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The Macrokinetics of the Thermal Decomposition of Polymers

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The kinetics of the thermal decomposition of thermoplastic polymers have been reviewed. The influence of the external medium—inert and chemically active gases - on the rate of thermal decomposition has been discussed. Heat and mass exchange at the surface of a polymer undergoing degradation, and the influence of the rate of heating and the thermal flux power, have been examined.
The bibliography contains 67 references.

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I. INTRODUCTION

In connection with the continuous increase in the production and use of polymeric materials, their stability to various external factors, including thermal fluxes of different intensities, is acquiring exceptional importance. When a thermal flux acts on a polymer surface, heating and thermal degradation take place, and this is important from a number of viewpoints.

Many polymers are designed for use at high temperatures of the surrounding medium, and may also be subjected to powerful thermal fluxes from flames and other sources. A knowledge of the mechanism of the thermal decomposition of polymers can therefore be used to change their properties to create fire-resistant synthetic polymers.

Thermal degradation processes can be divided into two categories, according to the nature of the heat acting on the polymer (the thermal flux power and the temperature of the surrounding medium). The first corresponds to bulk processes of isothermal degradation of the polymer, and the second to surface degradation of the polymer, usually called linear thermal decomposition.

Detailed discussion of the isothermal degradation of polymers, examination of the theoretical aspects, and attempts to establish the dependence of the mechanism of the decomposition of polymers on their structure have been carried out by a number of workers, and comprehensive monographs on these topics have been written by Jellinek[1], Grassie[2], Madorsky[3], and others[4,5].

The extrapolation of data on isothermal kinetics in a block to the range of rates of degradation usually encountered in surface thermal degradation and combustion is apparently unjustified[6].

To determine the macrokinetic characteristics of combustion, the efficiency of ablation heat protection, the efficiency of fire-resistant polymer coatings, and the parameters of other processes characterised by high temperatures and high thermal fluxes, it is necessary to know the regular kinetic features of the thermal decomposition and the influence of the surrounding atmosphere, the rate of heating of the polymer surface or the thermal flux power, the structure of the polymer, the thermochemical and thermophysical properties of the polymers, etc.

According to existing ideas[5], polymers can be divided into three classes, according to the type of thermal degradation: the first undergo complete degradation with rupture of the main chain; the second type includes the removal of lateral fragments, and these polymers give volatile gaseous products and a coke residue; and the third type consists of cross-linked polymers which give small quantities of volatile products and a large quantity of coke.

Without going into the details of the mechanism of thermal degradation, the main task today is to establish the limiting stage of the thermal decomposition of polymers at high temperatures and the relationship between the macrokinetics of this process and the kinetic characteristics of the low-temperature "isothermal" degradation. This problem can be solved only by analysing published experimental data on high-temperature thermal decomposition.

The simplest case is the thermal degradation and thermal decomposition of thermoplastic polymers, when the polymer is completely converted to gases, without leaving a residue. In this case it is possible to study the phenomenon of high-temperature degradation and thermal decomposition under quasi-stationary conditions. With polymers of the second and third types, however, a carbonised residue will gradually accumulate on the surface of the condensed phase, leading to a continuous change in the conditions of heat and mass transfer at the interface between the gas and condensed phases. The present paper analyses published experimental data on the thermal decomposition of thermoplastic polymers.

II. PROCEDURES FOR STUDYING THE THERMAL DECOMPOSITION OF POLYMERS

A number of methods have now been developed for studying the macrokinetic characteristics of thermal decomposition in the range of temperatures and rates of thermal decomposition not accessible to classical isothermal methods. They are based on the measurement of the rate of mass loss by the specimen being studied, and on the analysis of the volatile products[3]. An important problem is the measurement of the temperature of the surrounding medium, the temperature of the surface of the polymer undergoing thermal decomposition, and the thermal flux at the surface of the specimen.

The composition of the degradation products under the conditions of high-temperature thermal decomposition characterises not only the processes taking place in the condensed phase but also the secondary reactions taking place in the heating zone. Analysis of the dependence of the degradation products of polymers on the temperature of the sur-

rounding medium[7] showed that increase in the temperature of the surrounding medium leads to a significant decrease in the yield of monomer as a result of secondary reactions for polymethyl methacrylate (PMMA), poly-α-methylstyrene, polystyrene (PS), polypropylene (PP), and other polymers (see Table 1). The yield of monomer in the thermal decomposition is strongly influenced by the conditions of the experiment[7].

Table 1. Yield of monomer (mass % of the total quantity of volatile products) in the thermal decomposition of various organic polymers in a vacuum at elevated temperatures[7].

Polymer	T, °C		
	500	800	1200
Polyethylene	0.03	5.5	26.4
Polypropylene	0.4	17.9	15.8
Polyisobutene	36.5	69.0	13.0
Polystyrene	51.0	10.5	0.6
Polymethyl methacrylate	94.2	91.8	12.9
Polytetrafluoroethylene	96.6	91.2	78.1
Poly-α-methylstyrene	100	88.5	37.7

In the methods developed for studying thermal decomposition, the polymer is heated in different ways: 1) by the heat flux from a heated plate[8-13]; 2) by the heat flux from a massive heat-conducting block[14-16]; 3) by a radiant thermal flux[17-19]; 4) by convective heating in a stream of hot gas[20-24]; 5) by the thermal flux from a diffusion flame formed close to the surface of the polymer specimen, which is swept by a stream of gaseous oxidising agent[25-33], etc.

The first studies of the thermal decomposition of polymers were carried out by Schultz and Dekker[8]. The essential feature of their method is that the polymer specimen is pressed with a constant force by means of a load against the flat surface of a metal plate heated by an electric current. The junction of a platinum–platinum/rhodium thermocouple with a diameter (d) of 50 μm was welded to the centre of the plate above the specimen being tested. The heated-plate method was subsequently developed by other workers[9,10,12,13].

Other workers[34,35] used a porous plate instead of a continuous plate to heat the specimens. In their opinion, the use of a continuous plate to study the thermal decomposition leads to an increase in the rate of the thermal decomposition as a result of the elution (erosion) of the molten liquid layer of polymer from the gap between the specimen and the heater by the flux of thermal decomposition products. Many of the data which they obtained, however, show a marked scatter even for materials which sublime. It is possible that in the thermal decomposition of thermoplastic polymers, the liquid layer flowed into the pores of the plate before volatilising, so that the porous-plate technique has not found application in thermal decomposition studies.

The use of massive copper or aluminium blocks instead of a plate heater has been proposed[14] to obtain linear thermal decomposition with the highest possible levels of thermal flux and rate of thermal decomposition. A heater and a thermistor are mounted on the lateral surface of the block. The junction of a microthermocouple is stamped into the lower end face. The system used to supply the specimen and record the rate of linear thermal decomposition was the same as in Ref.8. The instruments with a heating block solved extremely simply the problem of measuring the thermal flux q_s. Thus placing two Constantan junctions separated by a distance l in the lower part of the copper block having a cross-section close to the area of the end fact (S) of the specimen undergoing thermal decomposition makes it possible, from the readings of the resulting differential Constantan–copper–Constantan thermocouple ΔT_{bl}, to find

$$q_s = \lambda_m \Delta T_{bl}/l$$

where λ_m is the thermal conductivity of copper.

In contrast to previous methods in other studies[21,22,24] etc., the surface of the polymer specimen was heated by a flow of heated gases.

In Ref.22, the temperature of the heated gases was varied from 500 °C to 950 °C, and the flow rate was varied in the range 30–60 cm s^{-1}. The temperature of the polymer surface and the temperature profile along the axis of the specimen were measured by introducing Chromel/Alumel thermocouples with a wire diameter of 50 μm.

In Ref.21, the surface of the specimen undergoing thermal decomposition was swept with the exhaust gases from a small laboratory rocket motor—the products of the combustion of a C_3H_8–O_2–N_2 mixture —and the rate of the thermal decomposition was measured. The concentration of oxygen in the surrounding atmosphere varied from 12 mole % to 83 mole %. The temperature of the stream at the end of the rocket motor jet was 1100 °C. The density of the thermal flux was ~20 cal cm^{-2} s^{-1}. The rate of thermal decomposition was determined by the change in the length of the specimen undergoing thermal decomposition when it was swept by the combustion products for 9 s.

In Ref.24, a method for studying the high-temperature thermal decomposition of polymers in a stream of heated gases was proposed, which made it possible to record the mass rate of thermal decomposition, the temperature of the polymer surface, and the temperature of the stream of gases.

Polymer specimens with an initial mass of ~(2–3) × 10^{-3} g and initial diameter d_0 = 1–1.5 mm were taken for the study of the thermal decomposition. The specimen was placed on the junction of a Pt–Pt/Rh thermocouple (wire diameter 20 μm), the ends of which were brought through a two-channel sheath with diameter 1 mm and through an amplifier to the recording apparatus. The thermal decomposition was carried out in a stream of gases, heated by an electric furnace, and the rate of flow was kept constant (4 cm s^{-1}). When introduced into the furnace, the polymer specimen melted, covered the junction of the thermocouple, and hung from it as a liquid drop. The thermocouple junction was then in the surface layer of the specimen, and recorded a temperature close to the temperature of the surface of the polymer. The change in the mass of the specimen was recorded using an electronic microbalance based on an MKh-1S mechano-electronic device—an electronic valve with a moveable anode. The signal from the mechano-electronic device was passed through an electronic transformer and amplifier and recorded by an N-115 oscillograph. Typical curves giving the change in the mass of the specimen and temperature are shown in Fig.1. When the specimen is introduced into the stream of heated gases, in the first period (I) the specimen is heated to a temperature T_s, which changes little during the thermal decomposition of the polymer specimen. When the thermal decomposition is complete, the thermocouple records the temperature of the stream T_∞.

The degradation of small polymer specimens in a stream of heated gases under the conditions of thermal decomposition and combustion has been studied[26]. The experimental assembly included two electrical heating coils, between which the polymer specimens (diameter 1–2 mm) were placed, at the

end of a horizontal glass fibre. The coils were heated to ~1000 °C. The diameter of the specimen was measured photographically during the thermal decomposition and combustion to within 1.27×10^{-3} cm. The temperature of the polymer surface was estimated using a thermocouple, on which the polymer specimen was placed. As in the previous case, the temperature of the specimen increased rapidly in the first period, after which it remained practically constant until the specimen disappeared completely, when it increased sharply, recording the temperature of the external medium. The moment of complete volatilisation of the polymer was recorded photographically.

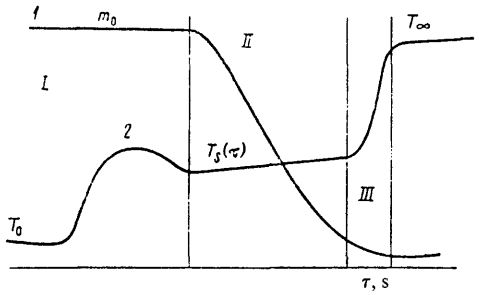


Figure 1. Change in mass (m) (*1*) and temperature (*2*) during thermal decomposition: *I*) heating of the polymer, *II*) thermal decomposition, *III*) recording of the flow temperature T_∞.

To increase the thermal flux at the polymer surface under conditions in which the polymer was swept by a stream of heated gases, a method was developed[25] in which a planar diffusion flame was established above the surface of the polymer. The temperature profile in the condensed phase was measured by a thermocouple placed inside the specimen. Cylindrical PMMA specimens with diameter 1.9 cm and length 3.71 cm were studied. The rate of linear thermal decomposition was determined in the stationary region by measuring the time required for the thermal decomposition of a specimen with a thickness of 1.27 cm. In addition to the thermocouple method, the temperature of the surface was measured using spectral methods, by recording the emission spectra of PMMA at a wavelength of 5.8 μm (the characteristic band of the C=O bond in the monomer), and determining T_S from their intensity. The optical measurements of the temperature of the surface (T_{SO}) gave a reproducible dependence of the temperature on the concentration of oxygen in the stream. The values of T_{SO} obtained were only a few degrees higher than the values measured by other methods.

The thermocouple measurements were carried out using Pt–Pt/Rh thermocouples with diameter 15 μm. In all cases, a region of relatively slow increase in temperature was observed before the thermocouple came out on to the surface. The extent of this region decreased sharply with increase in the rate of thermal decomposition. From the change in the nature of the thermocouple noise, it was concluded that there is a liquid layer on the surface of the PMMA undergoing thermal decomposition. The temperature profile in the condensed phase under the conditions of "quasi-stationary" thermal decomposition was assumed to obey Mikhel'son's equation[36]

$$T_{(x)} - T_0 = (T_s - T_0)\exp(-Ux/a) \quad (1)$$

where x is the distance from the surface, $T_{(x)}$ the current temperature, T_0 the initial temperature, T_S the temperature of the surface, a the coefficient of temperature change in the polymer, and U the rate of linear thermal decomposition. The authors[25] found the temperature of the surface by analysing their temperature profile data using the semilogarithmic relationship of Eqn.(1).

Other authors[34,37] studied combustion processes using an apparatus similar to that developed in Ref.25. An optical device was used to keep the surface of the specimen at the same distance from the front of the jet through which the oxidising agent was passed. In Ref.38 the polymer specimen was swept not by a counter stream but by a stream in the same direction, and "candle combustion" took place. All the measurements of the mass rate of thermal decomposition under the conditions of candle combustion were carried out when stationary conditions had been reached.

In Ref.19, thermal decomposition under combustion conditions was studied using planar polymer discs with thickness 3–5 cm and thermal decomposition surface area from 60 cm^2 to 100 cm^2. The specimen was placed in a quartz tube of length 61 cm and diameter 17 cm. A nitrogen–oxygen mixture with a given O_2/N_2 ratio was passed through the tube at a rate of 50–70 litre min^{-1}. The apparatus was fitted with two additional powerful sources of thermal radiation, which were directed on to the surface of the polymer being studied. The mass rate of thermal decomposition was measured continuously by an electronic balance. To investigate the influence of various factors on the rate of thermal decomposition ($\dot{m}$), the influence of the thermal decomposition surface area on the value of $\dot{m}$ was first studied. Extrapolation of the data on the dependence of $\dot{m}$ on S gave different values of the surface area at which $\dot{m}$ no longer depends on S; 3.0 m^2 for polystyrene, 2.5 m^2 for polymethyl methacrylate, 0.5 m^2 for polyethylene, and 0.3 m^2 for polypropylene.

To exclude completely the influence of heat losses from the specimen to the surrounding medium, that is to eliminate the influence of the surface area of the heated specimen on the mass rate of thermal decomposition, a method was proposed[33] for studying thermal decomposition under the conditions of the diffusion combustion of a spherical specimen completely surrounded by a flame. The polymer specimen with diameter 10 mm was fixed by a quartz capillary-holder on a vertical ceramic tube with outer diameter 1–1.5 mm. This ceramic tube was firmly connected to the horizontal rod of a mechano-electronic device, which recorded the change in the mass of the specimen undergoing thermal decomposition under combustion conditions. The power of the thermal flux to the surface of the polymer was controlled by changing from 20% to 100% the proportion of oxygen in the $N_2 + O_2$ mixture, supplied through a quartz tube with diameter 70 mm. The specimen was ignited by a gas burner, which was switched off immediately after the specimen began to burn. The thermal flux to the polymer surface was measured using a thermocouple probe, the shape of which coincided with the shape of the isothermal surface of the specimen. The temperature profile in the specimen and the temperature of the thermal decomposition surface were measured by a thermocouple placed inside the specimen at a distance of 1 mm from the surface. The diameter of the Pt–Pt/Rh wire used for the thermocouples was 0.02–0.03 mm. The external thermocouple probe was firmly connected to the linear displacement meter, whose readings were recorded on an oscillograph film. The moment when the outer thermocouple probe touched the polymer surface was recorded from the

response of the mechano-electronic device on the oscillograph film, and also visually using a KM-6 cathetometer and time recorder. An advantage of this method is that the change in the mass of the specimen undergoing thermal decomposition and the temperature profile in the gas and condensed phases are recorded on the same time coordinates.

The values of the maximum temperature of the flame (T_f), the temperature of the surface (T_S), and the temperature gradient (dT/dr), determined using the external thermocouple probe, are given in Table 2.

Table 2. Temperature measurements during the combustion of spherical PMMA specimens in an $N_2 + O_2$ atmosphere[33].

O_2, %	T_f, °C	T_S, °C	dT/dr, K cm^{-1}*
20	1350	460	5050
25	1520	480	6200
30	1660	500	7400

*Radius of the specimen in the measurements 4.5 cm.

The temperature of the surface and the temperature gradient at high oxygen concentrations (greater than 30 mass %) were measured by means of an internal thermocouple which emerged into the gas phase; this moment was recorded optically and determined from the sharp break on the curve giving the change in temperature. In Ref.30, an apparatus was proposed for determining the rate of degradation under conditions of thermal decomposition and combustion, in which a cylindrical reaction vessel with diameter 0.8 cm and height 1 cm was connected to a quartz rod, acting as the rod of an electronic balance. In this apparatus it was possible to carry out the thermal decomposition in a stream of air and inert gas. The planar heater, with diameter 0.9 cm, was placed at a distance of 0.8 cm from the specimen surface. The instrument developed makes it possible to record simultaneously the temperature of the specimen undergoing thermal decomposition and the change in its mass.

III. MEASUREMENT OF THE TEMPERATURE OF THE SURFACE OF POLYMERS DURING THERMAL DECOMPOSITION

Data on the kinetics of the degradation of polymers are usually correlated using the Arrhenius expression for the rate of thermal decomposition

$$\dot{m} = A \exp(-E/RT_s) . \qquad (2)$$

If the kinetic data are described by this relationship, the data obtained in one temperature range can be used to predict the behaviour of the polymer in other temperature ranges.

Success in correlation has been restricted to the knowledge of such quantities as T_S and the thermodynamic properties of a specific polymer[6]. When the experiments are carried out in the low-temperature range up to 300 °C, and when the degradation takes place in the "kinetic range", that is when the characteristic heating time of the specimen is much less than the chemical reaction time, the temperature of the polymer is equal to the temperature of the reaction vessel or the temperature of the surrounding medium.

Shteinberg[15] examined the physical picture of the endothermic bulk decomposition (gasification) of a sphere of substance whose kinetics corresponded to Eqn.(2). By introducing characteristic time scales, namely the heating time of the sphere

$$\tau_h = \frac{r^2}{a}$$

where r is the characteristic dimension of the specimen, and a is the thermal conductivity, and the decomposition time of the substance at a temperature T_S

$$\tau_r = [K_0 \exp(-E/RT_s)]^{-1}$$

he estimated the relative thickness of the reaction layer Δ.

At comparatively low temperatures T_S (Fig.2*a*), $\tau_h \ll \tau_r$, and all the substance can be heated to a temperature $T \cong T_S$ (the temperature gradient along the thickness of the specimen is practically zero) long before any significant fraction of it decomposes, $\Delta = r$. With increase in T_S (Fig.2*b*), the decomposition time τ_r becomes commensurate with the heating time τ_h, and $\Delta < r$. In the limit when $\tau_h/\tau_r \gg 1$ (Fig.2*c*), the thickness of the reaction layer is much less than the thickness of the material $\Delta/r \ll 1$, that is degradation takes place close to the hot surface, and moves together with the heating wave. The temperature profile in the condensed phase is determined by the ratio between the rate of movement of the heating wave and the thermophysical characteristics of the polymer specimen in accordance with the Mikhel'son equation[36]. When the degradation is carried out under thermal decomposition conditions, the temperature measurement involves considerable difficulties. In early studies of linear thermal decomposition by the heated-phase method[8–13], and also in thermal decomposition by a heated metal block[14–16], the thermocouple designed to record the surface temperature was fixed in the metallic heater. The temperature of the heater was taken as the temperature of the surface.

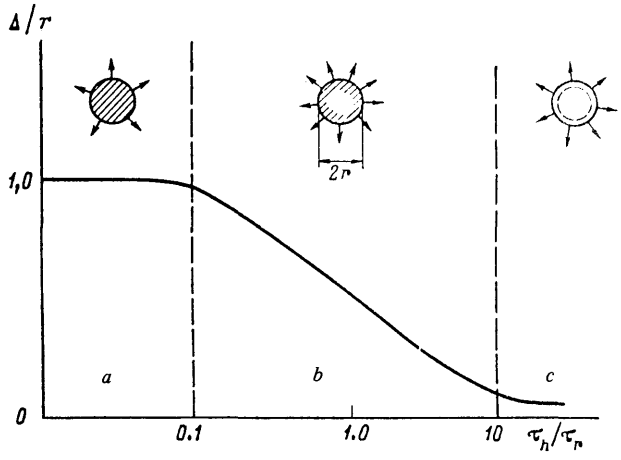


Figure 2. Dependence of the relative thickness of the reaction layer on the ratio of the characteristic times of thermal relaxation τ_h and decomposition τ_r.[15]

Cantrell[10] was the first to draw attention to the fact that the temperature of the surface undergoing thermal decomposition was different from the temperature of the heated block.

With change in the temperature of the heater T_0 from 8 °C to 60 °C, the rate of the linear thermal decomposition of solid carbon dioxide increased by a factor of less than 2, and the temperature of the surface T_S increased from −52 °C to −42 °C. An interesting feature is the appreciable superheating of the surface of dry ice compared with the temperature of equilibrium sublimation, corresponding to a pressure of gas in the film of ~1 atm. It was pointed out that for small T_0, $T_S \cong T_0$, and at high T_0 and high rates of linear thermal decomposition, the effect of the film may be significant, and $T_S < T_0$. Cantrell examined the problem of the transfer of heat in the gas gap formed by the linear thermal decomposition between the heater plate and the polymer, and obtained an equation relating the thickness of the gap (z) to the geometric dimensions of the specimen (r), the rate of linear thermal decomposition (U), the density of the substance (ρ), the viscosity of the thermal decomposition products (γ), and the force (W) pressing the polymer against the heated surface

$$z = \frac{3}{2}(\pi r^4 \gamma \rho U / W)^{1/3} . \quad (3)$$

In his experiments on the linear thermal decomposition of PMMA, Shteinberg[16] recorded the linear rate of decomposition and the thermal flux to the specimen surface q_1, which is given by:

$$q_1 = \lambda (T_0 - T_s)/z \quad (4)$$

where T_0 is the temperature of the heater. Eqns.(2)–(4) were used to calculate the values of ΔT, which are given in Fig.3.

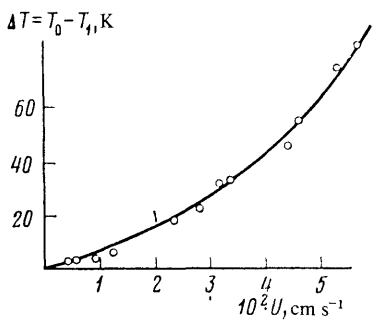


Figure 3. Change in the temperature drop through the gas film with increase in the rate of thermal decomposition of PMMA.[14]

The values of the thermophysical constants of the gas in the calculations were taken for the heavy hydrocarbon octane at the temperature of the plate. For the highest rates of thermal decomposition achieved in the experiments, the calculated thickness of the gas gap did not exceed 30 μm.

Tkachenko and co-workers[14] studied the thermal decomposition of linear and cross-linked PMMA. The temperatures of the surface of the material undergoing thermal decomposition at medium rates of thermal decomposition were calculated as in the previous case, but for high rates, assuming that T_S is constant, the temperature was found graphically from the equation:

$$\frac{mr}{W^{1/3}} = \left(\frac{32}{\pi}\right)^{1/3} \frac{\lambda (T_0 - T_s)}{\nu^{1/3}[c(T_s - T_\infty) + Q]} .$$

The values of T_S obtained were 450 °C for linear PMMA, and 475 °C for cross-linked PMMA.

In a study of the linear thermal decomposition of PE and PMMA,[23] the dependence of the temperature of the surface of the polymers undergoing thermal decomposition on the temperature of the surrounding medium was measured, and it was shown that they gradually increase.

A study of linear thermal decomposition in a stream of heated gases in the temperature range 500–950 °C [22,39] showed that the temperature of the surface and the temperature profile in the condensed phase are the same, irrespective of the conditions of the experiment.

Table 3. Temperatures of the surface (T_S) in the combustion of various polymers[25,40].

Polymer	λ, μm	T_s, °C	
		in air	in oxygen
Polyethylene	6.9	511	570
Polyisobutene	6.9	428	469
Polyester-polyurethane rubber	8.75	—	507
Polypropylene glycol-polyurethane rubber	8.75	—	492
Polymethylmethacrylate	8.75	417.417	477—490.527

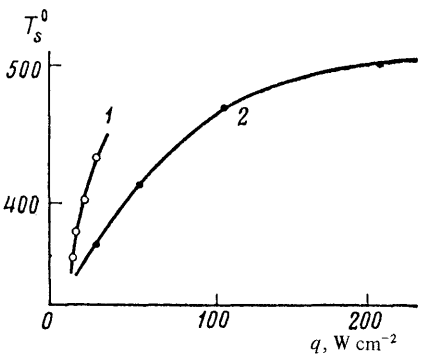


Figure 4. Influence of the thermal flux on the temperature of a PMMA surface during thermal decomposition: *1*) data from Ref.17, *2*) data from Ref.18.

The increase in the rate of linear thermal decomposition was attributed to the increase in the rate of volatilisation of the degradation products from the surface.

Infrared radiation has been used[40] to measure the temperature of the surface of burning fuels and polymer binding agents. This method was used to measure the temperatures of the surface of polymers during combustion in air and in an oxygen atmosphere.

The data in Table 3 show that for combustion in oxygen, T_S is 40–60 K greater than for combustion in air. The same method has been used[25] to determine the temperature of the surface in the thermal decomposition of PMMA during combustion.

Published data[17,18] on the influence of the thermal flux on the temperature of thermal decomposition show that with increase in the thermal flux to a surface, its temperature

increases (Fig.4). The dependence is more marked at low thermal fluxes. The lack of agreement in the published data[17,18] is due either to the inaccuracy of the determination of the thermal flux to the polymer surface or to the inaccuracy of the temperature determination.

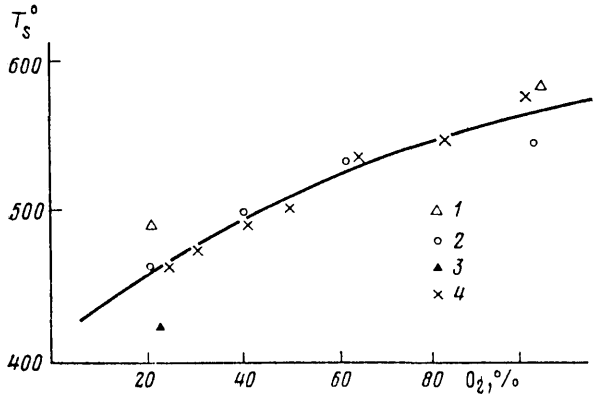


Figure 5. Dependence of the surface temperature of a PMMA specimen undergoing thermal decomposition under combustion conditions on $[O_2]$: *1*) Ref.25, *2*) Ref.26, *3*) Ref.33, *4*) Ref.44.

Table 4. Surface temperatures and combustion constants for polymers in air[26].

Material	T_s, °C	K, s cm^{-2}	
		expt.	theor.
Polyethylene	538.500*	39.8	57
Polypropylene	528	40.4	—
Nylon-6	542	29.4	—
Polymethylmethacrylate	416	36.3	57
Polystyrene-butadiene	—	44.1	—
Polyvinyl acetate	—	25.4	—
Cellulose acetate	309	6.1	—
Polystyrene	480** 494 480*	57.6	61
Polycarbonate	578	11.6	—
Phenol resin	—	80.5	—
Polyamide	—	29.7	—

* —[43], ** [42].

The influence of the oxygen concentration on T for the surface of a burning PMMA specimen was studied by other workers[34,41], and the results are given in Fig.5.

The experimental values of the temperatures of the surface and the rates of combustion for a number of polymers are given in Table 4.

Systematic studies of the influence of the temperature of the surrounding medium on the temperature of the surface of thermoplastic polymers undergoing thermal decomposition in a stream of heated gases have been carried out[24], and the results are given in Table 5.

IV. INFLUENCE OF OXIDISING AGENTS AND CHEMICALLY ACTIVE GASES ON THE THERMAL DECOMPOSITION OF THERMOPLASTIC POLYMERS

Studies carried out by many authors on the influence of oxygen on the rate of "bulk" degradation, studied thermogravimetrically, have shown that the presence of oxygen in the surrounding atmosphere usually leads to a marked increase in the rate of the bulk degradation of thermoplastic polymers[44,45]. In thermal decomposition, however, we are dealing with much higher temperatures, thermal fluxes, rates of heating of the specimen, and rates of degradation, so that it was necessary to determine the role of chemically active gases and oxygen in this range.

Table 5. Values of T_s (°C) in the thermal decomposition of thermoplastic polymers in a stream of heated gases[24].

Polymer	T_s					
	500	600	700	800	900	1000
PMMA	410	440	460	470	480	485
POM	450	490	515	530	535	540
PS	465	500	525	545	555	565
PE	485	535	570	595	610	620
PP	480	525	560	585	600	610

In Ref.21, the surface of a porous polymer was heated in the exhaust from a laboratory jet motor—the combustion products of a C_3H_8–O_2–N_2 mixture. The concentration of oxygen in the surrounding atmosphere was varied from 12 mole % to 83 mole %. A study of the rates of the thermal decomposition of PS and PMMA showed that the rate of the thermal decomposition is not sensitive to oxygen. In another series of experiments, a porous specimen was used and the concentration of any test gas passed through it was accurately controlled. The influence of N_2, O_2, ClO_3F, NO, NO_2, Cl_2, HCl, NH_3, and SO_2 on the thermal decomposition of PS and PMMA was studied. The rate of the thermal decomposition of PMMA and PS decreased with increase in the rate of supply of the test gases, but the introduction of NO_2 and Cl_2 led to a slight increase in the rate of the thermal decomposition of PS. The decrease in the rate of degradation with increase in the supply of test gases was related to the increase in the proportion of heat used up in heating the gas, and the decrease in the heat used to heat the polymer.

The influence of the concentration of oxygen on the thermal decomposition of PS and PMMA in a stream of gas heated to a temperature of 700 °C has been studied[22]. Increase in the O_2 concentration has no influence on the rate of the linear thermal decomposition of PS, and leads to a slight increase in the rate for PMMA.

A study of the influence of oxygen on the rate of the linear thermal decomposition of polystyrene, styrene–butadiene copolymers, and mixtures of polystyrene with o-phthalic acid, maleic acid, and propylene glycol[46] showed that at rates of thermal decomposition comparable with the rates observed in the combustion of polymers, oxygen has no influence on the rate of the linear thermal decomposition.

In Ref.24, the influence of the composition of the surrounding atmosphere was investigated by studying the thermal decomposition of PMMA in a stream of helium, nitrogen, and air. The values of the "volatilisation" constants for spherical specimens in a stream of heated gases, and their thermal conductivities, are given in Table 6.

At medium temperatures of the surrounding medium, the volatilisation constant is greater in helium, in which the thermal conductivity is almost ten times that for nitrogen and air. With increase in T_∞, this difference decreases, as a result of the increase in the contribution of radiation from the heating furnace to the total thermal flux. Thus at a temperature of ~1000 °C, the radiative thermal flux to the polymer surface is ~0.1 cal cm^{-2} s^{-1}, and the convective thermal flux ~0.05 cal cm^{-1} s^{-1}.

Table 6. Volatilisation constants 10^3 K, cm^2 s^{-1} for PMMA.

Gas streat	10^6 λ, cal $cm^{-1}s^{-1}K^{-1}$*	T_∞°					
		400	500	600	700	800	900
Nitrogen	98	0.5	2.5	4.8	7.0	9.6	13.0
Air	99	0.4	2.2	4.2	6.2	—	—
Helium	670	1.5	3.0	5.0	7.5	11.0	15.5

*The values of λ were taken for the gases at a temperature of 500 °C.[47]

From the neutron activation analysis of hot molten polypropylene[38], it was concluded that oxygen from the surrounding atmosphere is sorbed in the molten polymer layer. Examination of the thermal balance showed that an appreciable proportion of the heat is liberated in oxidation at the surface. It was concluded that if the contribution from external parameters is excluded, the combustion of the polymer is determined by its stability towards thermal oxidation.

On the basis of the results of Ref.29, the authors of Ref.48 examined the propagation of a flame over a polypropylene surface. They found that the temperature of the polymer surface increases from 350 °C to 500 °C with increase in the concentration of oxygen in the stream from 21% to 28%. As in the previous study, they found that the temperature of the flame remains constant at 1308 °C. This was taken as proof of the participation of oxygen in the thermal decomposition of polypropylene and the heating of the surface. Although analogous data were obtained for PMMA, it was stated that in the case of PMMA, surface oxidation does not take place.

The ^{13}C NMR spectra of molten PMMA formed during the combustion of a specimen coincide with the spectra of the original specimen[49]. This confirms indirectly that oxygen does not take part in the reaction in the condensed phase. The combustion of PMMA and MMA in a stream of oxidising agent has been studied, and the temperature profiles and the profiles of the products of the thermal decomposition of the polymer and their subsequent transformation obtained[50]. From an analysis of the profiles of the concentrations of the products in the gas phase and the temperature profiles, it was concluded that the earlier suggestion[29,37,48] that oxidation processes take place on the surface of the condensed phase is not justified. Other conditions being equal, the escape of oxygen through the diffusion flame is the same for the polymer and the monomer, and amounts to 0.5 mole %. This quantity of oxygen is too small for an exothermic reaction to take place on the surface. Oxygen can catalyse only the thermal oxidation of the gaseous thermal decomposition products, but cannot have any significant influence on the thermal decomposition of the condensed phase, since there is a fairly powerful stream of monomer from the surface.

V. MACROKINETICS OF THE THERMAL DECOMPOSITION OF THE POLYMERS

As shown in section I, in the thermal decomposition of polymers, the supply of heat to the surface can take place by one single mechanism or by several mechanisms simultaneously (radiation, convection, conduction, etc.).

Thermal decomposition usually takes place under "quasi-stationary" conditions, when the heat absorbed by the chemical degradation reaction is equal to the heat supplied to the polymer. To determine accurately by formal kinetics the dependence of the mass rate of degradation on the external conditions in each specific case it is necessary to solve the non-stationary thermal conductivity equation, after which the familiar temperature distribution $T(x, \tau)$ within the specimen can be used to determine the mass rate of degradation as

$$\frac{dm(x,\tau)}{d\tau} = K_0 \int_V \rho \exp\left[-\frac{E}{RT(x,\tau)}\right] dV$$

where ρ is the density of the material, K_0 the pre-exponential factor, and E the activation energy of degradation.

The analytical solution of the non-stationary thermal conductivity equation with a sufficient accuracy, even in the spherically symmetrical case for the bulk thermal degradation in a molten polymer and varying thermal flux over the surface of a sphere represents an extremely complex problem, and can be carried out only in particular cases. For many thermal decomposition problems, however, it is sometimes sufficient to examine only the thermal balance equation:

$$q_1 + q_2 + q_3 = \frac{dm}{d\tau} \cdot L + q_4$$

where q_1 is the radiation thermal flux, q_2 the convection or conduction thermal flux, q_3 the thermal flux through the specimen holder, $\frac{dm}{d\tau} \cdot L$ the absorption of heat as a result of the chemical degradation reaction (L is the heat of gasification), and q_4 is the heat used to heat the specimen. The thermal flux of the radiation from the surrounding non-isothermal cavity with an emissivity different from unity is determined in accordance with the geometry of the surroundings and the arrangement of the specimen relative to the surroundings, and is proportional to the emissivity of the material ε.

For an isothermal cavity with a surface area much greater than the surface area of the spherical specimen, the surface absorption is given by[51]:

$$q_1 = 4\pi r^2(\tau)\varepsilon\sigma(T_1^4 - T_s^4)$$

where $r(\tau)$ is the current radius of the sphere, and T_1 and T_S the temperatures of the cavity and the polymer surface.

If the thermal decomposition is carried out in a laminar stream of hot gas, the convective thermal flux to the polymer surface is given by[52]

$$q_2 = \frac{\overline{Nu} \cdot \lambda_f}{d(\tau)} (T_2 - T_s) \cdot S$$

where $d(\tau)$ is the diameter of the sphere, S the area of the sphere, T_2 the temperature of the gas, λ_f the thermal conductivity of the gas at a temperature $(T_2 + T_3)/2$, $\overline{Nu}$ the Nusselt number, which is determined by the geometric dimensions of the specimen and the physical conditions of flow, and $\overline{Nu} = f(Re, Pr)$ is a function of the Reynolds and Prandtl numbers.

For a sphere swept by a gas stream $Pr = 1$, and for small $Re \to 0$, $\overline{Nu} \to 2$, and for intermediate values $Re = (0-100)$, $\overline{Nu} = 2(1 + 0.08Re^{2/3})$.[53]

For the thermal decomposition of a polymer specimen in a stationary heated atmosphere, the parameter describing the nature of the motion is not *Re* but another dimensionless quantity—the Grashof number[53]

$$Gr = gd^3\gamma\Delta T/\nu^2$$

where g is the acceleration due to gravity, ν the kinematic viscosity, γ the coefficient of volume expansion of the medium, and ΔT the temperature difference responsible for the convection. For gases, $\gamma \sim 1/T$ and

$$Gr = \frac{gd^3}{\nu^2} \cdot \frac{\Delta T}{T} .$$

For heat exchange by conduction, the thermal flux to the surface of a sphere will be given by the equation

$$q_2' = \lambda_f \left.\frac{dT}{dr}\right|_{r=r(\tau)} \cdot S$$

where $S = 4\pi r^2(\tau)$ is the area of the surface of the sphere.

The thermal flux q_3 must be determined or calculated in each specific case, depending on the type of holder (quartz capillary, support, thermocouple wire, etc.). In thermal decomposition experiments it is desirable to decrease the flux q_3, since it is difficult to estimate its magnitude with sufficient accuracy, as it may show a complex dependence on the geometric dimensions. q_3 can be estimated for the thermal decomposition of a specimen on the junction of a Pt–Pt/Rh thermocouple with diameter $\delta = 0.02$–0.05 mm. The emissivity of platinum is assumed to be zero[47,54]. The purely convective heating of the wire is examined under the most favourable conditions, when its axis of symmetry is perpendicular to the thermal flux. The thermal conductivity equation for the temperature distribution along the axis of the wire from the surface of the specimen has the form

$$\lambda_{Pt} \cdot \frac{\partial^2 T(x)}{\partial x^2} = \frac{\overline{Nu}\lambda_f}{2\delta} [T_2(x) - T_3(x)] \frac{dS}{dV} \qquad (5)$$

with boundary conditions

$$T_3(x)|_{x=0} = T_s,\ T_3(\infty) = T_2(\infty)$$

where $T_3(x)$ and $T_2(x)$ are the temperatures of the wire and the gas at a distance x along the axis of the thermocouple, $dS/dV = 2\pi\delta\Delta x/\pi\delta^2\Delta x = 2/\delta$; and λ_{Pt} the thermal conductivity of platinum. For the gas it will be assumed that $Pr = 1$. The temperature fields and the flux rate fields at the polymer surface are then similar

$$\frac{T_2 - T_3}{v_0} = \frac{T_2(x) - T_s}{v(x)} \qquad (6)$$

where v_0 and $v(x)$ are the flux rates at a sufficient distance from the specimen and at a distance x from the specimen.

For small values $1 < Re < 4$, the following equation is applicable[52]

$$Nu \approx 0.891 \cdot \left(\frac{v_0 2\delta}{\nu}\right) \cdot 0.33 \qquad (7)$$

From Eqns.(6), (7), and (5),

$$\lambda_{Pt}\left[\frac{\partial T_3(x)}{\partial x}\right]^2 = \int_0^{\infty} \frac{2\lambda_f}{\delta^2}\left[\frac{T_2(x) - T_s}{T_2 - T_3}\right]^{0,33} \cdot 0.891\,[T_2(x) - T_3(x)]\left(\frac{v_0 2\delta}{\nu}\right)^{0,33} dT_3(x) .$$

The maximum value of the integral is obtained for $T_2(x) = T_2$

$$\left.\frac{dT_3(x)}{dx}\right|_{x=0} = \sqrt{\frac{\overline{Nu}}{\delta^2} \cdot \frac{\lambda_f}{\lambda_{Pt}}} \cdot (T_2 - T_3)$$

$$q_3 = 2\lambda_{Pt} \cdot S \left.\frac{dT_3}{dx}\right|_{x=0} = 2\lambda_{Pt}\pi\delta \sqrt{Nu\frac{\lambda_f}{\lambda_{Pt}}} (T_2 - T_s) .$$

The maximum value of q_3 for the thermal decomposition of a polymer drop on a Pt–Pt/Rh thermocouple ($d = 0.02$–0.05 mm, $\lambda_f = 0.6 \times 10^{-4}$ cal cm^{-1} s^{-1} K^{-1}, $Nu = 0.5$, $\delta = 0.0025$ cm, $\lambda_{Pt} = 0.8$ cal cm^{-1} s^{-1} K^{-1}, $(T_2 - T_S \cong 250°)$ is $\sim 0.5 \times 10^{-2}$ cal cm^{-2} s^{-1}.

To estimate q_4, the heat used to heat the specimen, it is necessary to solve the non-stationary thermal conductivity equation. For the thermal decomposition of a uniformly heated specimen, however, this term can be neglected. For large values of *Bi*, the surface degradation of a spherical specimen should take place with a quasi-stationary temperature profile, and q_4 will decrease with decrease in the current radius of the sphere, since *Bi* decreases. For high initial radii of a spherical specimen and high values of *Bi*, the temperature profile in the condensed phase will tend to the Mikhel'son distribution.

The heating term tends to the value $q_4 = c\rho U(T_S - T_0)$ or

$$q_4 = \frac{dm}{d\tau} \cdot c \cdot (T_s - T_0)$$

and this term can be combined with $L \cdot \frac{dm}{d\tau}$ to give:

$$q_1 + q_2 + q_3 = \frac{dm}{d}[L + c(T_s - T_0)] = \frac{dm}{d\tau} L_{eff} .$$

Thus depending on the diameter of the sphere, different effective heats of gasification of PMMA are obtained, from ~ 200 cal g^{-1} [55] for the completely heated specimens (diameter up to 1–2 mm), to ~ 400 cal g^{-1} [19,26] for linear thermal decomposition (large diameters).

For a heated drop of polymethyl methacrylate, the radiation flux for a drop diameter of about 1 mm and a temperature of the wall of the heater of 1000 °C is ~ 0.10 cal cm^{-2} s^{-1}. The degree of blackness of the polymer is 0.9.[42,54] The convective flux in this case is ~ 0.05 cal cm^{-2} s^{-1}. The value of q_3 is always smaller than 0.5×10^{-2} cal cm^{-2} s^{-1}, so that q_3 can be neglected, compared with the thermal flux. The thermal decomposition of the heated drop for a constant temperature throughout its volume is proportional to the mass of the specimen, that is

$$\frac{dm}{d\tau} = mK_0 \exp(-E/RT_s) .$$

The thermal balance equation with allowance for convection and radiation can be written as:

$$\frac{dm}{d\tau} = mK_0 \exp(-E/RT_s) = \frac{1}{L_{eff}} \cdot \sum_i q_i =$$
$$= \frac{S}{L_{eff}}\left[\varepsilon\sigma(T_1^4 - T_s^4) + \frac{Nu\lambda_f}{d}(T_2 - T_s)\right] \qquad (8)$$

where L_{eff} is the heat of gasification of the polymer.

The kinetic curve for the thermal decomposition of PMMA in Fig.1 gives the mass loss and the change in the temperature of the polymer specimen. Fig.1 shows that in the first period before the polymer specimen has melted, the thermocouple records the mean temperature between T_S and T_∞, but when the specimen has been heated and melted, it covers the junction of the thermocouple, which records the temperature of formation of the drop T_S.

In this period there is a considerable change in the density of the polymer sphere from 1.19 g cm^{-3} to ~ 0.8 g cm^{-3}, after which the density remains practically constant. The decrease in the density is due to the increase in the volume[26] (surface area) as a result of the formation of bubbles of the degraded monomer in the bulk. The monomer formed cannot leave the polymer surface immediately, since the rate of formation of the gas phase is greater than the rate of diffusion of the

bubble to the surface. With increase in the temperature of the specimen, the viscosity decreases, and the size of the bubbles reaching the surface is stabilised, and in this range (region II) it may be assumed that ρ is constant and equal to ~0.8.

Region III is characterised by small dimensions of the polymer drop, and in this region it is not possible to neglect the supply of heat through the holder (in the present case through the thermocouple) in the thermal balance equation.

Region II, in which the main mass loss takes place during thermal decomposition, is characterised by a constant smooth increase in the temperature of the drop from T_{s1} to T_{s2} (here we are dealing with the temperature of the entire drop, and not its surface, since all the specimen "boils" vigorously and there is good heat exchange within it, $dT/dr \to 0$).

To understand the increase in temperature in region II, Eqn.(7) is transformed, with the assumption that ρ = const, to the form:

$$L_{eff} \cdot K_0 \exp(-E/RT_s) = \frac{7{,}5\varepsilon\sigma(T_1^4 - T_s^4)}{d} + \frac{7{,}5\lambda_f Nu(T_2 - T_s)}{d^2} \quad (9)$$

It is obvious that with change in T_S by 30–40 K, the difference ($T_1^4 - T_S^4$) remains practically unchanged, but the difference ($T_2 - T_S$) decreases by ~5–7%. Thus by introducing the symbols

$$75\varepsilon\sigma(T_1^4 - T_s^4)/L_{eff}K_0 = A,\ 75\lambda_f Nu(T_2 - T_s)/L_{eff}K_0 = B_0$$

Eqn.(9) can be transferred to:

$$\exp(-E/RT_s) = \frac{A}{d} + \frac{B}{d^2} \quad (10)$$

Eqn.(10) shows that with decrease in the diameter during the experiment, both terms in the right-hand side increase, leading to an increase in T_S. To follow the dependence of the temperature of the heated drop T_S on the magnitude of the thermal flux, the diameter of the drop in Eqn.(9) is fixed:

$$d = \text{const};\ \frac{75\varepsilon\sigma}{dL_{eff}K_0} = C;\ \frac{75\lambda_f Nu}{d^2 L_{eff}K_0} = D$$

$$\exp(-E/RT_s) = C(T_1^4 - T_s^4) + D(T_2 - T_s). \quad (11)$$

Fig.6 gives the graphical solution of Eqn.(11), the intersection of curves *1* and *4*, and gives the required "quasi-equilibrium" temperature of the polymer specimen during thermal decomposition. It is obvious that with increase in the thermal flux to the polymer at a fixed diameter, the temperature of the specimen increases. For thermal fluxes which are not too large, there is only a slight change in the value of T_S.[56]

A number of papers[18,23,24,29,33] give data on the dependence of T_S for various thermoplastic polymers on either the thermal flux power or the temperature of the stream and the temperature of the radiant source, confirming the above conclusions.

Published data[24] on the mass rates of thermal decomposition and the corresponding temperatures were used to obtain graphically (Fig.7) the values of the kinetic parameters for the thermal decomposition of various polymers, given in Table 7.

Data on the thermal decomposition of small and large spherical polymer specimens under combustion conditions have been published[26,33]. The flame zone in the combustion of spherical particles lies close to the polymer surface, and heat exchange between the flame and the surface of the sphere takes place by conduction[33]. According to the theory developed[57–60] for the combustion of hydrocarbon liquids from porous spheres and the combustion of single droplets, the mass rate of combustion can be represented as

$$\frac{dm}{d\tau} = \frac{4\pi\lambda_f r}{c_p} \ln\left[1 + \frac{c_p(T_f - T_s)}{\Delta H - a}\right] \quad (12)$$

where c_p is the heat capacity, $\Delta H = (L + c_p\Delta T)$ the enthalpy of gasification of the polymer, $a = Ra/\frac{dm}{d\tau}$ defines the contribution of the radiation from the flame, and T_f is the temperature of the flame. Eqn.(12) was obtained assuming conductive heat transfer by integrating the thermal flux from the flame over the surface of the specimen. Since the flame of thermoplastic polymers is transparent, the term a can be neglected, so that the integration of (12) with respect to time gives the law governing the change in the dimensions of the specimen during thermal combustion

$$d^2 = d_0^2 - \frac{8\lambda_f}{c_p\rho} \ln\left(1 + \frac{c_p\Delta T}{\Delta H}\right) \cdot \tau$$

Introducing the symbol

$$\frac{8\lambda_f}{c_p\rho} \ln\left(1 + \frac{c_p\Delta T}{\Delta H}\right) = K$$

gives

$$d^2 = d_0^2 - K\tau$$

the law obtained for the volatilisation of a drop of liquid[61].

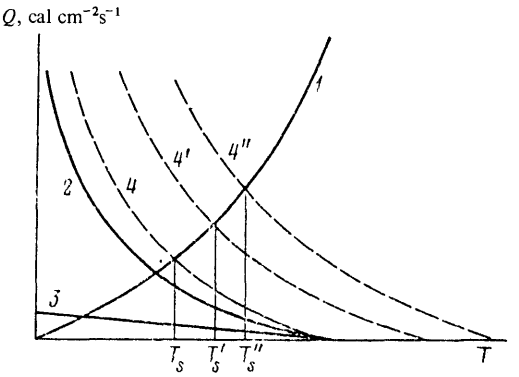


Figure 6. Graphical solution of Eqn.(11).

Table 7. Activation energies of the thermal decomposition of PMMA, PS, and PE.

Polymer	Data from Ref. 24	Other data	Refs.	Polymer	Data from Ref. 24	Other data	Refs.	Polymer	Data from Ref. 24	Other data	Refs.
PMMA	38	30	[3,51]	PE	35	45	[51]	PS	46	63	[51]
		31	[1]			20÷25	[75]			55	[5]
		29.6	[4]			46÷66	[1]			45÷55	[3]
		74	[25]			63	[5]			35	[75]
		40÷43	[15,16]			26÷63	[3]			25÷95	[21]

The change in the diameter of the polymer specimen with time is given in Fig.8.[26]

In this case and in the case of the combustion of large specimens (diameter up to 10 mm),[33] a linear time dependence of the surface area of the sphere is formally observed, since

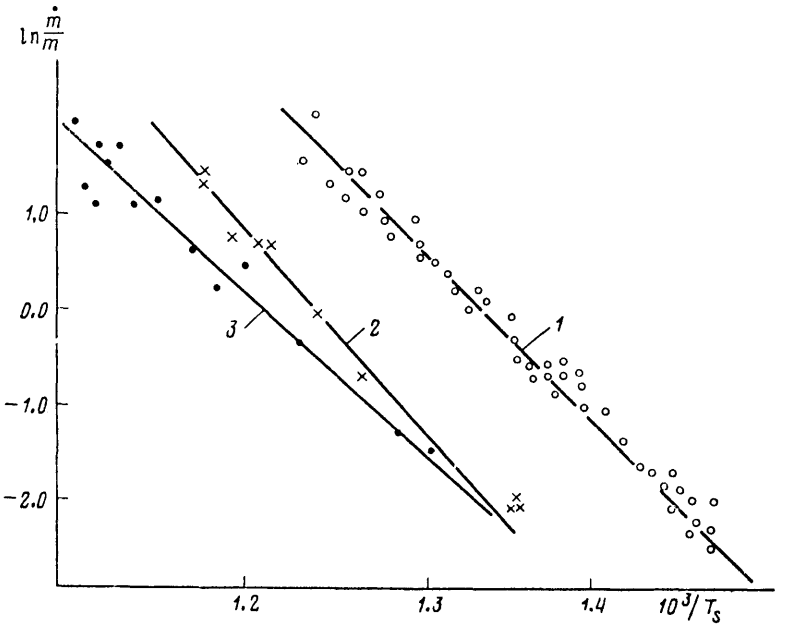


Figure 7. Plot of $\ln \dot{m}/m$ against $10^3/T$ during thermal decomposition: *1*) polymethyl methacrylate, *2*) polystyrene, *3*) polyethylene.

the rate of the process is determined by the rate of heat transfer from the flame to the polymer surface. The exact calculation of the kinetics of the thermal decomposition in the combustion of specimens with a large diameter is an extremely complex problem, because the process is non-stationary. Here, the situation is intermediate between bulk and linear thermal decomposition. In fact, the dependence of $\ln \dot{m}/m$ on $1/T_S$ for a fixed diameter and temperature within the sphere[33] gives a straight line with slope smaller than E but greater than $E/2$.[62] As with bulk thermal decomposition, the absolute values of the mass rates of thermal decomposition are determined by the power of the thermal flux to the polymer surface.

Research workers have paid most attention to the linear thermal decomposition of thermoplastic polymers[8–16]. In this case the temperature distribution in the condensed phase will be determined by Eqn.(2), as confirmed by the data in section II and Ref.43, obtained in a study of heat transfer during the combustion of polymers, and the rate of linear thermal decomposition can be calculated from the relationship[63]

$$U = K_0 \int_0^\infty \exp\left[-E/RT\,(U, x)\right] dx \,. \qquad (13)$$

The integral was calculated[64] using the Frank-Kamenetskii expansion of the exponent[53] to give

$$U^2 = aK_0 \exp(-E/RT_s) \frac{RT_s^2/E}{T_s - T_0 - \frac{1}{2}\frac{Q}{c\rho}} \,. \qquad (14)$$

The equation obtained is applicable for the model of the linear thermal decomposition of a semi-infinite mass. The effective energy of activation is equal to half the true activation energy. Linear thermal decomposition is usually studied using round rods of finite dimensions, for which heat losses from the lateral surface of the specimen may be significant[65]. Shteinberg[66] examined the regular features of linear thermal decomposition with heat losses, and determined the criterion for the change to the region in which external heat losses can be neglected. By assuming that the temperature field was one-dimensional, that is that the length of the specimen l was much greater than its diameter $d = 2r$, and that the heat losses are limited by external heat exchange between the lateral surface of the specimen and the surrounding medium, the thermal conductivity equation can be written in the form:

$$\frac{d^2T}{dx^2} + \frac{M}{\delta}\frac{dT}{dx} - \frac{QK_0}{ac}\exp(-E/RT_s) - \frac{Bi}{\delta^2} - (T\ T_\infty)$$

with boundary conditions

$$T|_{x=0} = T_s$$
$$T|_{x\to\infty} = T_\infty$$

where δ is the half-thickness of the plate (or radius of the cylinder), $M = U\delta/a$ is the Mikhel'son (Peclet) number, $Bi = \alpha\delta/\lambda$ the Biot number, and Q the heat of the reaction.

The expression obtained by Shteinberg for the rate of linear thermal decomposition has the form

$$U^2 = \frac{2aK_0T_s^2 \exp(-E/RT_s)}{E\left[(T_s - T_\infty)\left(1 + \sqrt{1 + 4Bi/M^2}\right) - \frac{Q}{C}\right]} \,.$$

For high rates of linear thermal decomposition and relatively small external heat losses, that is for $4Bi/M^2 \ll 1$, the limiting case of the thermal decomposition of a semi-infinite continuum of Eqn.(14) is obtained, and $U \sim \exp(E/2RT_S)$. For low rates, that is $4Bi/M^2 \gg 1$

$$U = \frac{K_0\delta RT_s^2 \exp(-E/RT_s)}{E(T_s - T_\infty)\sqrt{Bi}} \,. \qquad (15)$$

Eqn.(14) shows that with increase in the relative heat losses there is a qualitative change in the nature of the dependence of the rate of linear thermal decomposition on the temperature of the surface, $U \sim \exp(-E/RT_S)$. This is related to the fundamental difference in the dependence of

the width of the reaction zone on the parameters of the process. In the first case, $\Delta \cong a/U$, that is Δ increases without restriction with decrease in the rate of the process. In the second case, $\Delta = \delta\sqrt{Bi}$, that is it is practically constant, since it depends only on the defining dimension of the specimen and the heat exchange criterion Bi. Fig.9 gives the dependence of the rate of the linear thermal decomposition of polymethyl methacrylate on the reciprocal of the temperature of the surface on semilogarithmic coordinates.

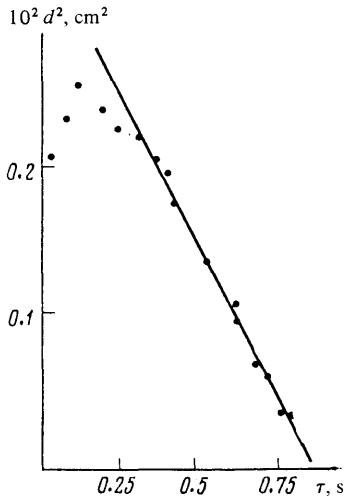


Figure 8. Change in the square of the drop diameter with time.

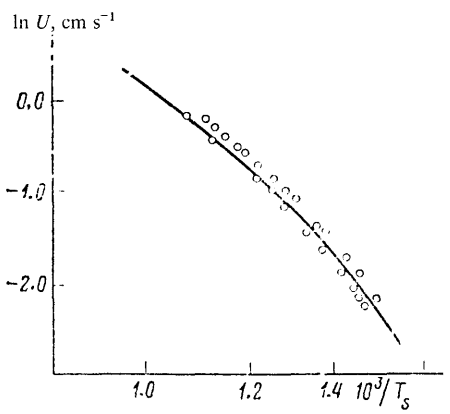


Figure 9. Dependence of the rate of the thermal decomposition of PMMA on $1/T_S$.[16]

Fig.9 shows that in the high-temperature range for large thermal fluxes, the effective value of the activation energy is $E/2$, and the pre-exponential term is equal to K_0. With decrease in the rate of linear thermal decomposition, there is a clearly defined change to the second range, where $U \sim \exp(-E/RT_S)$, that is the activation energy and the pre-exponential term acquire their true values.

It should be noted that the temperature distribution in the condensed phase during thermal decomposition will be more complex than the relationship given by Eqn.(2). Thus the distribution (2) was obtained from the solution of the thermal conductivity equation without a source or sink, with a boundary moving at a rate U. The true temperature distribution in the condensed phase can be obtained only with allowance for the chemical degradation reaction taking place in the surface layer of the condensed phase. In the surface layer of the molten polymer, where intensive degradation is taking place, the bubbles of gaseous degradation products lead to intensive mixing of the melt ("boiling"), and the heat transfer process differs considerably from conduction. The temperature gradient in this layer is $dT/dx \to 0$. For the second zone, where it is possible to neglect the chemical reaction, the temperature distribution along the x axis should be obtained from the solution of the thermal conductivity equation without a source, as in Ref.36, but only with allowance for the temperature dependence of the thermal conductivity coefficient, which increases markedly with increase in T in the range of temperatures produced during linear thermal decomposition on the surface of a polymer.

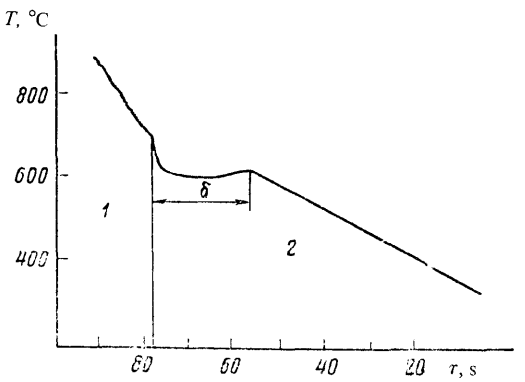


Figure 10. Temperature profile in the condensed phase in the thermal decomposition of thermoplastic polymers[67]; δ is the "boiling layer"; *1*) gas phase; *2*) condensed phase.

The existence of a boiling layer on a polymer surface during linear thermal decomposition was observed by a number of workers[25,67]. Fig.10 gives the temperature profile in the condensed phase obtained in Ref.67 for the thermal decomposition of PMMA. The thickness of the heated layer and the layer of melt in the thermal decomposition of polystyrene is inversely proportional to the rate of the thermal decomposition[43]. The same conclusion was reached in an analysis[25] of data on the thermal decomposition of polymethyl methacrylate Since the temperature distribution, as a result of intensive, heat exchange in the layer δ, is analogous to that shown in Fig.10, the rate of the linear thermal decomposition, in accordance with Eqn.(13), can be written as

$$U = K_0 \int_0^\infty e^{-E/RT(x)}\,dx = K_0 \int_0^\delta e^{-E/RT(x)}\,dx + K_0 \int_\delta^\infty e^{-E/RT(x)}\,dx . \quad (16)$$

Under the conditions of extensive heat exchange in the "boiling" layer, $T(x) \cong$ const in the range $0 \leq x \leq \delta$. Assuming that the reaction takes place at an appreciable rate only in the layer δ, the second integral in Eqn.(16) can be neglected,

and the rate of linear thermal decomposition is

$$U = K_0 e^{-E/RT_s} \int_0^{\delta} dx = K_0 \delta e^{-E/RT_s}$$

and the condition $\delta \sim 1/U$ gives $U^2 \cong K_0 e^{-E/RT_s}$, that is the same dependence of the rate of linear thermal decomposition on the reciprocal of the temperature as in Eqn.(14).

The kinetic characteristics of the degradation of PMMA, K_0 and E, obtained by the study of high-temperature thermal decomposition coincide with the values of K_0 and E obtained for "bulk isothermal" degradation[1,3]. This agreement indicates that on going from the low-temperature to the high-temperature range, the mechanism of the degradation apparently remains unchanged. The conclusions reached by various authors that the mechanism changes may be due chiefly either to the inaccuracy of the measurement of the temperature of the polymer surface during thermal decomposition or to the neglect of the complex macrokinetics in each specific case (the complex temperature profile, which changes with time and with change in the external conditions). Thus to reach final conclusions about the mechanism, it is necessary to carry out new studies with accurate allowance for all factors.

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