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NON-ISOTHERMAL THERMOGRAVIMETRY OF POLYMER

I. GENERAL MODEL INVOLVING FORMAL TERMINATION OF ACTIVE CENTRES

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A model of polymer decomposition is proposed which formally involves the termination of active centres. It yields reasonable activation energies for the decompositions of polypropylene, polyethylene, polystyrene and polymethyl methacrylate investigated by non-isothermal thermogravimetry. In the value of a formal reaction orders the model reflects the reaction conditions, such as initial sample weight, atmosphere, ventilation conditions, sample holder nature and shape, etc.

The non-isothermal kinetics of polymer degradation investigated by thermogravimetry is usually represented by a relatively simple equation

$$dc/dt = A/\beta \exp(-E/RT) f(c) \qquad (1)$$

where c is the conversion to volatile products, A and E are Arrhenius parameters, and $\beta = dT/dt$ is the rate of temperature rise. Such an approach may be criticized for the case $f(c) = (1-c)^n$, where n is a procedural reaction order, and also for the use of the Arrhenius dependence of the rate constant, etc. However, unless a better and equally simple alternative is put forward this approach, can hardly be abandoned. It has been shown that the values of system parameters A and E (and n) can be ascribed to an actual mechanism only in certain particular cases [1, 2]. Practically any perturbation of the experimental conditions leads to a change in the apparent E, bringing about a change in ln A in the same direction (compensation effect) [3].

A number of papers have dealt with the approximation of the value of the integral of the Arrhenius function $\int_{T_{init}}^{T} A/\beta \exp(-E/RT)\, dT$, and different methods of estimation of the parameters are thus available from both the integrated and the

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differential form of Eq. (1), but the general pattern of practical non-isothermal TG curve processing remains the same: the more or less obvious dependence of the obtained parameters on $f(c)$, and on other external measuring conditions, such as the mass of sample, the heating rate, the shape of the sample holder, the atmosphere, the ventilation conditions and experimental errors connected with non-equilibrium heat fluxes, the density of sample packing, etc. In spite of this, however, there still exists and naturally will exist an effort to compare the samples measured in different laboratories not only via the graphical record of a TG curve but also via system parameters.

The separation of the effects of these supplementary experimental conditions from the pure kinetic parameters characterizing the decomposition of a material as such may apparently be achieved through the choice of the decomposition model which accentuates the respective reaction conditions. Since the proper choice of the model may sometimes be the problem, methods of TG curve elaboration have been devised [4] which avoid the use of an analytical form of a model $f(c)$ for the determination of E; for a complete description of the process, however, $f(c)$ is needed.

The above ambiguity in the description of experimental TG curves stimulated us to consider a method of processing experimental data which involves the easy transition from one external experimental condition to another by changing one system parameter only. Until now, for a chosen model and change of the "external conditions", the congruency of different experimental weight *vs.* temperature curves was obtained by the rotation and shifting of coordinate axes, as shown by Adonyi [5].

In the present paper we put forward an idea of the formal termination of active centres in the mass and on the surface of decomposing polymer, through which all these side-effects may apparently be implemented. The model is exemplified by the decompositions of polystyrene, polypropylene, polymethyl methacrylate and polyethylene at different heating rates in a flow of nitrogen or air. The adaptability of such a model to given external experimental conditions is outlined.

Experimental

The thermogravimetry experiments were carried out on a Q-1500 D derivatograph (MOM, Budapest). The reaction vessel was an open platinum pan with a height of 12 mm, an upper diameter of 10 mm, and a lower diameter of 8 mm; the temperature in the sample was monitored with a thermocouple which simultaneously functioned as the holder of a reaction pan in a thermobalance system.

A flow of gas (nitrogen or air) at 6 l/h was introduced to the centre of the upper cross-section of the reaction pan. The rate of programmed heating was controlled by an independent thermocouple placed near the reaction pan. The temperature of the reaction system was determined independently by an off-line calculator, directly from the voltage of the thermocouple. The experimental points which may be used to describe the plot of the relative residual weight $(1-c)$ and temperature T are presented in an attached worksheet (Table 1). Even though such a presentation is not very current, we give it to allow the possibility of easy comparison with similar experiments in other laboratories.

Table 1 Worksheet of TG measurements on polypropylene, polystyrene, polymethyl methacrylate and polyethylene under 6 l/h of nitrogen or air (β is the heating rate)

Polymer	β, deg/min	Atmosphere	Temperature, K	$1-c$
Polypropylene P1	2.5	N_2	556.6	0.9841
			570.7	0.9788
			583.5	0.9735
			597.2	0.9630
			610.8	0.9471
			625.3	0.9233
			638.7	0.9962
			665.5	0.7381
			678.8	0.6005
			692.8	0.3942
			708.6	0.1217
Polypropylene P2	5	N_2	585.6	0.9876
			596.5	0.9801
			608.3	0.9702
			621.1	0.9578
			632.7	0.9404
			643.4	0.9132
			655.0	0.8734
			667.5	0.8139
			690.4	0.6104
			703.6	0.4417
Polypropylene P3	10	N_2	605.9	0.9868
			617.7	0.9816
			629.4	0.9763
			641.9	0.9683
			653.5	0.95
			664.2	0.9289
			676.7	0.8921
			689.8	0.8342
			701.2	0.7553

Table 1 (cont.)

Polymer	β, deg/min	Atmosphere	Temperature, K	$1-c$
			712.6	0.6262
			725.7	0.421
			739.5	0.1737
Polypropylene P4	2.5	air	485.7	0.9918
			498.7	0.9781
			512.7	0.9535
			526.5	0.9153
			539.7	0.8607
			553.8	0.7896
			568.0	0.6885
			582.7	0.5628
			596.3	0.4071
			610.9	0.2158
Polypropylene P5	5	air	494.5	0.9889
			505.5	0.975
			518.5	0.9583
			530.0	0.9333
			540.4	0.9028
			552.7	0.8556
			565	0.8
			578	0.725
			589.8	0.6278
			602.5	0.5056
			615.3	0.3472
			628.8	0.1611
Polypropylene P6	10	air	507.8	0.99
			519.8	0.98
			531.3	0.965
			543.5	0.9475
			555.8	0.9225
			567.1	0.895
			579.2	0.86
			591	0.82
			603.7	0.77
			617.3	0.7075
			629.9	0.625
			644.2	0.52
			658.5	0.38
Polystyrene S1	2.5	N_2	534.4	0.984
			547.6	0.9813
			561.7	0.9787
			574.9	0.9707

Table 1 (cont.)

Polymer	β, deg/min	Atmosphere	Temperature, K	$1-c$
			587.6	0.9547
			601.3	0.9067
			614.9	0.808
			628.4	0.6667
			642.7	0.48
			656.1	0.2773
			671.3	0.1173
Polystyrene S2	5	N_2	578	0.9847
			588.9	0.972
			599.8	0.9466
			611.6	0.9033
			623.4	0.827
			635	0.7074
			646.6	0.5547
			659.1	0.3842
			670.7	0.2239
			683.9	0.1043
Polystyrene S3	10	N_2	584.6	0.9841
			596.4	0.9735
			607.3	0.9549
			618.3	0.9204
			629.9	0.8594
			640.7	0.7745
			654	0.6472
			664.8	0.496
			678.1	0.3422
			690.4	0.1989
Polystyrene S4	10	air	579.4	0.9866
			590.2	0.9598
			601.1	0.8794
			612.9	0.7399
			624.7	0.5228
			637.2	0.3378
			650.6	0.2011
Polymethyl methacrylate M1	10	N_2	594.3	0.9873
			60?.3	0.9772
			616.2	0.9492
			627.9	0.8909
			638.9	0.7640
			649.3	0.5508
			662.7	0.3096
			676.1	0.1193

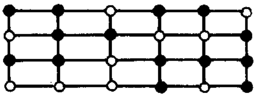
Table 1 (cont.)

Polymer	β, deg/min	Atmosphere	Temperature, K	$1-c$
Polyethylene E1	10	N_2	669.9	0.9854
			682.3	0.9766
			694.6	0.962
			706	0.9386
			718.2	0.9006
			731.3	0.8246
			743.3	0.6871
			755.4	0.4444
			769.2	0.1404

Polypropylene was powdered (<0.13 mesh), antioxidant-free Tatren HPS, a product of Slovnaft, Bratislava (average $Mw \cong 200{,}000$); polystyrene was powdered Vestyron, free of additives; polyethylene was a high-density polymer, free of stabilizers, a product of Slovnaft, Bratislava; polymethyl methacrylate was a product of ROHM and HAAS Inc.: type 8N, atactic. The weight of samples for TG measurements was 50 mg.

Introduction of model formally involving termination of reactive centres (T model)

The equation describing the actual weight loss dependent on linearly rising temperature was derived by assuming the following schematic representation of polymer "evaporation":



The open circles in the cross-section of the volume of evaporating sample designate the molecules formed in polymer decomposition and released into the gaseous phase. The full circles are the molecules of the condensed system. since the open circles are the potential sites of further decomposition and their distribution is uniform, the rate of weight loss may be expressed as follows:

$$-\frac{\mathrm{d}w}{\mathrm{d}t} = \overline{M}\cdot\frac{k_1(1-w)}{k_2(1-w)^m}[1-(1-w)^m] \tag{2}$$

where $\overline{M}$ is the average molecular weight of released molecules, $k_2(1-w)^m$ is the rate of disappearance of open circles due to mutual interactions, $k_1(1-w)[1-(1-w)^m]$ is the rate of their transformation to volatile products (k_1

and k_2 are rate constants), and m is the order of a formal termination. The last term of the product $k_1(1-w)[1-(1-w)^m]$ takes into account the fact that some of the reactive sites (open circles), $\sim(1-w)$, may terminate in mutual interactions, which negatively affects the reaction rate. Equation (2) for non-isothermal conditions, rewritten for the variable $c = 1-w$, is then

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{\mathrm{d}c}{\mathrm{d}T}\cdot\beta = k\cdot\frac{1-c^m}{c^{m-1}} \tag{3}$$

where k is a complex constant. Integration of Eq. (3), where k is again expressed in Arrhenius form as $k = A\exp(-E/RT)$, yields the equation

$$-\ln(1-c^m) = \frac{A}{\beta}\int_{T_{init}}^{T}\exp(-E/RT)\,\mathrm{d}T = \frac{A}{\beta}\cdot I \tag{4}$$

The integral I on the right-hand side may be satisfactorily represented by a rational expression [6] such as

$$I = Te^{-x}H(x) = Te^{-x}\left[\frac{x^3+18x^2+88x+96}{x^4+20x^3+120x^2+240x+120}\right]$$

where $x = E/RT$ and the following equation is then valid

$$\ln\left[-\frac{\ln(1-c^m)}{T\cdot H(x)}\right] = -E/RT+\ln\frac{A}{\beta} \tag{6}$$

which involves the activation energy in the slope $s = -E/RT$ and the pre-exponential factor in the intercept $q = \ln A/\beta$.

For higher values of x, $H(x) \approx RT/E$; least squares linearization of the experimental curve in terms of the coordinates

$$\ln\left[\frac{-\ln(1-c^m)}{T^2}\right] \quad \text{and} \quad 1/T$$

does not pose any problem. For the more general case of any x, the rapidly converging iteration procedure proposed in [6] may be recommended, again yielding the optimum values of E/R, $\ln A/\beta$ and correlation coefficient r. In our experience, the above values may be improved considerably through use of the correction factor f, which is usually very close to 1, so that

$$\ln\left[\frac{-\ln f(1-c^m)}{T\cdot H(x)}\right] = -E/RT+\ln A/\beta \tag{7}$$

This factor, which is in fact an integration constant of Eq. (4), involves the possible experimental errors in the determination of c; it shifts the values of E and $\ln A$ along the pencil-like valley [3] of the E *vs.* $\ln A$ plot to the optimum position of a given experiment. Using Eq. (7) for the experimental points in the conversion interval $c\langle 0\text{–}0.3\rangle$, we first determined the values of the slope E/R and the intercept $\ln A/\beta$ for $f=1$, and we then change the factor f until the optimum value of correlation coefficient r is attained.

Results and discussion

A survey of the activation energies of the thermal decompositions of the examined polymers determined by thermogravimetry (Table 2) indicates that there is a relatively large scatter in their values, which may be understood only by taking into account the different external conditions of the experiments, such as the sample history, the initial weight of polymer, the rate of heating, etc.

Table 2 Survey of activation energies of decomposition of examined polymers

Polymer	Atmosphere	E, kJ/mol	Remark	Reference
Polystyrene	N_2	178	initiator of polymerization: AIBN	7
	N_2	260	initiator of polymerization: AIBN	7
	N_2	240	initiator of of polymerization: DCP	8
Polypropylene	N_2	255		8
Polyethylene	N_2	290		8
Polyethylene	N_2	290		8
Polystyrene	N_2	180	isothermal	9
		205	non-isothermal	9
		234–255		9
Polypropylene	inert	244		10
	N_2	276		11
	oxygen	82	isothermal	11
Polymethyl methacrylate	N_2	207		12
	N_2	210		13
	N_2	224	isothermal	13
	N_2	129		14
Polypropylene	N_2	193–234	T model $m=2$	
Polypropylene	air	885–115	T model $m=1.5$	
Polystyrene	N_2	156–159	T model $m=1$	
Polymethyl methacrylate	N_2	167	T model $m=0.5$	
Polyethylene	N_2	281	T model $m=1.5$	

In the case of polymers examined in nitrogen, the non-isothermal TG records show the order of thermal stability to be as follows: polyethylene > polypropylene > polymethyl methacrylate ⩾ polystyrene (Fig. 1). The activation energy and pre-exponential factor values determined for different values of m are listed in Table 3. If the values of E are compared with those

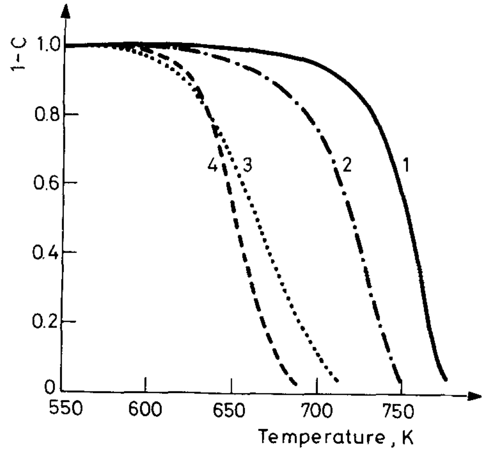


Fig. 1 Non-isothermal TG curves of polymers in nitrogen (6 l/h) 1 – polyethylene, 2 – polypropylene, 3 – polystyrene, 4 – polymethyl methacrylate. Heating rate: 10 deg/min

determined by the isoconversional method by Flynn [4] for several heating rates (in nitrogen), good accordance with the T model is obtained for $m = 1$ for polystyrene, $m = 2$ for polypropylene, $m = 1.5$ for polyethylene, and $m = 0.5$ for polymethyl methacrylate. The T model implies that the replacement of nitrogen by air of oxygen should lead to a decrease in m, as if the termination occurred with more difficulty, or the rate of initiation were higher. This seems reasonable, since "good" values of the activation energy of polymer decomposition in air were found only when m was lower than in nitrogen.

For polystyrene in nitrogen, we found that the remaining part of the curve for $c\langle 0.3–0.8\rangle$ provides the same activation energy value as that for $c\langle 0–0.3\rangle$ if m is higher (1.8 in our case).

Comparison with other models

It may be shown on several different models referred to in the literature that a shift in the parameter m of the termination model T to a lower or higher value permits transition from one reaction mechanism to another (Table 4). The models

Table 3 Optimum values of activation energy and ln A/β (β is the heating rate in deg/min) of respective polymers for termination model and assumed termination parameters m. Conversion c is in the interval ⟨0–0.3⟩ (r is correlation coefficient)

Polymer	Heating rate, deg/min	Atmosphere	E, kJ/mol	ln A/β	r	f	m
Polypropylene							
P1	2.5	N_2	193.0	28.944	−0.9995	1.0003	2
P2	5	N_2	201.6	29.894	−0.9988	1.000	2
P3	10	N_2	230.9	33.414	−0.9980	1.0001	2
P4	2.5	air	115.2	19.541	−0.9994	0.9982	1.5
P5	5	air	104.1	16.483	−0.9996	0.9980	1.5
P6	10	air	88.2	11.932	−0.9995	0.9976	1.5
Polystyrene							
S1	2.5	N_2	169.1	28.286	−0.9966	1.0154	1
S2	5	N_2	156.1	25.284	−0.9999	0.9996	1
S3	10	N_2	156.3	24.712	−0.9995	1.0035	1
c=0–0.3							
S3	10	N_2	158.6	24.416	−0.9991	0.9500	1.8
c=0.3–0.8							
S4	10	air	119.2	19.792	−0.9994	0.9430	0.5
Polymethyl methalcrylate							
M1	10	N_2	166.8	27.451	−0.9998	1.071	0.5
Polyethylene							
E1	10	N_2	281.3	40.746	−0.9993	1.0008	1.5

Table 4 Comparison of some models used for the interpretation of non-isothermal TG curve of polypropylene (P5) (heating rate 5 deg/min), air 6 l/h (models denoted as in [15])

Model	$F(c)$	E, kJ/mol	ln A/β	r	f	m	n
D 4	$1-2/3c-(1-c)^{\frac{2}{3}}$	172.3	28.51	−0.9935	—	—	—
D 3	$[1-(1-c)^{\frac{1}{3}}]^2$	174.1	28.96	−0.9940	—	—	—
D 2	$(1-c)\ln(1-c)+c$	171.4	29.79	−0.9932	—	—	—
F 1	$-\ln(1-c)$	84.3	13.00	−0.9940	—	—	1
F n	$1-(1-c)^{1-n}/(1-n)$	88.6	14.07	−0.9959	—	—	2
		93.1	15.12	−0.9973	—	—	3
		97.7	16.13	−0.9981	—	—	4
		82.1	12.64	−0.9928	—	—	0.5
		80.2	12.01	−0.9915	—	—	0
T	$-\ln(1-c^m)$	169.7	30.07	−0.9929	1	2	—
		143.2	24.26	−0.9994	0.9997	2	—
T	~F 1	84.3	13.00	−0.9940	1	1	—
		104.1	16.48	−0.9996	0.998	1.5	—

D4, D3 and D2 denote the heterogeneous, diffusion-controlled processes described by Wadsworth, Jander and Ginstling-Bronshtein [16]. They are well compatible with the T model if $m = 2$ ($f = 1$). The values of parameter $m = 1$ correspond to a current exponential law for $n = 1$, which seems to be suitable [14] for the description of the decompositions of polymers which leave no residue. On increase of the apparent reaction order n, the activation energy slightly increases.

The case $m = 0.5$ corresponds to the random depolymerization model for a number $L = 2$ of carbon atoms in the smallest chain that does not evaporate. Within the interval $m = 0.5$–1, the model involves the isothermal maximum cases as mentioned in [17], but the maximum may move over the whole interval of c from 0 to 1.

The theoretical non-isothermal TG curves calculated for the T model and different m, and for parameters taken from experiment P 6 evaluated for $m = 2$, quite clearly demonstrate the flexibility of the model used (Fig. 2).

A decrease of the m value towards zero leads to TG curves with steeper and steeper slopes and in the limiting case $m = 0$, the TG record is a straight line parallel with the coordinate of residual weights.

Random depolymerization and model involving formal termination of reactive centres

The flexibility of the proposed model involving the formal termination of reactive centres may additionally be demonstrated through a comparison with the random

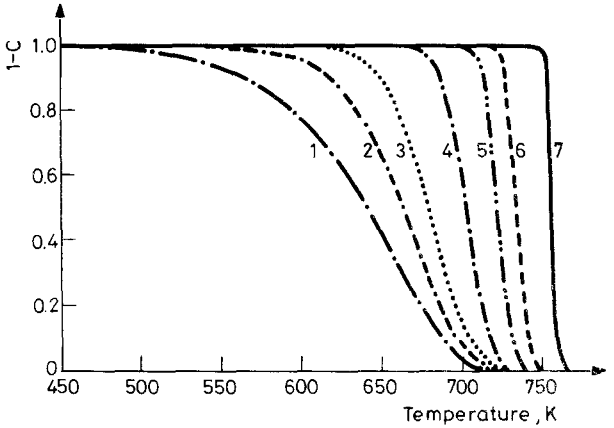


Fig. 2 Theoretical non-isothermal TG curves calculated for T model. Parameters originally obtained for sample of polypropylene P6 ($m = 2$, $f = 0.9997$, $r = -0.9991$, $\ln A/\beta = 19.08$, $E = 126.3$ kJ/mol); $m = 2$ (curve 1), 1 (curve 2), 0.5 (curve 3), 0.1 (curve 4), 0.01 (curve 5), 0.001 (curve 6), 0.000001 (curve 7)

depolymerization equation put forward by Simha and Wall [18]:

$$c = 1-(1-\alpha)^{L-1}\left[1+\alpha\cdot\frac{(N-L)(L-1)}{N}\right] \tag{8}$$

where N is the initial number of carbon atoms in the polymer chain, L is the number of carbon atoms in the smallest chain that does not evaporate, and α is the fraction of broken bonds, expressed under isothermal conditions as

$$\alpha = 1-e^{-lt} \tag{9}$$

where l is the rate constant of chain scission. If we consider the analytical form of a T model obtained by the integration of Eq. (2) under isothermal conditions for $f=1$, we have

$$\ln(1-c^{m}) = -kt \tag{10}$$

from which

$$c = (1-c^{-kt})^{1/m} \tag{11}$$

Of course, we do not know whether the constant l can be identified with k; if this is so, we may put

$$c = \alpha^{1/m} \tag{12}$$

We therefore performed a comparison of Eqs (8) and (12) in logarithmic coordinates (the values of α were 0.05, 0.1, 0.2, 0.25 and 0.3) for different values of N and L, and found that within $\alpha\langle 0\text{–}0.3\rangle$ a more or less good linear dependence may be obtained for the coordinates

$$\ln\left\{1-(1-\alpha)^{L-1}\left[1+\alpha\frac{(N-L)(L-1)}{N}\right]\right\} \quad vs.\ \ln\alpha$$

the slope of which should correspond to $1/m$, while the intercept involves the deviation from random depolymerization kinetics. It was ascertained that there is a relatively slight effect of the initial molecular weight of the polymer (Table 5) on the slope. From the plot of m *vs.* L (Fig. 3), we may see that for $m=0.5$, $L=2$, and the polymer volatilization is governed by random depolymerization (polymethyl methacrylate). At the same time, by choosing $m=0.5$ for polymethyl methacrylate, we "a priori" assume that the obtained value of the activation energy corresponds to that of random chain scission. The value $m=2$ considered for the degradation of polypropylene in nitrogen corresponds to $L=27$, while $m=1$ for polystyrene corresponds to $L=15$. The activation energy obtained in this way reflects the process of random scission.

The reported values $L=34$ for polyethylene, $L=24$ for polypropylene and $L=9$

Table 5 Calculated values of slope s and intercept q of dependences (8) and (12) for different values of L and N (r = correlation coefficient). (for $\alpha = 0.05$, 0.1, 0.15, 0.2, 0.25, 0.3)

L	N	q	$s = 1/m$	r
2	100	−0.1610	1.8470	0.9998
	1,000	−0.01996	1.9820	0.9999
	2,000	−0.01011	1.9909	0.9999
3	1,000	0.7570	1.8794	0.9999
	10,000	0.7755	1.8955	0.9999
	20,000	0.7765	1.8965	0.9999
4	1,000	1.1389	1.7807	0.9999
	20,000	1.1589	1.7977	0.9995
	100,000	1.1597	1.7984	0.9993
	10,000,000	1.1599	1.7986	0.9995
5	10,000,000	1.3705	1.7037	0.9988
6	10,000,000	1.4805	1.6128	0.9979
10	10,000,000	1.5350	1.2898	0.9909
12	10,000,000	1.4584	1.1521	0.9855
14	10,000,000	1.3594	1.0293	0.9792
20	10,000,000	1.0481	0.7384	0.9561
25	10,000,000	0.8281	0.5658	0.9353
30	10,000,000	0.6534	0.4381	0.9155

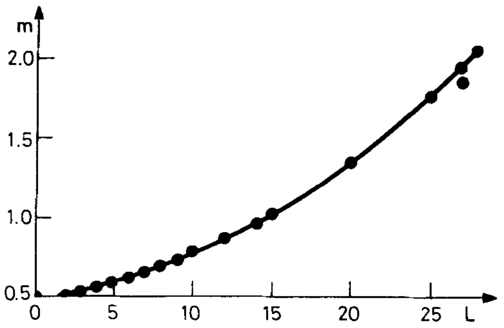


Fig. 3 Dependence of m on L for c 0–0.3

for polystyrene [18] are in quite good accordance for such a rough estimation. It should be remembered, however, that under non-isothermal conditions and with a statistical mode of polymer degradation, L would also change with temperature.

In air, the shifts in L and m to lower values compared with those in nitrogen may be interpreted in terms of the formation of lower molecular weight products due to polymer peroxidation.

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Zusammenfassung — Ein Modell für Zersetzungsreaktionen von Polymeren wurde entworfen, das auf dem Abbau von aktiven Zentren basiert. Es liefert richtige Aktivierungsenergien für die Zersetzung von Polypropylen, Polyäthylen, Polystyren und Polymethylmethakrylat (bestimmt durch nichtisotherme Thermogravimetrie) und macht es ausserdem möglich, die „äusseren“ Reaktionsbedingungen, wie Einwaage, Atmosphäre, Ventillationsbedingungen, Art und Form des Probenhalters usw. zu berücksichtigen.

Резюме — Предложена модель разложения полимера, которая формально включает обрыв активных центров. Такая модель дает возможность получать приемлемые энергии активации реакций разложения полиэтилена, полипропилена, полистирола и полиметилметакрилата, изученных неизотермической термогравиметрией. Предложенная модель допускает включение таких «внешних» условий реакций, как начальный вес образца, атмосферы, условий продувки, характера и формы держателя образца и т. п.