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Thermal Degradation Kinetics and Surface Pyrolysis of Vinyl Polymers

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Explicit expressions are obtained for the surface regression rates of pyrolyzing vinyl polymers. Thermal degradation of the polymer in a subsurface reaction zone is assumed rate limiting. Emphasis is placed on determination of the proper degradation mechanism (e.g., mode of initiation and magnitude of the kinetic chain length compared to the degree of polymerization), development of kinetic data, and derivation of corresponding expressions for the rate of mass loss. The method of calculation is based on a matched asymptotic expansion scheme, with the nondimensional activation energy, $\mathcal{E} = E/R^0T_s \gg 1$, treated as the expansion parameter. Results are displayed for polytetrafluoroethylene and compared to experimental results with fair success for polymethylmethacrylate and polystyrene.

Nomenclature

A = $[\Delta H_s(q_0 + N_w)]^{1/2}\delta \exp[\mathcal{E}_w(1 - \gamma)]$
B = pre-exponential factor in rate constants, sec^{-1}
c = specific heat at constant pressure
d = thermal diffusivity deep within polymer
E = activation energy in rate constants, cal/mole
$\mathcal{E}$ = E/RT_s, nondimensional activation energy
F = $\mathcal{E}(1 - \Theta)$, inner variable
G = function defined after Eq. (47)
h = specific enthalpy
h_i^0 = enthalpy of formation of species i at T_∞
H = $h/c_{p\infty}T_s$ nondimensional specific enthalpy
ΔH = $H_m - H_p$
K = thermal degradation rate constant, polystyrene, Eq. (10)
K' = thermal degradation rate constant, teflon, Eq. (3)
k_i = rate constant for initiation at chain ends, PMMA, Eq. (1)
k_{sc} = random scission rate constant, polystyrene, Eq. (11)
k_w = weak links scission rate constant, polystyrene, Eq. (15)
l = d/r, width of the conduction region
M_m = monomer molar mass
m = mass of sample in isothermal bulk degradation
m_0 = initial mass of sample in isothermal bulk degradation
N_w = number of weak links per monomer unit, polystyrene, Eq. (18)
n = order of the degradation reaction, Eq. (26)
P = degree of polymerization
P_0 = initial degree of polymerization
P_c = critical chain length, at or below which the chain evaporates rather than being further degraded
P_k = kinetic chain length
q = $1/P$
q_0 = $1/P_0$
q = $q\kappa_p/(q_0 + N_w)$
r = surface linear regression rate, cm/sec
$\mathcal{R}^2$ = nondimensional regression rate, Eq. (27)
R^0 = universal gas constant
T = temperature, °K
t = time
V_i = velocity of species i with respect to that of nondegraded polymer
v_i = V_i/r
y = physical coordinate, normal to regressing surface, >0 into gas phase
Y = y/l
α = E_{ps}/E_{sc}
β = B_{ps}/B_{sc}
γ = E_{ps}/E_w
δ = B_{ps}/B_w
κ_i = $\rho_i/\rho_{p\infty}$
Γ = $\Sigma_i\kappa_i(c_i/c_{p\infty})(1 + v_i)$
λ = coefficient of thermal conductivity
Λ = $\lambda/\lambda_{p\infty}$
η = $Y\mathcal{E}$, inner coordinate
$\dot{\omega}_i$ = rate of production of species i, g/sec cm^3
Ω_i = $\omega_i d/r^2\rho_{p\infty}$
ρ = density
Θ = T/T_s

Subscripts

i = any species present in the sample
m = monomer

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p = polymer (nondegraded or nonvolatilized)
pm = polymethylmethacrylate (PMMA)
ps = polystyrene
sc = random scission component, polystyrene
s = surface
w = weak links scission component, polystyrene
T = polytetrafluoroethylene (teflon)
0 = initial conditions in bulk degradation
∞ = conditions deep within sample

Introduction

DATA on the steady-state linear surface regression rates at measured surface temperatures, for materials exposed to intense surface heating, have been obtained by pressing the sample against a heated plate[1,2] and by immersing the sample either in the exhaust jet of a rocket motor[3] or in a jet of oxygen that burns with the pyrolysis products.[4] The surface temperature is measured by a thermocouple that is either imbedded in the hot plate[1] or interposed between the hot plate and the sample surface,[2] or it is inferred by monitoring the thermal radiation from the sample surface.[3,4] Occasionally, the temperature profile in the sample is measured by imbedded thermocouples.[4]

Because of their interest as binders in composite propellants and as ablative protection materials, vinyl polymers have frequently been used in these experiments. Results are available mainly for polymethylmethacrylate (PMMA)[1,2,4] and polystyrene.[2,3] These results have been interpreted as indicating that the rate limiting process is desorption from the surface of monomer units created in the subsurface thermal degradation of the polymer.[1,3,4] On the other hand, some authors have attempted to obtain mathematical expressions for the dependence of surface pyrolysis rate on surface temperature by assuming that the rate limiting step is the thermal degradation of the polymer in a subsurface reaction zone.[5–8] In particular, it has been shown from one such result[6] that the apparent activation energy for PMMA, obtained from surface pyrolysis experiments, is in rough correspondence with results of isothermal bulk degradation experiments.

Unfortunately, the theoretical expressions developed previously for regression rates controlled by in-depth reactions, suffer from rough approximations, the importance of which is difficult to assess. The present study is intended to obtain explicit relations between surface regression rate (as limited by the thermal degradation of the polymer) and surface temperature, which are rigorously valid in the limit of large activation energy.

The relations will be developed using a matched asymptotic expansion scheme. Results will be obtained for the general case of a degradation reaction of order between 0 and 1 with respect to the mass of nondegraded polymer and will be applied to the cases of PMMA and polytetrafluoroethylene (teflon). Comparison with experimental results will be given for PMMA; apparently no direct measurements of the surface temperature have been performed for ablating teflon. Since experimental results on surface regression of polystyrene are available, a theoretical regression rate relation will be developed for this polymer, taking into account the detailed degradation reaction mechanism inferred from extensive isothermal bulk degradation studies.

I. Isothermal Bulk Degradation Results

The first task is to obtain kinetic expressions from homogeneous isothermal bulk degradation data. Although textbooks[9,10] have been written on thermal degradation of polymers, there is still controversy over mechanisms and rate constants. Different types of mechanisms and corresponding mathematical rate expressions may be found in Refs. 9–13. Degradation is believed to involve depolymerization initiated at chain ends, at random points along the chain, or at isolated "weak links." Free radicals formed during initiation cause chain propagation ("unzipping"), characterized by the kinetic chain length P_k (number of monomer units produced on the average for one initiation). Termination of propagation occurs where the free radical is stabilized. This mechanism can be complicated by intermolecular transfer, wherein a free radical is stabilized by abstracting an H atom from a nearby inactive chain and thereby breaking the latter at random, or by intramolecular transfer, wherein a free radical combines with an H atom from its own chain, resulting in products larger than a monomer unit. The mechanisms of thermal degradation differ from one polymer to another essentially because of the mode of initiation and the magnitude of the kinetic chain length compared to the degree of polymerization.

Polymethylmethacrylate (PMMA)

Observation of residue molecular weight vs extent of volatilization, initial rate of volatile formation vs initial molecular weight, and products of degradation (almost exclusively monomer, at least up to 800°C)[10] suggest that the thermal degradation of PMMA involves initiation at chain ends, unzipping, insignificant intermolecular transfer and second-order termination.[9] The kinetic chain length is found to be fairly large (2×10^3 or higher at a temperature of 220°C).[9]

When the initial degree of polymerization is less than the kinetic chain length, the rate of mass loss has been expressed as[9]

$$-dm/dt = k_i m$$

$$k_i = B_{pm}\exp(-E_{pm}/R^0T) = 2.82\times10^9\exp(-31{,}000/R^0T),\ \mathrm{sec}^{-1} \qquad (1)$$

where k_i is the rate constant for the initiation at a chain end. In comparing experiment with theory Gordon[14] finds

$$k_i = 10^{9.0\pm1.5}\exp[-(29.6\pm4.4)\times10^3/R^0T],\ \mathrm{sec}^{-1} \qquad (2)$$

which brackets the result given in Eq. (1). Although no mention is made of the degree of polymerization for the samples used in surface pyrolysis,[1,2,4] it seems safe to assume that Eq. (1) will apply.

Polytetrafluoroethylene (teflon)

Reference 15 gives evidence that the product of teflon degradation is essentially monomer (in the range 360–510°C). This finding is supported by Ref. 10 (in the range up to 800°C). Intermolecular transfer does not occur. Initiation occurs at random along the chains and is followed by unzipping with a fairly short kinetic chain length and termination by disproportionation. Over most of the conversion to monomer the rate of mass loss is first order and can be expressed as[15]

$$-dm/dt = mK',\ K' = B_T\exp(-E_T/R^0T) = 3\times10^{19}\times\exp(-83{,}000/R^0T),\ \mathrm{sec}^{-1} \qquad (3)$$

These conclusions are also reached in Ref. 10, where K' is given as

$$K' = 4.7\times10^{18}\exp(-80{,}500/R^0T),\ \mathrm{sec}^{-1} \qquad (4)$$

Equation (3) can be confirmed theoretically by assuming an initial degree of polymerization much larger than the kinetic chain length.[15] Under these conditions K', a combination of initiation, propagation and termination rates, is independent of the initial degree of polymerization.

Polystyrene

Contradictory results and interpretations have been reported concerning polystyrene degradation. This somewhat lengthy section should illustrate the problem. The main features of the isothermal experimental results for polystyrene are as follows.

1) The products of the thermal degradation of polystyrene are mainly monomer ($\approx 40\%$ in weight), dimer, trimer, and tetramer in the temperature range up to 500°C.[10,16]

2) The molecular weight of the residue initially drops very sharply and then more gradually as volatilization progresses.[16,17] Furthermore, for a given initial degree of polymerization, the curve of residue molecular weight vs extent of volatilization is fairly insensitive to temperature changes.[17]

3) A plot of the rate of production of volatile products, at a given temperature, vs extent of volatilization shows a pronounced maximum at about 30–40% volatilization[16,17]; the maximum increases as the temperature increases.[16]

Jellinek[9] explains 2 as a result of the rapid breaking of a finite number of weak links distributed at random over the polymer chain backbone. This is followed by the true depolymerization reaction, characterized by initiation at the chain ends and unzipping with a short kinetic chain length. This true depolymerization is described by a zero-order reaction rate as follows. Letting the effective degree of polymerization, after all weak links have been eliminated, be $P_f = P_0/(1 + w_0)$, where w_0 is the number of weak links in a polymer chain of length P_0, we have m_0/P_fM_m chains in the sample after the initial breakdown. Since $P_f \gg P_k$, the number of chains remains constant during most of the reaction. The rate at which chain ends are activated is k_im_0/P_fM_m. For each activated chain end, P_k monomer units on the average are produced. Therefore

$$dm/dt = -(P_k/P_f)k_im_0 \tag{5}$$

Jellinek,[9] disputing 3, maintains that his experimental $m(t)$ results, for a given temperature, are straight lines over most of the reaction and therefore imply a zero-order reaction, in agreement with Eq. (5). From these results he finds

$$P_kk_i = 3.54 \times 10^{13} \exp(-44{,}700/R^0T),\ \mathrm{sec}^{-1} \tag{6}$$

which can be used only if the mechanism proposed by Jellinek and Eq. (5) are accepted.

Alternatively, in Ref. 13, observations 1–3 are explained by a process of depolymerization due to random initiation along the chains, unzipping with a very short kinetic chain length, and an important contribution from intermolecular transfer, resulting in further random scission of the chains. An added feature (introduced in Ref. 18) is the postulate of a critical chain length P_c at, or below which the chain will evaporate rather than be further degraded. The value of P_c is given approximately[19] by $P_c = E_b/E_v$, where E_v and E_b are, respectively, the energy required to evaporate one monomer molecule, and the energy to break one C—C bond in the corresponding polymer backbone. The results obtained in Refs. 13 and 18 can also be derived from Ref. 8. If k_r is the rate constant for random splitting (combining random initiation and intermolecular transfer) of any one bond, then the rate of mass loss is obtained as[13]

$$-m_0^{-1}dm/d\tau = (1 + P_c)P_c \exp(-P_c\tau)(1 - e^{-\tau}), \qquad \tau = k_rt \tag{7}$$

which possesses the maximum value $P_c[P_c/(P_c + 1)]^{P_c}$ at

$$\left.\frac{m_0 - m}{m_0}\right|_{\max} = 1 - \frac{(1 + 2P_c)}{(1 + P_c)}\left(\frac{P_c}{P_c + 1}\right)^{P_c} \tag{8}$$

For any reasonable choice of P_c, this maximum occurs at[13] $(m_0 - m)/m_0 \approx 25\%$. Also, the degree of polymerization of the residue for such a process is found[18] to drop sharply as volatilization progresses. Therefore Eq. (7) would offer a qualitative explanation of the observation on polystyrene. Accepting this explanation, we can use the value $P_c \approx 7$ (Ref. 9, p. 100) and the maxima observed at several temperatures in Ref. 16, to obtain from Eq. (7) evaluated at the maximum, the result

$$k_r = 1.54 \times 10^{14} \exp(-55{,}000/R^0T),\ \mathrm{sec}^{-1} \tag{9}$$

A third view is held in Refs. 17, 20, and 21. The idea of rapid breaking of weak links is revived to explain observation 2. Breaking of the weak links is considered to result in stable molecules by disproportionation. The volatile products arise from unzipping initiated at chain ends, the products larger than monomers being due to intramolecular transfer. A maximum in the rate curve occurs because new chain ends are continually created by breaking of the weak links, until they are exhausted. Random scission by intermolecular transfer is ruled out as a cause of the initial sharp molecular weight drop by showing[21] that the molecular weight drop can be separated experimentally from the production of volatiles which presumably promotes intermolecular transfer as a by-product of unzipping. In Ref. 20, the weak links are postulated to represent abnormalities in the disposition of the elements in the chain, rather than inclusion of oxygen.[9] If this mechanism is correct, then neither Eq. (5) nor Eq. (7) can be used. Reference 22, however, offers a theory which fits the conclusions of Refs. 17, 20, and 21.

For a second-order termination of the chain propagation reaction, under the assumption $P_0 \gg P_k$, the rate of mass loss is expressed as[22,11]

$$-dm/dt = mKq^{1/2} \tag{10}$$

where K is a combination of initiation, propagation and termination rates, and $q = P^{-1}$. Although Eq. (7) applies only for isothermal systems,[13,18] Eq. (10) is applicable under nonisothermal conditions, as well as in the presence of intramolecular transfer.[22] Equation (10) must be coupled with an equation for the rate of change of q. To explain the sharp drop of molecular weight, Ref. 22 considers three possible components added to end-initiated unzipping, viz., a random scission, weak links scission, or intermolecular transfer scission. In the case of a random scission component, the equation for the rate of change of q can be found to be[22,11]

$$dq/dt = k_{sc}(1 - q) \tag{11}$$

Equations (10) and (11) predict curves of q vs m/m_0 and dm/dt vs m/m_0 which agree with observations 2 and 3 of Ref. 14. The last part of observation 2 is explained by assuming that the activation energies for K and k_{sc} are fairly close.

Gordon[23] states without proof that a weak links scission theory should fit the observations as well as Eq. (11). An equation for q for this case can be derived as follows. If on the average there are w weak links and n normal bonds per original chain at some time t during degradation, then the number of monomer units that have been produced is $(n_0 - n)m_0q_0/M_m$, since scission of weak links does not result in monomer formation[17] and since m_0q_0/M_m is the number of original chains in the sample. For $P_0 \gg P_k$, it then follows that

$$m = m_0 - (n_0 - n)m_0q_0 \approx nm_0q_0 \tag{12}$$

since $n_0 \approx q^{-1}$. The number-average degree of polymerization of the residue is (Ref. 9, p. 15)

$$q^{-1} = m[(s + 1)m_0q_0 - (m_0 - m)]^{-1} \tag{13}$$

where $s = (w_0 - w) + (n_0 - n)$ is the number of bonds broken per original chain. In view of the first identity of Eq. (12), Eq. (13) can be written as

$$q^{-1} = m[m_0q_0(1 + N_w/q_0 - w)]^{-1} \tag{14}$$

where the original number of weak links per monomer unit is

$N_w = q_0 w_0$. The rate at which weak bonds are broken is

$$-dw/dt = k_w w \tag{15}$$

from which w can be eliminated by use of Eq. (14) to obtain

$$d(mq)/dt = k_w(m_0 q_0 + m_0 N_w - mq) \tag{16}$$

Equations (10) and (16) constitute the two independent differential equations which describe the time development of m and q in the weak links scission theory.

If no normal bonds are broken, then $m = m_0$, and Eq. (16) becomes

$$dq/dt = k_w(q_0 + N_w - q) \tag{17}$$

from which it is seen that q increases to $q_0 + N_w$ when all weak links are broken. Since the initial sharp drop in molecular weight is interpreted in Ref. 20 as breaking of weak links with little volatilization, the number of weak links per monomer unit can be estimated from q_0 and q_f, the value of q after the sharp initial drop; the result is $N_w = q_f - q_0$, which is found[20] to vary between about 10^{-4} and 8×10^{-4}, depending on the mode of polymerization and on q_0. If no weak bonds are broken, then $k_w = 0$ and, from Eq. (16), one obtains $mq \approx$ const, which predicts a linear relationship between P and percent volatilization, a fact which is observed for PMMA of high-molecular weight (Ref. 9, p. 68) and apparently also is observed for polystyrene after all weak links have been eliminated.[21]

From Eq. (10) applied initially, a knowledge of q_0 and the data of Ref. 16, the value of K can be obtained as

$$K = B_{ps}\exp(-E_{ps}/R^0T) = 4.6 \times 10^{17} \times \exp(-58{,}000/R^0T),\ \mathrm{sec}^{-1} \tag{18}$$

Although no data has been published for k_w, its value can be estimated from $P(t)$ curves for different temperatures given in Ref. 17; at very small times Eq. (17) is applicable and reduces approximately to $q - q_0 \approx N_w k_w t$, in which N_w can be evaluated from Ref. 20, and for which a 40°C temperature increase can be introduced as a correction to the $q(t)$ curves,[20] to obtain

$$k_w = B_w\exp(-E_w/R^0T) = 1.8 \times 10^{19} \times \exp(-65{,}000/R^0T),\ \mathrm{sec}^{-1} \tag{19}$$

If the random scission component theory is accepted, then at small times $q - q_0 \approx k_{sc}t$, and the data implies

$$k_{sc} = B_{sc}\exp(-E_{sc}/R^0T) = 7.8 \times 10^{15} \times \exp(-65{,}000/R^0T),\ \mathrm{sec}^{-1} \tag{20}$$

It is found that indeed E_w, or E_{sc}, is close enough to E_{ps} to explain the latter part of observation 2 according to the results of Ref. 22. Although the weak links component theory developed herein agrees well with the experimental results,[17,20,21] since most investigators favor the random scission component theory,[10] both will be applied to polystyrene surface regression rate computations.

II. Surface Regression Rate Computation

General Equations

During steady linear regression there exists a coordinate system in which time derivatives vanish from the conservation equations. Letting y denote the coordinate normal to the sample surface in this system, with $y > 0$ corresponding to the gas phase, we find that species and energy conservation equations can be written as

$$r d\rho_i/dy = -d(\rho_i V_i)/dy + \dot{\omega}_i \tag{21}$$

and

$$(dT/dy)\sum_i \rho_i c_i(r + V_i) = d(\lambda dT/dy)/dy - \sum_i h_i\dot{\omega}_i \tag{22}$$

where symbols are defined in the nomenclature.

A suitable nondimensional form for Eqs. (21) and (22) is

$$d\kappa_i/dY = -d(\kappa_i v_i)/dY + \Omega_i \tag{23}$$

and

$$\Gamma d\Theta/dY = d(\Lambda d\Theta/dY)/dY - \sum_i H_i\Omega_i \tag{24}$$

where $\kappa_i \equiv \rho_i/\rho_{p\infty}$, $v_i \equiv V_i/r$, $\Omega_i \equiv \dot{\omega}_i\lambda_{p\infty}/c_{p\infty}\rho_{p\infty}{}^2r^2$, $\Theta \equiv T/T_s$, $\Gamma \equiv \Sigma_i\kappa_i(c_i/c_{p\infty})(1 + v_i)$, $\Lambda \equiv \lambda/\lambda_{p\infty}$, $H_i \equiv h_i/c_{p\infty}T_s$, and $Y \equiv yr(\rho_p c_p/\lambda_p)_\infty$.

If no significant degradation of the polymer were to take place, and if ρ_p, c_p and λ_p were not to change appreciably, then Eq. (24) would possess the simple heat-conduction solution

$$\Theta = \Theta_\infty + (1 - \Theta_\infty)\exp(Y) \tag{25}$$

Rate of Mass Loss for Order between 0 and 1

For a reaction of order n,

$$\dot{\omega}_p = -\dot{\omega}_m = -B\rho_p{}^n\exp(-E/R^0T),\ 0 \leq n \leq 1 \tag{26}$$

PMMA and teflon correspond to $n = 1$, whereas polystyrene is somewhat more complicated. The nondimensional regression rate R is defined by

$$r^2 = \mathcal{R}^2\mathcal{E}^{-1}Be^{-\mathcal{E}}\lambda_{p\infty}/c_{p\infty}\rho_{p\infty}{}^{2-n} \tag{27}$$

where $\mathcal{E} = E/R^0T_s$. If we assume that $v_p = 0$, then Eq. (23) for $i = p$ and Eq. (24) become

$$d\kappa_p/dY = -\kappa_p{}^n(\mathcal{E}/\mathcal{R}^2)\exp[\mathcal{E}(1 - \Theta^{-1})] \tag{28}$$

and

$$\Gamma d\Theta/dY = d(\Lambda d\Theta/dY)/dY - \Delta H\kappa_p{}^n(\mathcal{E}/\mathcal{R}^2) \times \exp[\mathcal{E}(1 - \Theta^{-1})] \tag{29}$$

respectively, where $\Delta H \equiv H_m - H_p$ may depend on Θ.

Although thermal expansion of the solid in the heated reaction zone will cause $v_p > 0$, this effect should be negligibly small since one expects small fractional changes in specific gravity, giving $V_p \ll r$ and therefore $v_p \ll 1$ in Eq. (3). On the other hand, in the hotter parts of the reaction zone, the abundance of either high-pressure or high-velocity gaseous products may physically detach polymer particles from the undegraded substrate and rapidly accelerate them to $v_p \gg 1$. For this reason, Eq. (28) is best viewed as describing polymer regression under conditions such that the condensed phase remains intact until vaporizing. High tensile strength of condensed polymer and the absence of foam or fizz zones would favor small v_p. Of course, the results should be qualitatively correct if $v_p \lesssim 1$.

In practice, $\mathcal{E}$ is always large enough that an asymptotic expansion in this parameter can be performed. From Eq. (29), when $\Theta^{-1} - 1 = O(1)$ the contribution of the chemical production term becomes negligible, the amount of volatiles produced is negligible and Eq. (29) becomes

$$d\Theta/dY = d^2\Theta/dY^2 \tag{30}$$

where it has been assumed that all properties of the polymer, prior to effective degradation, are constant. However, when Θ is sufficiently close to 1, so that $1 - \Theta = O(\mathcal{E}^{-1})$, the chemical production term must be taken into account.

A matched asymptotic expansion scheme is therefore indicated. In the outer region, Θ and Y are the variables and Eq. (30) is the differential equation. In the inner region, $F = \mathcal{E}(1 - \Theta)$ and $\eta = Yf(\mathcal{E})$ are the variables of order unity, with $f(\mathcal{E}) \to \infty$ as $\mathcal{E} \to \infty$, and the differential equations obtained from Eqs. (28) and (29) are

$$d\kappa_p/d\eta = -\kappa_p{}^n[\mathcal{E}/f(\mathcal{E})](1/\mathcal{R}^2)e^{-F}[1 + O(\mathcal{E}^{-1})] \tag{31}$$

and

$$\frac{f(\mathcal{E})}{\mathcal{E}^2}\,\frac{dF}{d\eta}\,\Gamma = \frac{d}{d\eta}\left(\Lambda\,\frac{dF}{d\eta}\right)\frac{f^2(\mathcal{E})}{\mathcal{E}^2} + \Delta H_s\,\frac{\kappa_p{}^n}{\mathcal{R}^2}\,e^{-F}[1 + O(\mathcal{E}^{-1})] \tag{32}$$

Only the choice $f(\mathcal{E}) = \mathcal{E}$ leads to a physically meaningful solution. If Γ is of order unity, then to lowest order the inner equations become

$$d\kappa_p/d\eta = -\kappa_p{}^n e^{-F}/\mathcal{R}^2 \tag{33}$$

and

$$d^2F/d\eta^2 = -\kappa_p{}^n e^{-F}\Delta H_s/\mathcal{R}^2 \tag{34}$$

where the assumption $\Lambda = 1$ has been introduced for the sake of simplicity (typically thermal conductivities of polymer and gaseous products are both of order 10^{-4} cal/sec cm°K).

It may be noted that in lowest order heat convection and heat conduction occur in the outer zone [Eq. (30)], polymer convection and polymer consumption occur in the inner zone [Eq. (33)], and heat conduction and chemical consumption of thermal energy occur in the inner zone [Eq. (34)]. Heat convection is negligible in the inner zone to order $\mathcal{E}^{-1}$, and diffusion of polymer and of degradation products is negligible everywhere to order $\mathcal{E}^{-1}$. This last result stems from the previously discussed assumption $v_p = 0$, which removes the diffusion term from Eq. (33), and from the assumption $\Gamma = O(1)$, which pushes the left-hand side of Eq. (32) to higher order. If $c_i = c_{p\infty}$ for all species, then $\Gamma = \Sigma_i \kappa_i \times (1 + v_i) = 1$ by mass conservation, thereby proving the ordering $\Gamma = O(1)$. In fact, reasonable departures from equal specific heats do not affect Γ greatly. For example, for a polymer-monomer binary system with $v_p = 0$, mass conservation shows that Γ can be written as $\Gamma = c_m/c_{p\infty} + \kappa_p(c_p - c_m)/c_{p\infty}$ which is of order unity for any realistic choice of properties.

The outer solution, from Eq. (30), is

$$\Theta_{\text{outer}} = \Theta_\infty + C_1 e^Y \tag{35}$$

By matching of inner and outer solutions, C_1 and a boundary condition for Eq. (34) are obtained. Thus, the expansions $\Theta_{\text{outer}} \sim \Theta_\infty + C_1(1 + \eta\mathcal{E}^{-1} + \ldots)$ and $\Theta_{\text{inner}} \sim 1 - \mathcal{E}^{-1} \times \lim_{\eta \to -\infty} F$ require that $C_1 = 1 - \Theta_\infty$ and $(F/\eta)_\infty = \Theta_\infty - 1$. Other boundary conditions for Eqs. (33) and (34) are $F(0) = 0$, $\kappa_p(-\infty) = 1$ and $\kappa_p(0) = \kappa_{p,s}$, where $\kappa_{p,s}$ will be assumed to be prescribed.

From Eqs. (33) and (34) it can easily be shown that

$$\kappa_p = (dF/d\eta + C_2)/\Delta H_s \tag{36}$$

where C_2 is obtained from the boundary conditions at $\eta \to -\infty$, viz., $C_2 = \Delta H_s + (1 - \Theta_\infty) > 0$. Substituting Eq. (36) into Eq. (34), one derives $d^2F/d\eta^2 = -De^{-F}(dF/d\eta + C_2)^n$, where $D \equiv \Delta H_s{}^{1-n}/\mathcal{R}^2$. Letting $g = dF/d\eta + C_2$, and looking for g as a function of F, we obtain

$$(g - C_2)dg/g^n = -De^{-F}dF \tag{37}$$

For $0 \leq n < 1$, Eq. (37) can be integrated readily between the appropriate values of g and F at $\eta = 0$ and $\eta \to -\infty$, yielding

$$[1/(2 - n)](g_\infty{}^{2-n} - g_s{}^{2-n}) - [C_2/(1 - n)] \times (g_\infty{}^{1-n} - g_s{}^{1-n}) = -D \tag{38}$$

where the boundary conditions on F have been applied. Since the boundary conditions on g are $g_\infty = \Delta H_s$ and $g_s = \Delta H_s \kappa_{p,s}$, we find from Eq. (38) that

$$\mathcal{R}^2 = (2 - n)(1 - n)[\Delta H_s(1 - \kappa_{p,s}{}^{2-n})(n - 1) + (\Delta H_s + 1 - \Theta_\infty)(2 - n)(1 - \kappa_{p,s}{}^{1-n})]^{-1} \tag{39}$$

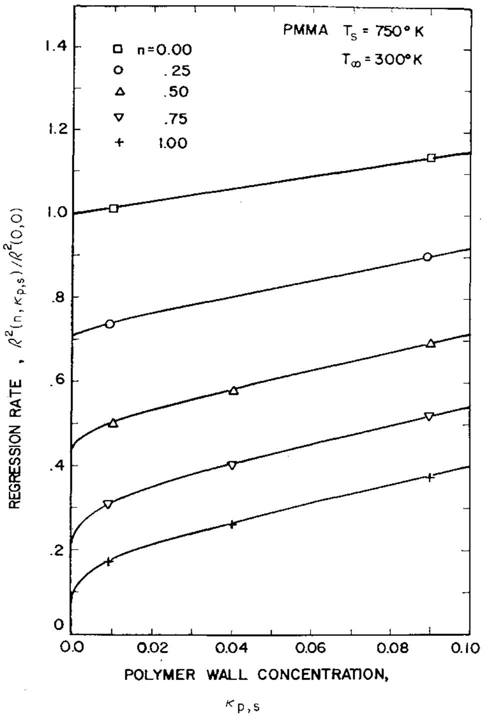

Fig. 1 Nondimensional regression rate vs. reaction order and polymer surface concentration.

For $n = 1$, the integral of Eq. (37) is

$$(g_\infty - g_s) - C_2 \ln(g_\infty/g_s) = -D \tag{40}$$

so that

$$\mathcal{R}^2 = [-(\Delta H_s + 1 - \Theta_\infty)\ln\kappa_{p,s} - \Delta H_s(1 - \kappa_{p,s})]^{-1} \tag{41}$$

Equations (39) and (41) constitute the asymptotic formulas for the regression rate that we intended to derive.

It may be noted that if one lets $\kappa_{p,s} \to 0$ in Eq. (39), then $\mathcal{R}^2$ approaches a finite limiting value that constitutes a logical definition of the regression rate for $0 \leq n < 1$. On the other hand, in Eq. (41) $\mathcal{R}^2 \to 0$ as $\kappa_{p,s} \to 0$. Physically this means that an infinite amount of time is required to eliminate all polymer for a first-order degradation reaction, and consequently the surface does not regress if its location is defined by $\kappa_{p,s} = 0$. For $n = 1$, the physically correct definition of the surface location must therefore correspond to a small nonzero value of $\kappa_{p,s}$. Fortunately the value of $\mathcal{R}^2$ is not strongly dependent on $\kappa_{p,s}$ for small values of $\kappa_{p,s}$ when $n = 1$, as may be inferred from the representative curves shown in Fig. 1, where $\mathcal{R}^2(0,0) = (\Delta H_s/2 + 1 - \Theta_\infty)^{-1}$. For $n = 1$ we have arbitrarily selected $\kappa_{p,s} = 0.01$.

Polystyrene, Weak Links Scission Component

For polystyrene, regardless of the scission mechanism, Eqs. (10) and (18) yield

$$\dot{\omega}_p = -B_{ps}\exp(-E_{ps}/R^0T)\rho_p q^{1/2} \tag{42}$$

which may be substituted into the definition of Ω_i in Eqs. (23) and (24). It is seen that these equations now contain the addition quantity $q = \mathrm{P}^{-1}$, for whose rate of change an additional equation must be written. For weak links scission, Eqs. (16) and (19) imply that this additional equation is

$$rd(q\kappa_p)/dy = B_w\exp(-E_w/R^0T)(q_0 + N_w - q\kappa_p) \tag{43}$$

After nondimensionalizing, we find that Eqs. (30) and (35) still describe the outer solution; the only modifications occur in the inner reaction zone. We define $\mathcal{R}^2$ by Eq. (27) with $n = 1$ and with B_w and $\mathcal{E}_w$, treat $\mathcal{E}_{ps}$ as the expansion

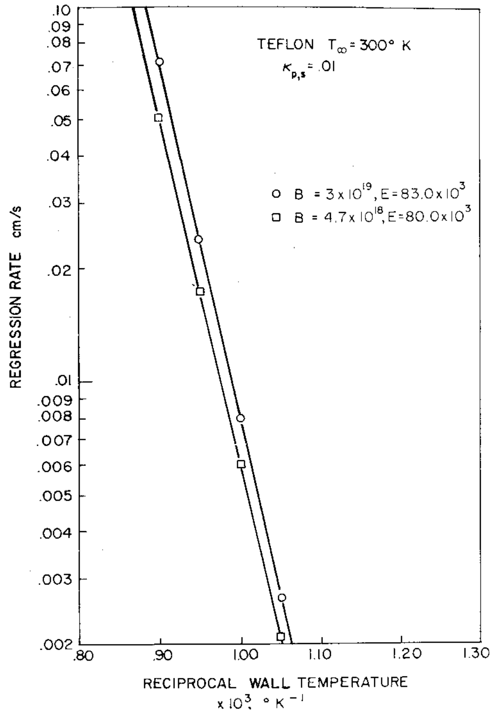

Fig. 2 Regression rate vs surface temperature, teflon.

parameter so that $\Theta = 1 - F\mathcal{E}_{ps}^{-1}$ and $\eta = Y\mathcal{E}_{ps}$, introduce the parameters $\gamma \equiv E_{ps}/E_w$ and $\delta \equiv B_{ps}/B_w$, and use $\tilde{q} \equiv q\kappa_p/(q_0 + N_w)$ as the third dependent variable. The inner equations which correspond to Eqs. (33) and (34) are then found to be

$$d\kappa_p/d\eta = -e^{-F}\kappa_p^{1/2}\tilde{q}^{1/2}A/\gamma\mathcal{R}^2\Delta H_s^{1/2} \tag{44}$$

$$d^2F/d\eta^2 = -e^{-F}\kappa_p^{1/2}\tilde{q}^{1/2}A\,\Delta H_s^{1/2}/\gamma\mathcal{R}^2 \tag{45}$$

and

$$d\tilde{q}/d\eta = e^{-F/\gamma}(1 - \tilde{q})/\gamma\mathcal{R}^2 \tag{46}$$

where $A \equiv [\Delta H_s(q_0 + N_w)]^{1/2}\delta \exp[\mathcal{E}_w(1 - \gamma)]$.

It is found from Eqs. (44) and (45) that Eq. (36) again relates κ_p to F, with the same value for C_2. The variable $\tilde{q}$ can be related approximately to κ_p by dividing Eq. (44) by Eq. (46), ignoring the factor $\exp[(\gamma^{-1} - 1)F]$ on the grounds that γ is close to unity, and then integrating from $-\infty$ to η. The result is

$$2(g^{1/2} - g_\infty^{1/2}) = -A[G(\tilde{q}) - G(\tilde{q}_0)] \tag{47}$$

where

$$G(\tilde{q}) \equiv -2\tilde{q}^{1/2} + \ln[(1 + \tilde{q}^{1/2})/(1 - \tilde{q}^{1/2})]$$

and where $g = \Delta H_s\kappa_p$ is defined above Eq. (37). Writing Eq. (46) as

$$(g - C_2)d\tilde{q}/dF = e^{-F/\gamma}(1 - \tilde{q})/\gamma\mathcal{R}^2$$

with $g(\tilde{q})$ obtained from Eq. (47), we can integrate from $\eta = -\infty$ to $\eta = 0$ in order to obtain an expression for $\mathcal{R}^2$. The result is

$$\mathcal{R}^2 = \{(\Delta H_s + 1 - \Theta_\infty)\ln[(1 - \tilde{q}_0)/(1 - \tilde{q}_s)] - I\}^{-1} \tag{48}$$

where

$$I \equiv \int_{\tilde{q}_0}^{q_s} [g(\tilde{q})/(1 - \tilde{q})]d\tilde{q}$$

Since $g(\tilde{q})$ is known, Eq. (48) constitutes the required theoretical expression for the regression rate.

To use Eq. (48), the surface value $\tilde{q}_s$ must be specified. From Eq. (48) it is seen that a meaningful solution is obtained only if $\tilde{q}_s < 1$. Since sufficiently small chain fragments vaporize readily, we define a critical degree of polymerization P_c at the surface. Then, by definition, $q_s = P_c^{-1}$, and therefore $\kappa_{p,s} = \tilde{q}_s(q_0 + N_w)P_c$ according to the definition of q. Since $g_s = \kappa_{p,s}\Delta H_s$, Eq. (47) can be evaluated at $\eta = 0$ to effect elimination of $\kappa_{p,s}$, thereby providing an equation for $\tilde{q}_s$. Since $\tilde{q}_s$ is expected to be very close to unity, we set $\tilde{q}_s = 1 - \epsilon$, assume $\epsilon \ll 1$, and expand Eq. (47) to obtain

$$\epsilon = \exp[-G(\tilde{q}_0) - 2\Delta H_s^{1/2}/A + (P_c^{1/2}/\delta)e^{\mathcal{E}w(\gamma - 1)} + \ln 2 - 2] \tag{49}$$

In Eq. (49) the value of A is rather small while all other terms are of order unity, so that ϵ is indeed small. Having determined $\tilde{q}_s$ from Eq. (49), we can evaluate I by numerical integration and then compute the regression rate from Eq. (48).

Since Eq. (47) implies that we can write I in the form

$$I = -\int_{g_\infty}^{g_s}\left(\frac{g}{\tilde{q}}\right)^{1/2}\frac{dg}{A}$$

an upper bound for I is easily found to be $\frac{2}{3}A^{-1}\tilde{q}_0^{-1/2}\Delta H_s^{3/2}$.

Polystyrene, Random Scission Component

For random scission Eqs. (11) and (20) imply that Eq. (43) must be replaced by

$$rdq/dy = B_{sc}\exp(-E_{sc}/R^0T)(1 - q). \tag{50}$$

Aside from this change, the situation is entirely analogous to that of the weak links component. We now employ B_{sc} and $\mathcal{E}_{sc}$ for defining $\mathcal{R}^2$ in Eq. (27), and we again treat $\mathcal{E}_{ps}$ as the expansion parameter. With the definitions $\alpha \equiv E_{ps}/E_{sc}$, $\beta = B_{ps}/B_{sc}$ and $C \equiv \beta\exp[\mathcal{E}_{sc}(1 - \alpha)]$, one finds, by proceeding in a manner analogous to that of the previous section, the result

$$\mathcal{R}^2 = \{(\Delta H_s + 1 - \Theta_\infty)\ln[(1 - q_0)/(1 - q_s)] - \Delta H_sJ\}^{-1} \tag{51}$$

where

$$J \equiv \int_{q_0}^{q_s}(1 - q)^{-1}\exp\{C[G(q_0) - G(q)]\}dq$$

Here G is the function defined after Eq. (47) and q_s is to be equated to P_c^{-1}. The integral J must be evaluated numerically. When this is done, it is found that the J term is negligible compared with the others in Eq. (51). A consequence of this result is that the regression rate for the random scission component, unlike that for the weak links component, becomes independent of the initial degree of polymerization when $P_0 \gg 1$.

III. Comparison with Experimental Data

Theoretical results for polytetrafluoroethylene are displayed in Fig. 2, as obtained with the data of Table 1 and with the two alternative rate coefficients given in Eqs. (3) and (4). Equations (27) and (41) for a first-order reaction with $\kappa_{p,s} = 0.01$ were used in the computation. There seems to be no experimental regression rate data with which Fig. 2 can be compared. The results are shown in the range of ablation applications, viz., T_s around 1000°K and r around 0.01 cm/sec. According to Eq. (3), these results do not depend on the initial degree of polymerization.

In Fig. 3, theoretical results from Eqs. (27) and (41) are shown for PMMA, using the data of Eqs. (1) and (2). These results are found not to be dependent on the initial degree of polymerization, so long as it is not too large ($P_0 \lesssim 2 \times 10^3$). At higher degrees of polymerization Eq. (1) becomes inapplicable. Experimental data plotted in Fig. 3 are taken from Ref. 2, in which the hot plate technique was used at

Table 1 Data used for regression rate computation

	Teflon	PMMA	Polystyrene
$\rho_{p\infty}$, g/cm^3	2.1 − 2.3 (Ref. 24)	1.18 − 1.19 (Ref. 24)	1.05 − 1.08 (Ref. 24)
$c_{p\infty}$, cal/g°K	0.25 (Ref. 24)	0.35 (Ref. 24)	0.32 − 0.35 (Ref. 24)
$\lambda_{p\infty}$, cal/sec cm°K	6.34×10^{-4} (Ref. 25)	5.0×10^{-4} (Ref. 26)	2.78×10^{-4} (Ref. 27)
d,cm^2/sec	1.2×10^{-3}	1.21×10^{-3}	0.83×10^{-3}
M_m, g/mole	100.02 (Ref. 24)	100.11 (Ref. 24)	104.14 (Ref. 24)
P_c	...	...	7 (Ref. 9, p. 100)
$h_m{}^0 - h_p{}^0$, cal/g	445 (Ref. 5, 28) (gaseous monomer)	130 (Ref. 27) (liq. monomer)	167 (Ref. 27) (liq. monomer)
$c_m(T)$(gas), cal/g°K	$0.193 + 1.35 \times 10^{-4}(T - 300)$ (Ref. 28)	?	$0.29 + 5.6 \times 10^{-4}(T - 300)$ (Ref. 29)
$c_p(T)$, cal/g°K	$0.254 + 3.36 \times 10^{-4}(T - 300)$ (Ref. 15)	?	$0.32 + 9.65 \times 10^{-4}(T - 300)$(Ref. 27)
$[h_m(\text{gas}) - h_m(\text{liq.})]_{T_\infty}$, cal/g	...	92 (Ref. 29)	105 (Ref. 29)
$(h_m - h_p)_T$, cal/g	$445 - 6.1 \times 10^{-2}(T - 300) - 10^{-4}(T - T_\infty)^2$	222[a]	$272 - 3 \times 10^{-2}(T - 300) - 2 \times 10^{-4}(T - 300)^2$

[a] Taken at this value for lack of information.

atmospheric pressure and the surface temperature was measured by a thermocouple interposed between the plate and the sample surface, from Ref. 1, in which the hot plate technique was used at atmospheric pressure with a thermocouple imbedded in the plate, and from Ref. 4, where surface pyrolysis was obtained by combustion of pyrolysis products with oxygen from an impinging jet. In Ref. 4 the surface temperature was measured either optically (measurement of thermal radiation) or from temperature profiles determined by fine thermocouples imbedded in the sample.

Substantial discrepancies appear between theory and experiment and also among the experiments themselves. It may be noted that the theoretical curve is found to agree well with the apparent activation energy of Ref. 2. At a given temperature, the theoretical magnitude of r is a factor of 2 below the experimental regression rate of Ref. 2. The highest theoretical curve falls within the scatter of the thermocouple measurements of Ref. 4. However, the theoretical curve does not agree with the optically inferred activation energy. Reference 4 indicates for this set of results an apparent activation energy of 35 kcal/mole, which cannot be accounted for by either the present theory (giving about 15 kcal/mole) or the desorption theory of Ref. 1 (giving about 9.2 kcal/mole).

It is interesting to note that, in Ref. 4, a "liquidlike" layer close to the surface of the sample is postulated from the temperature profile studies. Its extent is also found to increase with decreasing r. At $r = 0.028$ cm/sec, $T_s = 555$°C, the width of this layer is found to be a few hundredths of a millimeter. This liquidlike layer might well be interpreted as the region of effective thermal degradation, the thickness of which, according to the present theory, is of the order of $(\mathcal{E}r)^{-1}d \approx 2 \times 10^{-2}$ mm, where the values for PMMA in Table 1 and the previously stated r and T_s have been employed. The theoretically predicted effective degradation region also increases in width as r decreases, in agreement with the experimental observation.

It is also postulated in Ref. 4 that in hot plate experiments, since the liquidlike layer is "squeezed," the thermocouple mounted on the plate might measure a subsurface temperature in the liquidlike layer. From the present theory, the drop in temperature within the region of effective degradation is $\Delta T \sim T_s\mathcal{E}^{-1}$. If indeed the measured surface temperature T_{exp} can be interpreted as $T_s - \Delta T$, then the theoretical value r in term of T_{exp} would become, from Eq. (27), $r^2(T_{\text{exp}})/r^2(T_s) \approx e$. In other words, the theoretical curve would have to be raised by a factor of 1.6 (without affecting the apparent activation energy) to be plotted in conditions similar to that of the hot plate experimental data (namely r vs T_{exp}). This might explain part of the discrepancy between the theoretical results and the hot plate data [1,2] in Fig. 3.

In Fig. 4, theoretical results for polystyrene for the random scission theory [Eq. (51)] and for the weak links scission theory [Eq. (48)] are displayed. They are compared with the experimental data from Ref. 2, in which the hot plate technique was used at atmospheric pressure with a thermocouple between sample and plate, and from Ref. 3, where the surface heating is obtained from the exhaust jet of a laboratory rocket motor and the surface temperature measured by infrared radiation monitoring.

The theoretical results show practically no dependency on P_0 for the random scission component theory, and some measure of dependency for the weak links scission component theory. Also, in the latter case r increases as N_w is raised, which is expected on physical grounds. It should be noticed that an implicit effect of P_0 exists through N_w, since N_w is found[17] to depend on the initial degree of polymerization. The theoretical results for the weak links component are in excellent agreement with the data of Hansel and McAlevy.[3] Theoretical results for the random scission component lie farther from the experimental data of Ref. 3, a fact which may reinforce the already strong evidence of Refs. 17, 20, and 21 in favor of the weak links scission component.

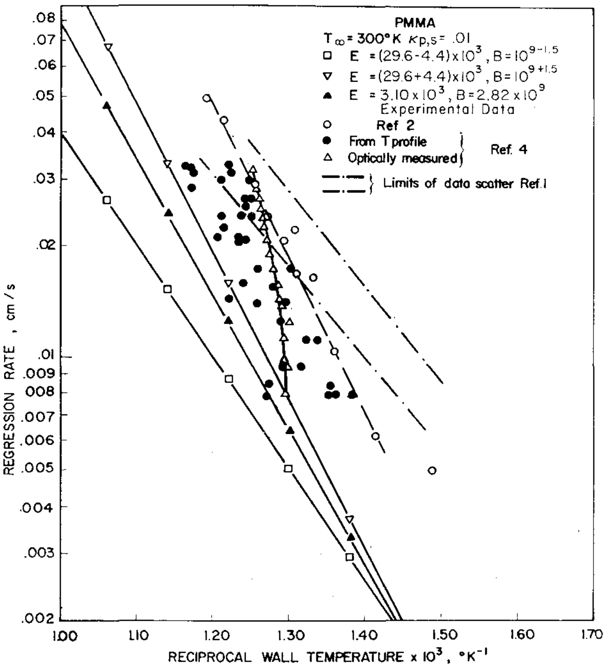

Fig. 3 Regression rate vs surface temperature, PMMA.

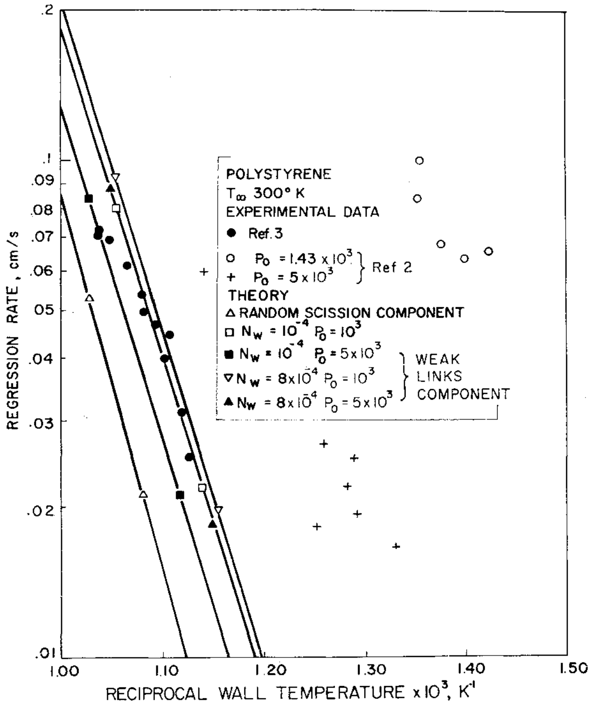

Fig. 4 Regression rate vs surface temperature, polystyrene.

It is interesting to note that softening and spreading of the polystyrene sample on the heating element is mentioned in Ref. 2. This may help to account for the wide divergence of the hot plate data from that of Ref. 3 and from the theory. Further support for this view may be provided by the observation that, as the degree of polymerization and therefore the viscosity of the sample increase, the discrepancy should diminish and the data should tend to approach the theory, a trend that can be found in Fig. 4.

In summary, although agreement of the present theoretical results with experiment is of necessity only partial because of discrepancies among experimental data, nevertheless the present weak links component theory appears to describe correctly the regression rate of polystyrene in an ablative environment. The first-order reaction theory developed herein for the linear regression rate of polymethylmethacrylate may or may not be applicable since it yields the correct activation energy but a regression rate that is somewhat low. In general, the particular matched asymptotic expansion scheme derived here for predicting from isothermal degradation data values of linear regression rates under intense surface heating, will be applicable to some polymers and not to others.

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