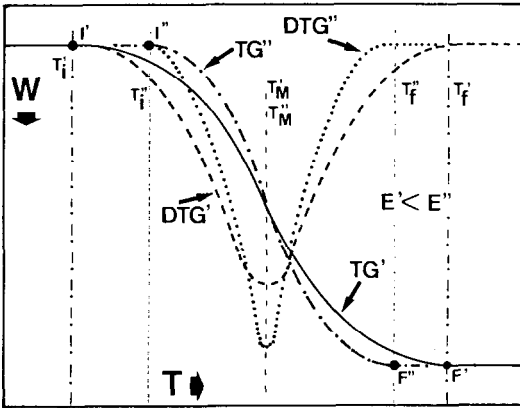

Fig.1 Formalized TG/DTG - curves.

As both temperature and time are conversion determining factors in non-isothermal conditions of TG, starting with the simplest law of formal kinetics for the time dependence of the conversion degree, α, (1) and for the temperature dependence of the reaction rate constant, k, (2), it is easy to understand that the steepnes of TG/DTG-curves is rather determined by the activation energy, E, of the process.

$$\frac{d\alpha}{dt} = \kappa f(\alpha); \quad f(\alpha) = (1-\alpha)^n \quad : \quad F(\alpha) = \kappa t \qquad (1)$$

$$\kappa = A \exp(-E/RT) \quad : \quad \frac{d\log\kappa}{dT} = E \frac{1}{2.303 RT^2} \qquad (2)$$

In Fig.1 it is shown that the width of the temperature range is as smaller as higher the activation energy, i.e. the temperature coefficient of the reaction. Therefore it may be hazardous to use other characteristics than T_i to specify the thermal stability of the sample.

Depending on the respective activation energies T_M-temperatures for inctance may coincid, even if the initial temperatures of degradation T_i are quite different as sketched in Fig.1.

QUANTITATIVE ESTIMATION OF TG-DATA

Quantitative estimation of TG-data supposes kinetic interpretation of TG/DTG curves.

Customary it is supposed that the rate equation of heterogeneous processes

$$d\alpha/dt = k(T)f(\alpha)g(\alpha,T)h(\sum_i x_i) \tag{3}$$

can be used in its simplified form, considering only temperature, $k(T)$, and conversion, $f(\alpha)$, dependent parameters.

$$d\alpha/dt = k(T)f(\alpha) \tag{4}$$

Conversion-temperature cross terms $g(\alpha,T)$ are assumed ineffective and all physical factors which may influence the heterogeneous process, like sample size and shape, as well as surrounding atmosphere and pressure are eliminated due to the constancy of chosen reaction conditions.

Taking into account the linear temperature programme used in TG

$$hr = dT/dt \tag{5}$$

hr being the heating rate in Ks^{-1}, rate equation (4) can be reformulated

$$d\alpha/dT = \{k(T)/hr\} f(\alpha) \tag{6}$$

and than explicited.

Temperature dependence is supposed to obey the Arrhenius law

$$k(T) = A\exp(-E/RT) \tag{7}$$

whilst conversion function is considered in its simplest form

$$f(\alpha) = (1-\alpha)^n \tag{8}$$

although for heterogeneous solid-gas reaction also more complicated expressions are encountered (ref.1).

In extension of the language of formal gas-phase kinetics, E is considered the activation energy and n the "reaction order" of the heterogeneous process in TG condition.

Eqn.(6) may be now explicited as follows

$$d\alpha/dT = \frac{A}{hr} \exp(-E/RT)(1-\alpha)^n \tag{9}$$

which is the basic equation of the non-isothermal kinetics of TG.

Separation of variables for integration of the differential rate equation (9) yields from the beginning two questions.

So the conversion integral supposes for solution the knowledge of the reaction order, n.

$$F(\alpha) = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} \tag{10}$$

As n has no physical meaning or support and therefore cannot be predicted, only trial and error method can be recommended to aproximate n for best fit of experimental data.

Concerning the temperature integral

$$I(T) = \int_{T_i}^T \frac{A}{hr} \exp(-E/RT) \ dT \tag{11}$$

no direct solution is accesible and in literature plenty of proposales are encountered for most accurate solution of the temperature integrale, including various computer programmes.(ref.2)

This explains also the multitude of methods recommended for kinetic interpretation of TG-data, customary classified in differential methods, which starts with the differential rate equation (9) and in integral methods.

Taking into account the aime of this paper, only one of these solutions will be discussed. According to Doyle (ref.3) the following approximate solution can be used if the ratio E/RT>15, condition fullfilled by majority of degradation processes:

$$\log F(\alpha) = \log(AE/R) -\log hr -2.315 - 0.457 \frac{E}{R} T^{-1} \tag{12}$$

This solution is the starting point of one of the promising kinetic interpretation methods proposed independently by Flynn and Wall (ref.4) and by Ozawa (ref.5) respectively.

For different heating rates and constant transformation degree, iso-α, eqn.(12) can be formulated as follows:

$$- \frac{d \log hr}{dT^{-1}} = 0.457 \frac{E}{R} \tag{13}$$

i.e. a series of parallel isoconversional straight lines will be obtained with slope as steeper as higher the activation energy of the process, as suggested in Fig.2.

As a consequence the shift of the temperature range of the degradation process with increasing heating rate to higher temperatures will be as more pronounced as smaller the respective activation energy.

KINETICS AND MECHANISM OF POLYMER DEGRADATION

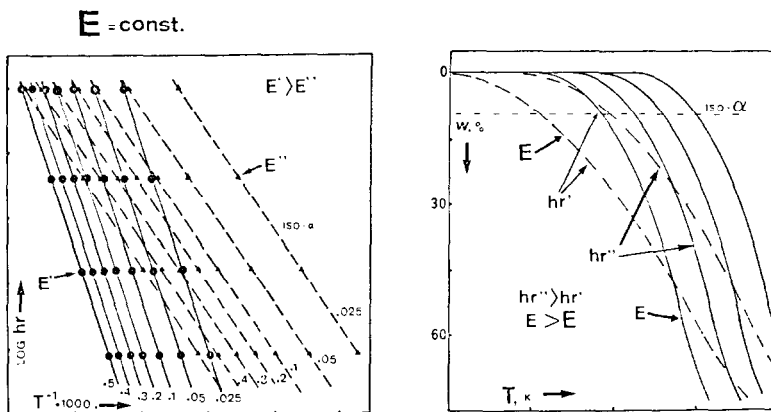Depending on the nature of the polymer and the structure of the

Fig.2 Formalized Flynn-Wall-Ozawa plot of degradation
processes with different activation energies

repeating unit during thermal degradation different reaction pro-
ducts result, monomer formation being rather the exception. For
vinylic polymers the following general scheme can be presented:
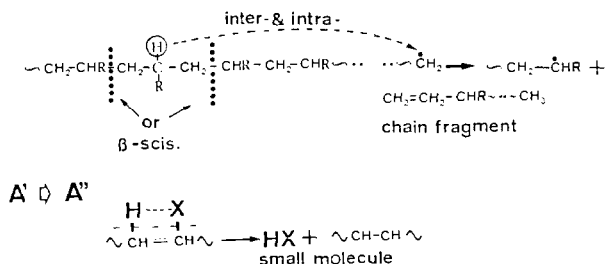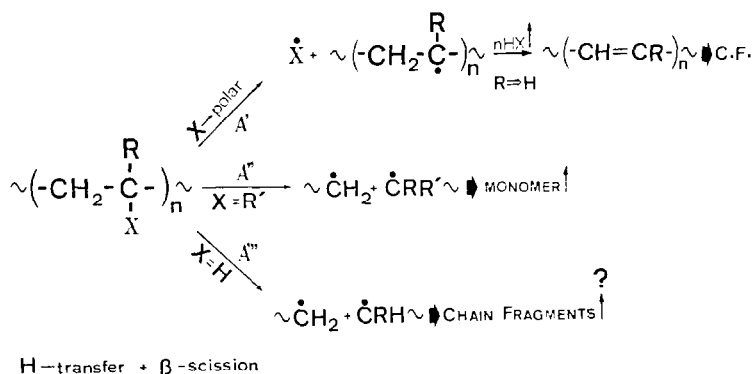
The effective reaction mechanism with side group scission (A')
or main chain scission (A" and A"') is related to the polar nature

of the X-substituent and the probability of monomer regeneration
(A") depends on the absence or the presence of mobil tertiary H-
atoms. In the latter case (A"') chain fragments of different length
and volatility are formed by inter- or intramoleculare H-transfer
followed by ß-scission. In principle the chain fragments must not
be volatile at temperature of formation.

By side group scission (A') small molecules ar formed in a first
degradation step, whilst the main chain is splitting off only in a
second step at higher temperatures. This first step can be assimi-
lated with a depolymerization in which "monomer molecules" are for-
med by consecutive elimination of the side groups "grafted" on the
main chain.(ref.6).

Typical TG/DTG curves of representatives of the three different
reaction mechanisms are shown in Fig.3. The mechanisms presented
are only limiting cases, however, real degradation occuring by
more ore less accentuated overlapping of these idealized processes.

Observed slope changes
in linear-poly(ethylene),
1-PE, degradation may be
explained by accumulation
of longer chain fragments
at lower temperatures and
their sudden evaporation
at higher temperatures.
This effect will be as mo-
re pronounced as smaller
the heating rate (ref.7).

Polycondensation poly-
mers will show in princi-
ple similar degradation
mechanism, only no monomer
molecules will be formed.

Consequently weight
loss measurements in poly-
mer degradation will be in
principle effective if de-
gradation occurs accordin-
gly to mechanisms A' or A"
when volatile small resp.
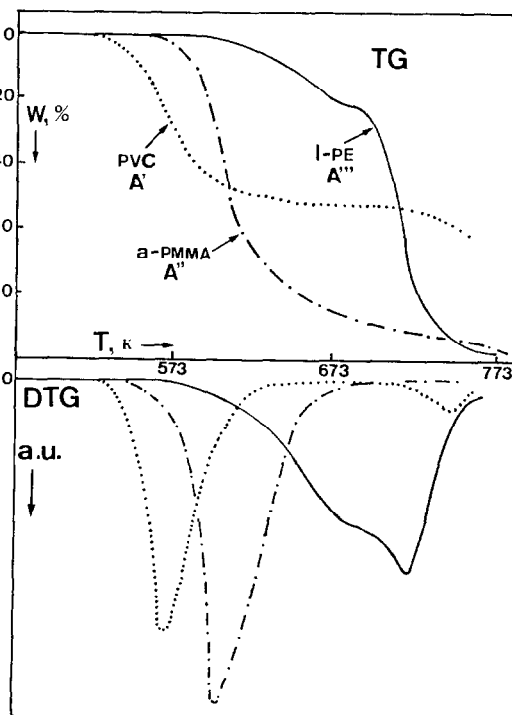monomer molecules are for-
med. On the contrary, if

Fig.3. Degradation in air of 20 mg
polymer samples. Hr = 0.21 Ks^{-1}
(Sample characteristics see ref.7)

chain fragments of different length are formed (A"'), weight loss measurements may fail. Here molecular weight measurements are quite more effective (see Fig.4). The effectiveness depends supplementary on the kinetic chain length of the degradation process, ν, and the temperature. As higher the temperature as smaller the fragments resulted in process A"'.
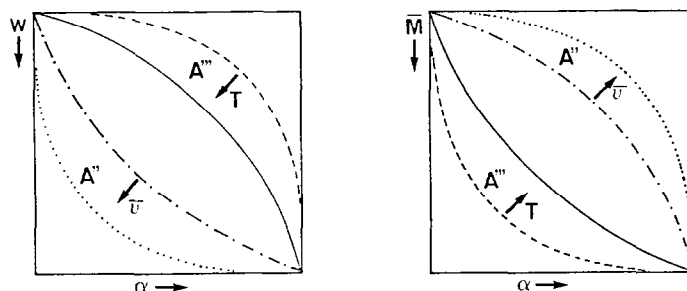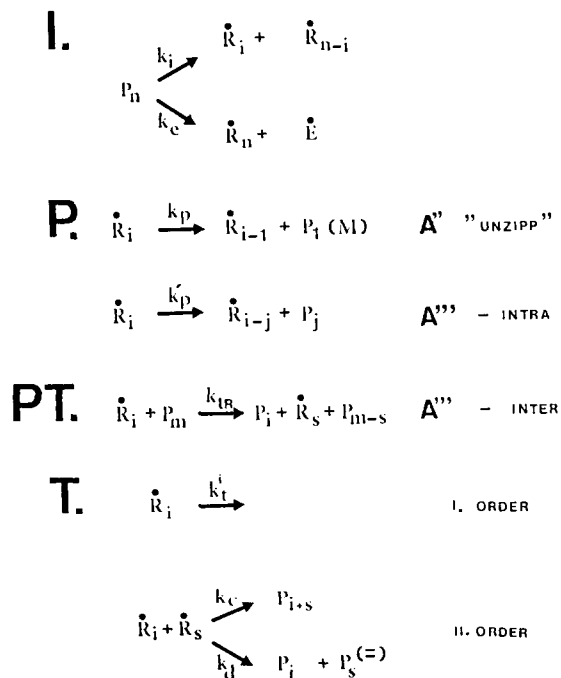

Fig.4 Formalized weight loss and molecular weight change curves in polymer degradation.

Thermal degradation of polymers occurs according to a radical chain mechanism, including initiation (I), propagation (P), propagation by transfer (PT) and termination (T) as shown below.

I.

$$P_n \begin{array}{c} \xrightarrow{k_j} \dot{R}_i + \dot{R}_{n-i} \\ \xrightarrow{k_e} \dot{R}_n + \dot{E} \end{array}$$

P.

$$\dot{R}_i \xrightarrow{k_p} \dot{R}_{i-1} + P_1 (M) \qquad A" \quad \text{"UNZIPP"}$$

$$\dot{R}_i \xrightarrow{k'_p} \dot{R}_{i-j} + P_j \qquad A"" \quad - \text{INTRA}$$

PT.

$$\dot{R}_i + P_m \xrightarrow{k_{tR}} P_i + \dot{R}_s + P_{m-s} \qquad A"' \quad - \text{INTER}$$

T.

$$\dot{R}_i \xrightarrow{k_t^i} \qquad \qquad \text{I. ORDER}$$

$$\dot{R}_i + \dot{R}_s \begin{array}{c} \xrightarrow{k_c} P_{i+s} \\ \xrightarrow{k_d} P_i + P_s^{(=)} \end{array} \qquad \text{II. ORDER}$$

Solution of rate equation assumes stationary state for radical concentration, i.e. egality between rates of initiation and of termination and depending on the nature of the elementary reactions involved, the kinetic chain length and distribution different solutions of overall reaction rate and activation energy are deduced. (ref.8).

Stationary state in chain reaction occurs allways only after an induction period wich is related with the "life time", τ, of the radicals. Essential featurs of radical accumulation during induction period are exemplified for simple depolymerization process.
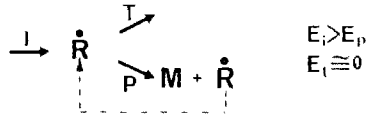
Rates of accumulation of radicals and monomer during induction period are given by the expressions:

$$d\left[\overset{\bullet}{R}\right]/dt = W_i - (V_p + V_t)\left[\overset{\bullet}{R}\right] \quad ; \quad d\left[M\right]/dt = V_p\left[\overset{\bullet}{R}\right]$$

Integration for radical concentration yields:

$$\left[\overset{\bullet}{R}\right] = \frac{W_i}{V_p + V_t}\left\{ 1 - \exp\left(-(V_p + V_t)t\right)\right\}$$

Using the notations $\tau = 1/(V_p + V_t)$ for the "life time" of the radicals and $\nu = V_p/(V_p + V_t)$ for the "kinetic chain length" of the chain process one obtains

$$\left[\overset{\bullet}{R}\right] = \tau\, W_i \left\{ 1 - \exp\,(-t/\tau)\right\}$$

and

$$W = d[M]/dt = \nu\, W_i \left\{ 1 - \exp(-t/\tau)\right\}$$

W being the overall reaction rate. It is easy to demonstrate that stationary state supposes $t \gg \tau$.

Variation of radical concentration, overall reaction rate and of product (monomer) concentration in simple chain reaction is shown in Fig.5 (ref.9).

In above equations V_i are the frequency factors of the respective elementary processes. They are concentration dependent in contrast to the rate constants.
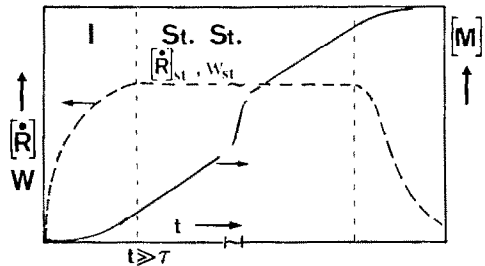
Fig.5. Evolution of simple chain.

In non-isothermal conditions of thermogravimetry, however, stationary state is allways perturbed and only at maximum reaction rate stationary state assumtion is valid. Consequently at the beginning of the degradation process conversion will depend mainly on activation energy of the initiation step, E_i, and than gradual tend the much smaller overall activation energy characteristic of the stationary state. This gradual decrease of activation energy during occurence of process will be observed in any radical chain reaction in non-isothermal condition. As a consequence activation energy will show an apparently conversion dependence, $E=E(\alpha)$.

Formalized Flynn-Wall-Ozawa plot for degradation process with conversion dependent activation energy, typical for thermal degradation of polymers in non-isothermal condition of TG is shown in Fig.6.
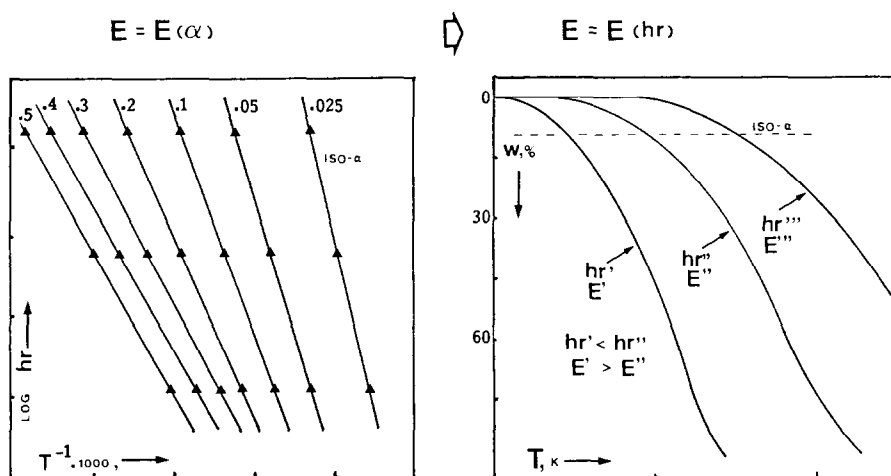

Fig.6 Formalized Flynn-Wall-Ozawa plot of degradation
process with conversion dependent activation energy.

It is evident that the temperature range is not only shifted to higher temperatures, but also as larger as higher the heating rate. That means that the temperature coefficient of the reaction (i.e. the activation energy) decreases with heating rate if a decrease with conversion degree of activation energy is observed. Vice versa is also valid and will be characteristic of parallel processes in thermogravimetric conditions. Theoretical shapes of TG/DTG curves for parallel processes are analysed by Flynn (ref.10) and Ozawa (ref.11).

It is easy to demonstrate that conversion dependent activation

energy will be allways accompanied by heating rate dependent acti-
vation energy.

Starting with the same approximate solution of Doyle - eqn.(12) -
and assuming at constant heating rate a given conversion range,
eqn.(12) can be reformulated as follows:
For iso-hr

$$\Delta \log F(\alpha) = \Delta \log (AE/R) - 0.457 \Delta(\frac{E}{R} T^{-1}) \qquad (14)$$

For E = const, $\Delta\log(AE/R)=0$, whilst for E = E(α) it can be assumed
that $\Delta\log(AE/R) \ll \Delta(\frac{E}{R} T^{-1})$.

Considering now the same conversion range, but at different hea-
ting rates, because of the identity

$$\left[\Delta \log F(\alpha)\right]_{hr'} \equiv \left[\Delta \log F(\alpha)\right]_{hr''} \qquad (15)$$

it will be also valid the identity

$$\left[\Delta (ET^{-1})\right]_{hr'} \equiv \left[\Delta (ET^{-1})\right]_{hr''} \qquad (16)$$

The only condition of validity of eqns. (15) and (16) is that
the reaction mechanism remains the same by changing the heating
rate. For simple radical chain mechanism this condition is respec-
ted.

Conversion independent activation energy Flynn-Wall-Ozawa plot
shows parallel iso-conversional straight lines as seen in Fig.2,
i.e. $\Delta(T^{-1})_{hr'} = \Delta(T^{-1})_{hr''}$ and therefore also constant activation
energy at different heating rates. On the contrary conversion de-
pendent activation energy results in non-parallel straight lines
(see Fig.6), i.e. $\Delta(T^{-1})_{hr'} \neq \Delta(T^{-1})_{hr''}$ and consequently activation
energy will show heating rate dependence too, $E_{hr'} \neq E_{hr''}$, because
of the imposed condition by eqn.(16).

Conversion and heating rate dependent activation energy predic-
ted by Flynn-Wall-Ozawa plot according to Fig.6 is obeserved du-
ring non-isothermal TG in air for Poly(vinylchloride) (ref.12),
Poly(vinylacetate) (ref.13), Poly(vinylalcohol) (ref.14) as well
as for the degradation in nitrogen of α-Cellulose (ref.15), an-
ionic Poly(methylmethacrylate) (ref.16) and Poly(ethyleneterephtha-
late) (ref.17).

Because of the temperature increase during TG degradation of
polymers the reaction mechanism itself may change as well due to
the heterogeneous character of the process, when diffusion can

concur the chemical process, but mainly due to the presence of
weak bonds. These weak bonds will split preferential at lower tem-
peratures, because the small apport of activation energy. As high-
er the temperature as more reduced the influence of weak bonds and
random scission will gain in importance. Parallel reactions will
occure in TG condition and theoretical aspects concerning conver-
sion and hr influences on shapes of TG/DTG curves are analysed in
literature (ref 11 and 12).

The same effect will be observed in presence of oxygen because
of the smaller activation energy of the radical generating process

$$P_n + O_2 \longrightarrow H\overset{\bullet}{O}_2 + \overset{\bullet}{R}_n$$
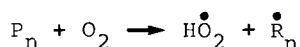
as compared to the thermal bond spliting reactions. Taking into ac-
count that volatile products will relative rapidly surround the
sample special in cruicible, the influence of oxygen will be obser-
ved mainly at the beginning of the degradation process of polymers
in TG condition.

No further straight lines are obtained in a Flynn-Wall-Ozawa
plot as shown in Fig.7 for the degradation of anionic Poly(styrene)
in air (ref.18). Even much more sophisticated diagrammes are ob-
tained for the degradation of linear Poly(ethylene) in air.

Complicated Flynn-Wall-Ozawa diagrammes are therefore indices
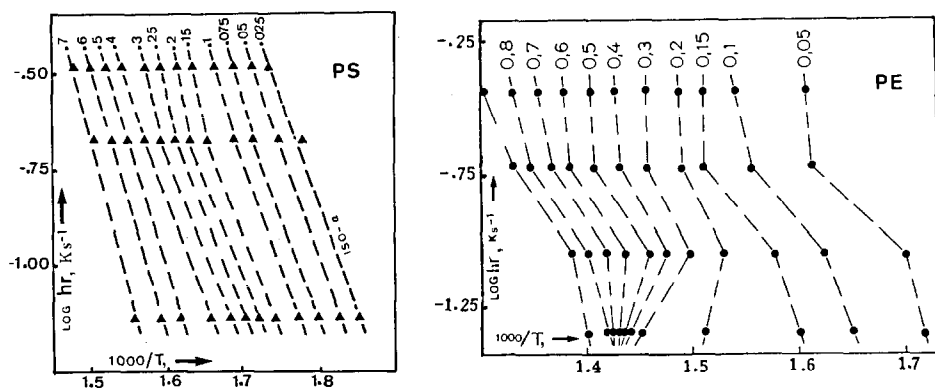of complicated degradation mechanismes.

Fig.7   Flynn-Wall-Ozawa-Diagrams of anionic Poly(styrene),
        M=52000 and of linear Poly(ethylene), SRM 1475 Nat.
        Bur.Stand., M=18310. TG in air, Sample size 20 mg

Finally some considerations concerning the constancy of the hea-
ting rate. Although constancy of heating rate in TG is general sup-

posed taking into account the used linear heating programme, paral-
lel measured DTA curves show that specially in the conversion
range due to the reaction heat the heating rate is perturbed in
the sample. Small sample size and low heating rate will reduce
this influence, however, but in detriment of the accuracy of the
measurement. Only DSC type heating will exclud the effect of reac-
tion heat. This type of heating, however, is up to now not applied
in TG. Kinetic estimation can consider variable heating rate and
general the trend of conversion dependence of activation energy is
preserved even if absolute values of activation energy are quite
different (ref.7).

In conclusion it can be stated the rigurous quantitative evalu-
ation of TG-data of polymers supposes multiple heating rate measu-
rements, because single heating rate data are dependent on condi-
tions used. By multiple heating rate measurements both the comple-
ity of degradation process and probable reaction mechansim as well
as belonging kinetic parameters are accesible.

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