Eur. Polym. J. Vol. 18, pp. 813 to 819, 1982
Printed in Great Britain. All rights reserved

0014-3057/82/090813-07\$03.00/0

REACTIONS OF METHYL RADICALS WITH POLYMERS—PART 1: ABSTRACTION REACTIONS WITH POLY(*p*-METHOXYSTYRENE)

N. A. Weir and M. Rujimethabhas
Chemistry Department, Lakehead University, Thunder Bay, Ontario,
P7B 5E1, Canada

(*Received* 22 *September* 1981)

Abstract—The kinetics of hydrogen abstraction by methyl radicals from poly(*p*-methoxystyrene) have been investigated, methyl radicals being produced by the photolysis ($\lambda = 254$ nm) of the polymer under high vacuum. A new differential equation has been derived to describe simultaneous diffusion and reaction of methyl radicals; its solution, along with experimentally determined yields of methane, have been used to obtain a value for the rate constant for H abstraction from the polymer. The value of this constant is compared with previous data for poly(styrene) and the apparent agreement is found to be fortuitous. Relative to similar gas phase abstractions, the rate constants are lower by about four orders of magnitude; some of the factors contributing to this difference are discussed.

INTRODUCTION

Direct and indirect evidence (ESR and product analyses, respectively) indicate that methyl radicals are formed during the irradiation of a number of polymers, e.g. poly(*p*-methoxystyrene) (PMOS) [1], poly(methyl methacrylate [2, 3] poly(vinyl acetophenone) [4] and poly(vinyl acetate) [5]. Because of their inherent high reactivity and high mobility within polymers, methyl radicals are important intermediates; their interactions with the polymer critically influence the general course of the photoreactions, and the nature of the products of photodegradation. They also act as potential initiators of subsequent free radical reactions, e.g. oxidation by generating radical centres on the polymer.

Despite the significance of such reactions as H abstraction from polymers, little kinetic information is available, research in this area having been impeded by experimental difficulties associated with measuring $\dot{C}H_3$ concentrations, and in defining the extent to which various reaction products are derived from homogeneous, as opposed to heterogeneous processes.

A study of the reactions of $\dot{C}H_3$ with a number of polymers [isotactic poly(propylene), poly(styrene) (PS) and low density poly(ethylene)] was recently made, $\dot{C}H_3$ being derived from the photolysis and thermolysis of 1,1 diphenyl ethyl-hydroperoxide; a rate constant for H abstraction from PS at 353 K of 1.6 $dm^3\ mol^{-1}\ sec^{-1}$ was reported. This value was regarded as being anomalously low, and various reasons were offered [6].

One disadvantage of a system in which the $\dot{C}H_3$ source is dispersed in the polymer is the lack of information on its distribution within a given polymer sample, this being the result of possible mutual incompatability of polymer and hydroperoxide. Hence a uniform distribution and hence rate of production of $\dot{C}H_3$ are by no means assured. In order to obtain kinetic data the previous workers [6] derived and solved a differential equation to represent the simultaneous diffusion and reaction of $\dot{C}H_3$. However, a solution appropriate to a steady state only was obtained, and its application is not necessarily justified in all cases.

The model also assumed a constant "source" term, and no allowance was made for the effect of film thickness, which is certainly significant in the photochemical production of radicals. In addition the rate constant for abstraction was derived from the relative rates of formation of CH_4 and C_2H_6, the classical technique used in gas phase kinetics. It is doubtful whether the application of such competitive kinetics is valid in the present case, since the CH_4 forming reaction is a gas–solid reaction while the C_2H_6 was supposed to result from the gas phase recombination of $\dot{C}H_3$ [6].

In order to eliminate possible ambiguities arising from these deficiencies, we have re-investigated abstraction by $\dot{C}H_3$ from PMOS the polymer itself being a photochemical source of $\dot{C}H_3$ on the high vacuum short-wave ($\lambda = 254$ nm) irradiation. The system has the additional advantage that the reactions do not require to be carried out at 353 K, at which temperature the polymer, or at least the lower molecular weight components of it, begin to undergo physical changes. In practice also, few photodegradation reactions occur at such high temperatures.

A new differential equation describing the simultaneous reaction and diffusion of $\dot{C}H_3$ has been derived, allowance being made for a thickness dependent source term; a solution applicable to both steady and non-steady state conditions has been obtained. Rate constants have been calculated directly using this equation and the experimentally determined CH_4 yields, and no competitive kinetics are assumed.

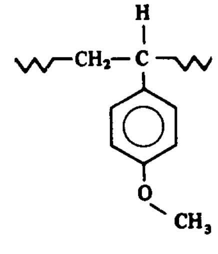
THEORETICAL

Mathematical model

Consider a thin polymer film of thickness L and surface area A aligned in the yz-plane as shown in Fig. 1. The film is irradiated with u.v. radiation of uniform intensity, I_0, the flux being emitted in a direction parallel to the x-axis.

In order to formulate an equation to describe simultaneous reaction and diffusion of methyl radicals, it is necessary to define the principal reactions involving methyl radicals produced in the photolyses of PMOS films which have recently been investigated in detail [1].

For convenience the polymer is represented as



$HPCH_3$ where H refers to the α-H which, according to the results of a recent study employing isotopic substitution at the α-position, is the most likely to be abstracted [7]. The short wave photolysis of PMOS gives rise to methyl radicals (fission of the CH_3—O bond), the reactions of which occur in both phases. It is therefore appropriate to outline the reactions which take place in gas and solid phases.

(a) *Reactions of $\dot{C}H_3$ in bulk polymer film*

$$HPCH_3 \xrightarrow[h\nu]{1} H\dot{P} + \dot{C}H_3 \quad (1)$$

$$HPCH_3 + \dot{C}H_3 \xrightarrow{2} \dot{P}CH_3 + CH_4 \quad (2)$$

$$\dot{C}H_3 + \dot{C}H_3 + M \xrightarrow{3} C_2H_6\,(M \text{ is a third body}) \quad (3)$$

$$\dot{P} + \dot{C}H_3 \xrightarrow{4} \text{Non-radical products} \quad (4)$$

where $\dot{P} \approx H\dot{P}$ or $\dot{P}CH_3$ (macroradicals). ($\dot{C}H_3$ addition to phenyl groups is also possible, but it was not investigated.)

(b) *Reactions of $\dot{C}H_3$ in the gas phase*

Concentrations of $\dot{C}H_3$ radicals in the gas phase may be derived from two sources, i.e. some may be formed by photolysis of the molecules in the surface layer of the film and enter the gas phase directly and others formed in the bulk polymer could conceivably diffuse out of the polymer matrix into the gas phase.

Simultaneous diffusion and reaction processes can be described by a continuity equation for an isotropic medium under isothermal conditions, i.e.:

$$\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i + S_i - L_i \quad (5)$$

where ∇^2 is the Laplacian operator which takes the form $\partial^2/\partial x^2$ in the one-dimensional case. Since in the experimental set-up products of methyl radical reactions are derived from the diffusion along the direction parallel to the x-axis, i.e. along the direction of formation due to the incident radiation, (5) takes the form:

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} + S_i - L_i \quad (6)$$

x and t are space and time variables, respectively. If i is identified as $\dot{C}H_3$ as in the present case, then $C_i = C_i(x, t)$ is the concentration of methyl radicals. D_i is the diffusion coefficient of $\dot{C}H_3$ and is assumed to be constant with respect to x and to concentration. For an anisotropic medium, D_i is direction dependent [8] but, to make the equation tractable, we have assumed the bulk polymer to be isotropic. S_i is the source term and is equal to the rate of production of $\dot{C}H_3$. For the present experimental conditions $S_i = I_0 \Phi_i e^{-\alpha x}$ (Lambert's Law). Here I_0 is the intensity of incident radiation, and Φ_i is the quantum yield for $\dot{C}H_3$ production, α is the absorption coefficient for u.v. radiation by the chromophore in the film, and x is the film thickness. For convenience, let $\beta = I_0 \Phi_i$ and $S_i = \beta e^{-\alpha x}$. L_i is the loss term which describes the depletion of methyl radicals due to chemical reactions.

We have neglected a term involving the mass transport due to convection, since in our experiment the photolysis was conducted in a static system. Mass transport due to thermal gradient has similarly been excluded [9]; this is justifiable on the grounds that the experiments were carried out isothermally.

Thus, the equation describing changes in the $\dot{C}H_3$ concentration ($\dot{C}H_3$) in bulk polymer film under isotropic and isothermal conditions may be expressed as:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} + \beta e^{-\alpha x} - k_2(HPCH_3)C - 2k_3C^2(M) - k_4(\dot{P})C \quad (7)$$

where $C = (\dot{C}H_3)$.

It is likely that the rate of recombination of methyl radicals in the film (in the presence of a third body M), $2k_3C^2(M)$, is much smaller than that in the gas phase, i.e. 2×10^{10} dm^3 mol^{-1} sec^{-1} [10, 11] because of the relative efficiencies of methyl radical collisions in the two media. Thus most of the C_2H_6 formed may be attributed to the gas phase reaction and the term $2k_3C^2(M)$ in (7) becomes relatively unimportant. On the other hand the formation of CH_4 via hydrogen atom abstraction by $\dot{C}H_3$ from the solid polymer (reaction 2) is likely to be more facile than the corresponding gas phase reaction of $\dot{C}H_3$ and H atoms, since the latter reaction is a termolecular process [12] which under the present high vacuum (10^{-7} torr)* con-

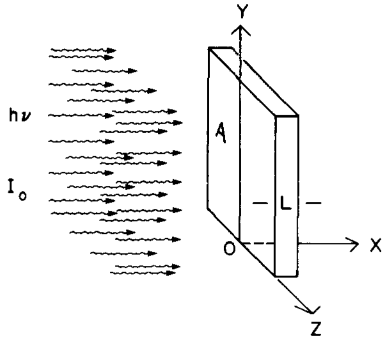


Fig. 1. Model of polymer film used to derive the differential equations. L is the thickness and A is the area exposed to u.v. radiation of incident intensity I_0.

---

* 1 torr = 133.322 Pa.

ditions would be unlikely. Thus the term $2k_3C^2(M)$ may be eliminated from Eqn (7).

The rates of reaction of $\dot{C}H_3$ with macroradicals ($\dot{P}$), other than those with which they could recombine in the cages in which they are initially formed together, are not likely to be significant since they require the mutual encounter of $\dot{C}H_3$ with large immobile radicals (cage collapse reactions would contribute no methane, hence could not be detected).

The high $\dot{C}H_3$ mobility could in part compensate for this, however, on account of its high reactivity and the relatively very high concentration of abstractable H atoms (relative to ($\dot{P}$)), it is reasonable to expect $\dot{C}H_3$ to participate in abstraction reactions at the expense of $\dot{C}H_3 + \dot{P}$ reactions. Thus the term $k_4(\dot{P})C$ may be regarded as insignificant in (7). Thus Eqn (7) may be simplified to:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} + \beta e^{-\alpha x} - k_2(\mathrm{HPCH_3})C \qquad (8)$$

Under the present experimental conditions, $(\dot{C}H_3) = C \ll (\mathrm{HPCH_3})$ as indicated by the total product yields. Thus the second-order term, $k_2(\mathrm{HPCH_3})C$, can be replaced by pseudo first-order kinetics, i.e. $k_2(\mathrm{HPCH_3}) = k$, where k is the apparent pseudo first-order rate constant. Therefore the observed rate of CH_4 formation is given approximately by Eqn (9):

$$\begin{aligned}\frac{d(CH_4)}{dt} &= k_2(\dot{C}H_3)(\mathrm{HPCH_3})\\ &= k(\dot{C}H_3)\\ &= kC \qquad (9)\end{aligned}$$

The differential equation becomes:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} + \beta e^{-\alpha x} - kC \qquad (10)$$

Time dependent solution to differential Eqn (10)

The differential equation (10) is solved for the following set of initial and boundary conditions:

$$\begin{aligned}&C(x, 0) = 0, 0 < x < L\\ &\left.\begin{aligned}C(0, t) = 0\\ C(L, t) = 0\end{aligned}\right\} t > 0\end{aligned}$$

and the solution (see appendix) is shown in Eqn (11).

$$C = \frac{\Phi I_0}{\alpha^2 D - k}\left[(e^{(\alpha^2 D - k)t} - 1)e^{-\alpha x} + \frac{\left\{\sinh\sqrt{\frac{k}{D}}(L - x) + e^{-\alpha L}\sinh\sqrt{\frac{k}{D}}x\right\}}{\sinh\sqrt{\frac{k}{D}}L}\right.$$

$$- e^{(\alpha^2 D - k)t}\frac{\{\sinh\alpha(L - x) + e^{-\alpha L}\sinh\alpha x\}}{\sinh\alpha L}$$

$$\left. + 2\pi L^2(\alpha^2 D - k)\sum_{n=1}^{\infty}\frac{\exp - \left[\left\{\left(\frac{n\pi}{L}\right)^2 D + k\right\}t\right] n\{(-1)^n e^{-\alpha L} - 1\}\sin\left(\frac{n\pi}{L}\right)x}{(n^2\pi^2 D + kL^2)(n^2\pi^2 + \alpha^2 L^2)}\right]. \qquad (11)$$

Writing $C(\bar{x}, t)$ to represent the average concentration of C over the thickness of the film, we obtain Eqn (12):

$$C(\bar{x}, t) = \frac{1}{b - a}\int_a^b C(x, t)\,dx \qquad (12)$$

where a and b represent the lower and upper limits of the film thickness between which the concentration of $\dot{C}H_3$ is averaged. The rate of production of CH_4 per unit area at various times may be calculated from $kC(\bar{x}, t)$. Thus the theoretical rate of production of CH_4, R_{CH_4} at time t for a film of area A, is:

$$R_{CH_4} = A \times k \times C(\bar{x}, t) \qquad (13)$$

and the concentration of CH_4 at various times may be calculated. Equation (13) is of the same form as (9) which relates C to the measured yield of CH_4.

The steady state solution to Eqn (10) for which $dc/dt = 0$ may also be solved under the same boundary conditions as imposed upon the non-steady state equation and the solution is given in Eqn (14).

$$\begin{aligned}C(x) = {}&\frac{\Phi I_0}{(D\alpha^2 - k)\sinh(\sqrt{k/D}L)}\\ &\times\left[\sinh\sqrt{\frac{k}{D}}(L - x) + e^{-\alpha L}\sinh\sqrt{\frac{k}{D}}x\right.\\ &\left.- e^{-\alpha x}\sinh\sqrt{\frac{k}{D}}L\right]. \qquad (14)\end{aligned}$$

The average value of $C(x)$ over the polymer film thickness may be found similar to that shown in (12) and is designated as $C(\bar{x})$. The theoretical rate of production of CH_4 from the steady state solution, R_{CH_4}, may also be calculated from Eqn (13) by replacing $C(\bar{x}, t)$ with $C(\bar{x})$.

EXPERIMENTAL

The details of the photolyses of films of PMOS have been described [1] and only a summary of the salient features is given below. Films of PMOS (4×10^{-4} cm thick) were photolysed under high vacuum (10^{-7} torr) conditions using 254 nm radiation. The temperature of the reactions was controlled to 298 ± 1 K. The gaseous products were analysed continuously and quantitatively by an in-line quadrupole mass spectrometer (Micromass Q7). Rates of formation of CH_4 were used to test our theoretical model, and to obtain information about methyl radical abstraction reactions with the polymer.

RESULTS AND DISCUSSIONS

Typical experimental data for CH_4 formation from a PMOS film 10^{-4} cm thick are shown by circular data points (A) in Fig. 2 (C_2H_6 is also formed, but not shown), and the results of the theoretical calculation for the CH_4 production (integrated over the total film thickness) are indicated by the triangular points. The same results are obtained from the non-steady state and the steady state calculations. It can be seen that the theoretical and experimental data coincide for reaction times of up to about 120 min, after which the experimental data deviate from linearity (this is discussed further below). Corresponding theoretical data were shown for a film of thickness 10^{-5} cm (B). It should be noted that the non-steady state solution yields the same results as the steady state one.

Figure 3 shows molecular weight changes in the same time scale as the above gaseous evolution reactions. Molecular weights have been normalized against the initial value for the undegraded polymer, i.e. $(\overline{M}_n)_t/(\overline{M}_n)_0$. It can be seen that a more abrupt change in molecular weight occurs around 90 min irradiation.

With the exceptions of the diffusion coefficient D for $\dot{C}H_3(D_{\dot{C}H_3})$ in PMOS and the rate constant, k, which was to be estimated, all the parameters used in the calculation were derived from experimental results [1] and these are shown in Table 1 (column 2). The absolute value of the quantum yield for $\dot{C}H_3$ formation cannot be obtained and it has therefore been estimated using the values for Φ_{CH_4} and $\Phi_{C_2H_6}$. Assuming that all of the $\dot{C}H_3$ radicals ended up as CH_4 and C_2H_6, the value of $\Phi_{\dot{C}H_3}$ would be $\Phi_{CH_4} + 2\Phi_{C_2H_6}$. This value is an upper limit, since it is expected that some of the $\dot{C}H_3$ may also undergo reaction (4). However, the contribution from (4) is not likely to be large, particularly in the initial stage of the photolysis when $\dot{C}H_3$ and $\dot{P}$ concentrations are likely to be small. $\Phi_{\dot{C}H_3}$ was therefore taken as 1×10^{-3} (based on the experimentally obtained values of Φ_{CH_4} and $\Phi_{C_2H_6}$ as 3.7×10^{-4} and 3.3×10^{-4}, respectively).

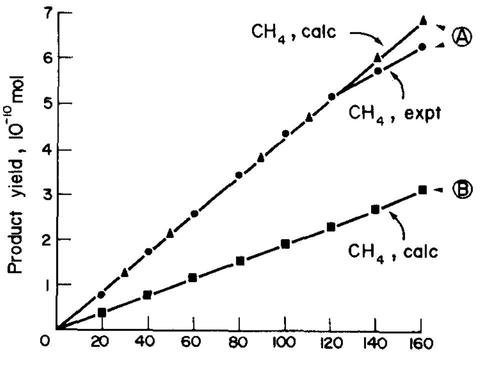


Fig. 2. Comparison of observed and theoretical yields of CH_4 as a function of reaction time, A-film thickness = 10^{-4} cm. B-film thickness = 10^{-5} cm-theoretical yield.

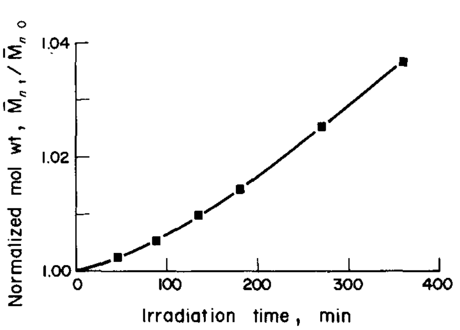


Fig. 3. Changes in molecular weight $(\overline{M}_n)_t$ as a function of time of irradiation of PMOS film at $\lambda = 254$ nm. Molecular weight changes normalized to $(\overline{M}_n)_0$ the molecular weight of undegraded polymer.

The diffusion coefficient for methyl radicals in PMOS has not been reported; previous workers [6] have used the corresponding value of the diffusion coefficients for CH_4 as an approximation in their studies of poly(styrene), e.g. D for CH_4 in PS is 10^{-7} cm^2 sec^{-1} at 353 K [6]. However, such an approximation would not appear to be justified in the present case for the following reasons:

(a) *Volume of diffusant*

From the vacuum u.v. absorption [13] and ESR [14, 15] studies, it is concluded that $\dot{C}H_3$ (in its ground state) assumes the D_{3h} point group and has an internuclear (C–H) distance of 0.107 nm [16]. This value is smaller than the corresponding value for C–H in CH_4 (i.e. 0.109 nm), as obtained from Raman spectroscopy [17]. Thus the effective volume of CH_4 is greater.

(b) *Polymer free volume*

If the structure and geometry of the two monomers (i.e. styrene and p-methoxy styrene) are considered, it is reasonable to conclude that the PMOS will have a larger free volume than the equivalent number of moles of PS.

The likely effects of these two factors on the value of $D_{\dot{C}H_3}$ in PMOS can be qualitatively assessed by considering the following empirical relationship

Table 1. Comparison of experimentally obtained parameters with those used in calculations to provide the best fit

Parameter	Experimental	Theoretical
α (cm^{-1})	5600	5600
I_0 (E cm^{-2} sec^{-1})	3.0×10^{-10}	3.7×10^{-10}
$\Phi_{\dot{C}H_3}$	1×10^{-3}	1.05×10^{-3}
D (cm^2 sec^{-1})	5×10^{-7}	5×10^{-7}
L (cm)	4×10^{-4}	4×10^{-4}
k (sec^{-1}), nonsteady state	—	15.7
k (sec^{-1}), steady state	—	15.6

between D, free volume and diffusant volume [18–21], i.e.

$$D = d\exp(-B/f) \qquad (15)$$

where D is the diffusion coefficient, d is related to the size and shape of the diffusant, B is associated with the smallest hole size required for diffusive jumps and f is the average fractional free volume of the polymer system. It can be seen that, for $\dot{C}H_3$ diffusing in PMOS, B is smaller, f is larger, and since the exponential term is more important, the overall result is an increased value for $D_{\dot{C}H_3}$ relative to D_{CH_4} in PS. The exact magnitude of this difference is impossible to calculate, but a plausible value of $5 \times 10^{-7}\,\mathrm{cm^2\,sec^{-1}}$ has been estimated and is used in the calculations.

Parameters listed in Table 1 (column 2) were used in conjunction with observed yields [1] and Eqns (13) and (9) to calculate k and k_2. The same procedure was used for non-steady state and steady state solutions, employing the same set of parameters in the calculations. Data are summarized in Table 2.

It appears that the value of $k_2(\pm 10\%)$, the rate constant for H abstraction from the polymer, is considerably lower than that previously implied and that for an analogous gas phase abstraction by $\dot{C}H_3$ in which the rate constant is at least four orders of magnitude higher [22]. This result is in general qualitative agreement with data obtained for H abstraction from PS, poly(ethylene) and poly(propylene), and it can perhaps be rationalized in terms of the Eyring formulation of the rate constant, i.e.

$$k_2 = \theta\exp\left(\frac{\Delta S\dagger}{R}\right)\exp\left(-\frac{\Delta E}{RT}\right) \qquad (16)$$

in which θ is a ratio of fundamental constants, and $\Delta S\dagger$ and ΔE are the entropy and energy of activation respectively.

In the gas phase both the $\dot{C}H_3$ and the molecule from which it abstracts have their classical translational energies, and undergo frequent collisions. At 298 K, however, PMOS is a glassy solid ($T_G = 362$ K) [23] in which the chains of the macromolecules are rigid, the only degree of freedom being low amplitude oscillations of the substituted phenyl groups around the C-phenyl axis [24]. Methyl radicals have potentially high mobility, but this is restricted to random displacements in the available free volume. In addition the formation of the transition state for abstraction of the tertiary H atoms (other abstractions are energetically unfavourable) requires a rather specific encounter of $\dot{C}H_3$ with the tertiary C atom, which is subject to unfavourable steric effects [25]. The overall effect of these factors is reflected in a low value of $\Delta S\dagger$, and hence in the value of k_2.

Table 2. Comparison of rate constants for H atom abstraction by methyl radical from films of poly(styrene) and poly(p-methoxystyrene)

Polymer	k ($\mathrm{sec^{-1}}$)	k_2 ($\mathrm{dm^3\,mol^{-1}\,sec^{-1}}$)	T (K)	Reference
PMOS	16 ± 2	2 ± 0.2	298	Present work
PS	16–25	1.3–1.9	353	[6]

For PMOS, the non-steady state and the steady state calculations yield the same rate constants (k and k_2).

Formation of radical centres on the tertiary C-atoms of the polymer accompanies abstraction. However, to attain the geometry associated with these sp^2 hybridized tertiary C-atoms (i.e. planar), displacements of adjacent bonds are required; since PMOS is well below its T_G at 298 K, segmental motion can only be achieved by the input of energy. Thus it follows that ΔE for the reaction will be higher than that for a small molecule in the gas phase, and from (16) it can be seen that k_2 will be correspondingly lower.

Also shown in Table 2 are data obtained for PS [6] which would be expected to react under identical conditions at a similar rate. The apparent agreement between the two sets of data is undoubtedly fortuitous, and attributable to the neglect of the factors mentioned in the Introduction. A temperature difference of 55 K would bring about a change in the rate constant for PS of at least two orders of magnitude.

The validity of the differential Eqn (10) and its solution (11) in representing total CH_4 formation from PMOS as a function of irradiation time can be assessed from Fig. 2(A) in which typical experimental data for a 10^{-4} cm thick film are compared with those calculated using the above determined value of k and other experimentally determined parameters, e.g. I_0. It can be seen that there is very good correspondence between the two sets of data for reaction periods of approximately 100 min after which the theoretical exceeds the observed yield. It can also be seen that the model can adequately represent reactions of thinner films, theoretical data being obtained for a film 10^{-5} cm thick (Fig. 2B) which had insufficient mechanical strength to be investigated experimentally. This model is particularly sensitive to film thickness, and it can be seen that about 50% of the CH_4 yield is formed within a 10^{-5} cm thick layer. Similar observation can also be made with the results of the theoretical calculation from the steady-state solution (14) and the experimental data for the yield of CH_4.

Slight modifications were made to the value of the various parameters to obtain the best fit between observed and theoretical data, and these are summarized in Table 1 (column 3). The discrepancy between experimental data and theoretical predictions beyond about 100 min reaction is not due to a mathematical limitation of the model, but rather the result of the following modifications of physical properties of the film brought about by the irradiation.

(a) *Diffusion characteristics*

It has been established that simultaneous chain scission and cross-linking occur during the photolysis of PMOS [1] the quantum yield for the latter being significantly greater. In the early stages of the reaction (<60 min) chain scission compensates to some extent, and consequently the molecular weight increases slowly. However, as the reaction proceeds and the system becomes more rigid, the effects of chain scission are overwhelmed by cross linking, and the molecular weight increases more rapidly.

Typical data are shown in Fig. 3, from which it can be seen that the more pronounced effects of cross linking coincide approximately in time with the observed deviations between experimental and theoretical data, and these can be ascribed to the effects of cross linking on diffusion coefficients of $\dot{C}H_3$ and CH_4.

It has been established [26, 27] that cross linking leads to a reduction in the values of diffusion coefficients of gases in polymers and it follows that not only will the $\dot{C}H_3$ mobility be reduced (and with it the probability of abstraction), but the diffusion of CH_4 out of the polymer will be impeded, and the observed rate of formation will decrease.

(b) *Optical effects*

Irradiation of PMOS leads to the formation of a number of polymer species which exhibit enhanced absorption in the u.v. and visible regions of the spectrum, consequently the absorption coefficient, α, will become a composite term which will be time dependent.

In addition, the absorbing species formed in the surface layers will act as internal filters and the effective u.v. intensity reaching lower layers within the film will decrease [28]. The changing absorption pattern will probably also change the quantum yield for $\dot{C}H_3$ formation.

Effects (a) and (b) will be reflected in non-constant (i.e. time dependent) values of parameters such as α, Φ and D; since no allowance was made for this effect in deriving Eqn (10), it follows that it is unsuitable for predicting behaviour beyond about 100 min.

In summary a new differential equation representing the simultaneous diffusion and reactions of $\dot{C}H_3$ radicals within PMOS films has been derived, solved (for non-steady state and steady state conditions) and used in conjunction with experimental data for CH_4 production by photolysis of PMOS to obtain a rate constant for $\dot{C}H_3$ abstraction from the polymer. The system has the advantage that $\dot{C}H_3$ is derived directly from the polymer by photolysis and not from another solute molecule dispersed in the film.

Unlike others [6] the present model employs a source term ($\beta e^{-\alpha x}$) which includes a number of measurable and variable parameters associated with the film (e.g. thickness) and it allows the rate constant to be calculated directly, without the need to invoke competitive kinetics.

It is evident from this investigation that the steady state and non-steady state calculations yield the same rate constants, k and k_2 (Table 2). While the steady state solution offers simpler calculation, the non-steady state solution is more general.

Acknowledgements—The authors acknowledge the generous support of the Natural Sciences and Engineering Research Council of Canada, and the technical assistance of Mr S. T. Spivak and Mr G. Anderson of this University.

REFERENCES

1. N. A. Weir and T. H. Milkie, *Polym. Degrad. Stabil.* **1**, 105 (1979).
2. G. Geuskens and C. David, *Makromolek. Chem.* **165**, 273 (1973).
3. Y. Hajimoto, N. Tamura and S. Okamoto, *J. Polym. Sci.* **A 3**, 255 (1965).
4. N. A. Weir and T. H. Milkie, *J. Polym. Sci., Polym. Chem. Ed.* **17**, 3723 (1979).
5. K. Tsuji, *Rep. Progr. Polym. Phys., Japan.* **17**, 553 (1974).
6. O. A. Zaporozhskaya, L. L. Yasina and V. S. Pudov, *J. phys. Chem.*, Russia **53**, 1394 (1979).
7. N. A. Weir, M. Rujimethabhas and P. Q. Clothier, *Eur. Polym. J.* **17**, 431 (1981).
8. J. Crank, *The Mathematics of Diffusion.* Oxford University Press, London (1956).
9. L. D. Landua and E. M. Lifshitz, *Fluid Mechanics*, p. 222. Pergamon Press, London (1959).
10. N. Basco, D. G. L. James and R. D. Stuart, *Int. J. Chem. Kinet.* **2**, 215 (1970).
11. H. E. van den Berg, A. B. Callear and R. J. Nostrom, *Chem. Phys. Lett.* **4**, 101 (1969).
12. S. W. Benson, *The Foundations of Chemical Kinetics*, 361. McGraw-Hill, New York (1960).
13. G. Herzberg and J. Shoosmith, *Can. J. Phys.* **34**, 523 (1956).
14. M. Karplus, *J. chem. Phys.* **30**, 15 (1959).
15. L. Kaplan, *Free Radicals* (Edited by J. K. Kochi), Vol. II, p. 361. John Wiley, New York (1973).
16. G. Herzberg, *Proc. R. Soc.* **262A**, 291 (1961).
17. B. P. Stoicheff, C. Cumming, G. E. St. John and H. L. Welsh, *J. chem. Phys.* **20**, 498 (1952).
18. M. H. Cohen and D. Turnbull, *J. chem. Phys.* **31**, 1164 (1959).
19. H. Fujita, *Diffusion in Polymers* (Edited by J. Crank and G. S. Park), Chapter 3. Academic Press, New York (1968).
20. M. Kawakami, H. Iwanaga and S. Kagawa, *Bull. chem. Soc. Japan* **54**, 869 (1981).
21. A. Kreituss and H. L. Frisch, *J. Polym. Sci., Polym. Phys. Ed.* **19**, 889 (1981).
22. V. N. Kondrat'ev, *Chemical Kinetics of Gas Reactions*, p. 265, Pergamon Press, London (1964).
23. C. A. Brighton, G. Pritchard and G. A. Skinner, *Styrene Polymers*, Applied Science Publisher, London (1979).
24. R. E. Wetton, *Dielectric Properties of Polymers* (Edited by F. E. Karasz), Plenum Press, New York (1972).
25. L. Dulog and K. H. David, *Makromolek. Chem.* **177**, 1717 (1976).
26. A. Aitken and R. M. Barrer, *Trans. Faraday Soc.* **51**, 116 (1955).
27. R. Greenwood and N. A. Weir, *J. appl. Polym. Sci.* **19**, 1409 (1974).
28. N. A. Weir, *J. appl. Polym. Sci.* **17**, 401 (1973).
29. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Chapter 12, Oxford University Press, London (1959).
30. E. T. Copson, *An Introduction to the Theory of Functions of a Complex Variable*, Chapter 4, Oxford University Press, London (1959).

MATHEMATICAL APPENDIX

The solution to the differential Eqn (10) may now be solved, by first rearranging it as follows:

$$\frac{\partial^2 C}{\partial x^2} - \frac{k}{D}C - \frac{1}{D}\frac{\partial C}{\partial t} = -\frac{\beta}{D}e^{-\alpha x} = -\gamma e^{-\alpha x} \qquad (A1)$$

where $\gamma = \beta/D$. (A1) is Laplace transformed; we obtained

$$\frac{d^2\overline{C}}{dx^2} - \frac{k}{D}\overline{C} - \frac{1}{D}(p\overline{C} - \overline{C}_0) = -\frac{\gamma}{p}e^{-\alpha x} \qquad (A2)$$

$$\overline{C} = \int_0^\infty e^{-pt}C(x, t)\,dt.$$

Applying the initial condition:

$$C(0, x) = 0, \quad \text{thus } \overline{C}_0 = 0.$$

The subsidiary equation is:

$$\frac{d^2\overline{C}}{dx^2} - \frac{k}{D}\overline{C} - \frac{p}{D}\overline{C} = -\frac{\gamma}{p}e^{-\alpha x}. \tag{A3}$$

Putting $\mathcal{D} \equiv d/dx$, (A3) may now be written as:

$$\left[\mathcal{D}^2 - \left(\frac{k}{D} + \frac{p}{D}\right)\right]\overline{C} = -\frac{\gamma}{p}e^{-\alpha x} \tag{A4}$$

The auxiliary equation of (A4) is

$$\left[\omega^2 - \left(\frac{k}{D} + \frac{p}{D}\right)\right]\overline{C} = 0$$

$$\omega = \pm\sqrt{\frac{k+p}{D}}$$

Thus

$$\overline{C} = A\exp\left(\sqrt{\frac{k+p}{D}}\,x\right) + B\exp\left(-\sqrt{\frac{k+p}{D}}\,x\right)$$

where A and B are integration constants.

From the particular integral of (A4) we get

$$\overline{C} = -\frac{\gamma e^{-\alpha x}}{p\left\{\alpha^2 - \left(\frac{k+p}{D}\right)\right\}}$$

Thus the general solution for $\overline{C}$ is

$$\overline{C} = A\exp\left(\sqrt{\frac{k+p}{D}}\right)x + B\exp\left(-\sqrt{\frac{k+p}{D}}\right)x - \frac{\gamma}{p}\left[\frac{e^{-\alpha x}}{\left\{\alpha^2 - \left(\frac{k+p}{D}\right)\right\}}\right] \tag{A5}$$

Writing $\xi = \sqrt{\frac{k+p}{D}}$, we have

$$\overline{C} = Ae^{\xi x} + Be^{-\xi x} - \frac{\gamma}{p}\left[\frac{e^{-\alpha x}}{\alpha^2 - \xi^2}\right] \tag{A6}$$

Applying the boundary conditions to (A6),

$$\left.\begin{matrix} C(t, 0) = 0 \\ C(t, L) = 0 \end{matrix}\right\} t > 0$$

Hence

$$0 = A + B - \frac{\gamma}{p}\left[\frac{1}{\alpha^2 - \xi^2}\right] \tag{A7}$$

$$0 = Ae^{\xi L} + Be^{-\xi L} - \frac{\gamma}{p}\left[\frac{e^{-\alpha L}}{\alpha^2 - \xi^2}\right] \tag{A8}$$

Solving (A7) and (A8) for A and B, we get

$$A = \frac{\gamma}{p}\left[\frac{e^{-\alpha L} - e^{-\xi L}}{(\alpha^2 - \xi^2)(e^{\xi L} - e^{-\xi L})}\right]$$

$$B = \frac{\gamma}{p}\left[\frac{e^{-\alpha L} - e^{\xi L}}{(\alpha^2 - \xi^2)(e^{-\xi L} - e^{\xi L})}\right]$$

Thus the particular solution for $\overline{C}$ may be written as:

$$\overline{C} = \frac{\gamma}{p}\frac{1}{(\alpha^2 - \xi^2)}\left[\frac{(e^{-\alpha L} - e^{-\xi L})e^{\xi x}}{(e^{\xi L} - e^{-\xi L})} - \frac{(e^{-\alpha L} - e^{\xi L})e^{-\xi x}}{(e^{\xi L} - e^{-\xi L})}\right] + \frac{\gamma}{p}\left[\frac{e^{-\alpha x}}{\xi^2 - \alpha^2}\right]. \tag{A9}$$

$$\overline{C} = T_1 + T_2$$

where T_1 is used to notify the first term and T_2 the second term of (A9).

T_2 may be partial fractioned as shown:

$$T_2 = \frac{\gamma D}{\alpha^2 D - k}\left[\frac{1}{p + (k - \alpha^2 D)} - \frac{1}{p}\right]e^{-\alpha x}$$

From the standard table of Laplace transforms, the inverse of T_2 may be found (say C_2):

$$C_2 = \frac{\gamma D}{\alpha^2 D - k}[(e^{(\alpha^2 D - k)t} - 1)e^{-\alpha x}] \tag{A10}$$

The inverse of T_1 cannot be found in the standard tables so we have followed a standard procedure of the Inversion Theorem for the Laplace transformation as outlined by Carslaw and Jaeger[29] in which use is made of the Cauchy's theorem of residues[29,30]. The result of the inverse transformation of T_1 is C_1 (not shown separately, but shown in the final solution). Thus the final solution for C is $C = C_1 + C_2$; after the substitution of $\gamma D = \beta = \Phi I_0$ followed by rearrangement, we have Eqn (11).