

PHOTODEGRADATION AND HIGH TEMPERATURE DEGRADATION OF POLYMERS

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INTRODUCTION

Photodegradation and high temperature degradation of polymers have become of increasing interest in recent years. Whereas degradation of polymers by high energy radiation has been studied extensively, photodegradation has been neglected. However, these two types of degradation show great similarities as far as secondary reactions are concerned. The primary step in the photodegradation is more specific than that in high energy radiation because of the magnitudes of energy involved. The penetrating power of high energy radiation is appreciably greater than that of ultra-violet light, which can, therefore, usually produce significant changes only in the surface layers of polymers, or in thin polymer films.

The mechanism of photodegradation can be studied in solution or with the bulk polymers in the form of films. Chain scission, crosslinking and the production of monomer and other small molecular weight compounds can take place. The chain scission reaction is usually of the random type and can be followed by molecular weight measurements. Crosslinking is indicated by the polymer becoming progressively insoluble. Smaller products are usually analysed in a mass spectrometer or in a chromatograph. A survey of the published work is given in this paper, which also considers, briefly, degradation caused by photosensitization.

The field of high temperature degradation (above 500°) of polymers is in its infancy as far as the published literature reveals. Great efforts are being made to find new heat-stable polymers in the semi-inorganic and inorganic fields. In the present paper the results of high temperature degradation are reviewed. These are mainly of an analytical nature but they give some indication of the processes involved. Rate measurements above 500° have so far not been published, but it is expected that publications including rate measurements will be forthcoming in the near future. The experimental difficulties due to the great rate of the reactions at these elevated temperatures are quite considerable.

The analytical techniques used are mainly mass spectrometry and chromatography. Differential thermal analysis will also become more prominent in this field.

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Some theoretical considerations

Two reactions may take place when polymers are exposed to ultra-violet light: chain scission and crosslinking. These processes are of major

importance, since they affect profoundly the molecular weight and physical properties of polymers. Besides these two reactions, other reactions also take place which may lead to transformation of the polymer side groups, the formation of new groups and evolution of low molecular weight compounds.

It is advantageous to separate experimentally these two major reactions, chain scission and crosslinking, in polymers where they tend to occur simultaneously. This can be done by irradiating dilute polymer solutions and irradiating polymer films at low temperatures when the mobility of polymer radicals becomes very small. The crosslinking reaction will be suppressed under such conditions.

Chain scission may be considered first. One can distinguish a number of reactions, which are also prominent in thermal reactions:

- (i) random chain scission;
- (ii) random chain scission accompanied by formation of monomer at the newly formed chain ends;
- (iii) reverse polymerization which consists of chain end initiation, depropagation (unzipping producing monomer), and termination.

These reactions have been discussed in some detail elsewhere¹.

The random chain scission reaction is always characterized by a sharp decrease in polymer chain length with the formation of negligible amounts of monomer or very short chains. It can be represented, whatever the cause of degradation, by,

$$\frac{1}{P_t} - \frac{1}{P_0} = k t \quad (1)$$

where P_0 is the number average chain length at the beginning of the reaction and P_t the number average chain length at time t of the degradation process; k is a rate constant.

We may now consider a random chain scission taking place in a dilute polymer solution contained in a cylindrical reaction vessel with plane parallel windows, which is irradiated with a monochromatic parallel beam of ultra-violet light of sufficient frequency to bring about chain scission. The rate of breaking main chain links is then given by,

$$-\frac{dn}{dt} = \phi_s I'_{\text{abs}} \quad (2)$$

where n is the concentration of main chain links (number of main chain links/cm³) present at time t , I'_{abs} the average number of quanta absorbed by each cm³ of the solution per second and ϕ_s the quantum yield with respect to chain scission (this is the number of main chain links broken for each quantum absorbed). Equation (2) can be integrated easily if ϕ_s and I'_{abs} are constant and leads to² (only a small percentage of links is assumed to be ruptured),

$$\frac{s}{P_0} = \frac{1}{P_t} - \frac{1}{P_0} = \frac{\phi_s I'_{\text{abs}} t}{n_0} \quad (3)$$

where n_0 is the initial concentration of main chain links in the polymer

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solution and s the average number of main chain links broken for each original chain (s/P_0 is also referred to as the degree of degradation). Thus ϕ_s can be evaluated if I'_{abs} , n_0 , P_t and P_0 are known.

Actually, equation (3) is valid for a reaction vessel of any shape. If the special case is considered where the reaction vessel is cylindrical and where the Beer-Lambert law is obeyed, one can write,

$$\frac{s}{P_0} = \frac{1}{P_t} - \frac{1}{P_0} = \frac{k_1(1 - e^{-k_2 n_0 l}) I_0 t}{n_0} \quad (4)$$

where k_1 is a rate constant, k_2 an optical constant, l the length of the reaction vessel and I_0 the incident light intensity (quanta $\text{cm}^{-2} \text{sec}^{-1}$).

If the light absorption is small, equation (4) can be written,

$$\frac{s}{P_0} = \frac{1}{P_t} - \frac{1}{P_0} = \phi_s \frac{2 \cdot 303 E}{n_0 l} I_0 t \quad (5)$$

where $E = \log \frac{I_0}{I_t}$. I_t is the transmitted light intensity and E is the optical

density. The quantum yield is also given by $\phi_s = k_1 l$. Equation (5) shows that a straight line should be obtained by plotting s/P_0 against t , independent of initial polymer concentration (as long as s is small) and initial chain length P_0 , provided I_0 and E are constant. E is directly proportional to n_0 . The degree of degradation and experimental rate constant $k_{\text{exp}} = \phi_s \frac{2 \cdot 303 E I_0}{n_0 l}$ should be proportional to the first power of the light intensity. If appreciable "repolymerization" (combination of polymer radicals) were to take place, this would no longer be the case.

The treatment of photodegradation of polymer films is somewhat more complicated than degradation in solution. A polymer film may be considered exposed to a parallel beam of monochromatic ultra-violet light incident at a right angle to the film. The absorption of light may be subject to the Beer-Lambert law. Random chain scission only may be considered at this juncture. The average number of links broken in each original polymer chain in the film will be a function of the distance of this chain from the exposed film surface. As far as the over-all number average chain length or molecular weight are concerned, it does not matter how the total number of chain scissions in the film is distributed throughout the film; however, the over-all viscosity or weight average chain lengths and molecular size distribution will be a function of the average viscosity and weight average chain lengths and size distribution in each layer of the film.

This problem has been treated for a film consisting of polymer chains of one size only (homogeneous polymer)³ and for films having initially a random distribution in each layer of the film⁴. For a random chain scission reaction of such a film the ratio of weight to number average chain length remains constant for a large extent of degradation ($P_w/P_n = 2$). An initially homogeneous polymer sample acquires a random distribution when $s > 6$.

A homogeneous polymer sample as treated by the author³ may be considered first. The over-all average number of scissions \bar{s} for each original

chain in a film of thickness x_1 (this is the total number of main chain scissions in the film divided by the total number of original chains) is given by,

$$\bar{\alpha} = \frac{\bar{s}}{P_0} = \frac{1}{P_t} - \frac{1}{P_0} = \frac{ktI_0}{m_1x_1} (1 - e^{-ax_1}) \quad (6)$$

where $\bar{\alpha}$ is the overall degree of degradation, I_0 the incident light intensity, k a rate constant, a an optical constant, m_1 the number of monomer units for each cm^3 of the film, x_1 the thickness of the film, t the time of irradiation, P_0 the original number average chain length and P_t the number average chain length for the whole film at time t of the irradiation process.

For small light absorption equation (6) becomes,

$$\frac{\bar{s}}{P_0} = \frac{1}{P_t} - \frac{1}{P_0} = \frac{ktI_0a}{m_1} \quad (6a)$$

The degree of degradation α_x at the distance x from the exposed film surface is,

$$\alpha_x = \frac{s_x}{P_0} = \alpha_0 e^{-ax} \quad (7)$$

where α_0 is the degree of degradation at the exposed film surface and is given by,

$$\alpha_0 = \frac{ktI_0a}{m_1} \quad (7a)$$

The number average size distributions for degraded films were calculated as a function of exposure conditions; from this information all average chain length can in principle be computed numerically. This size distribution is given by,

$$n_{P,t} = -\frac{1}{ax_1P_0} \left\{ (P_0 - P) \left[\frac{(1 - \alpha_{x_1})^{P+1}}{P+1} - \frac{(1 - \alpha_0)^{P+1}}{P+1} - \frac{(1 - \alpha_{x_1})^P}{P} + \frac{(1 - \alpha_0)^P}{P} \right] - \frac{2}{P} \left[(1 - \alpha_{x_1})^P - (1 - \alpha_0)^P \right] \right\} \quad (8)$$

For the original chains left undegraded, the number is

$$n_{P_0,t} = -\frac{1}{ax_1P_0} \int_{\alpha_0}^{\alpha_{x_1}} \frac{e^{-\alpha x P_0}}{\alpha x} d\alpha x \quad (8a)$$

$n_{P,t}$ and $n_{P_0,t}$ refer respectively to the number of chains of length P and P_0 at time t of the irradiation process in one base mole of polymer. α_0 and α_{x_1} are the degrees of degradation at the incident surface and opposite surface respectively. The expression for the weight average chain length P_w was given in explicit form,

$$P_{w,t} = \frac{1}{ax_1P_0} \left\{ \frac{1}{\alpha_{x_1}^2} [\alpha_{x_1}(P_0 - 1) + 2][1 - (1 - \alpha_{x_1})^{P_0}(\alpha_{x_1}P_0 + 1)] - \frac{1}{\alpha_0^2} [\alpha_0(P_0 - 1) + 2][1 - (1 - \alpha_0)^{P_0}(\alpha_0P_0 + 1)] \right\} + n_{P_0,t}P_0^2 \quad (9)$$

If the optical density of the film, the incident light intensity I_0 , the film thickness x_1 , P_0 and P_w are known, α_0 and with it α_{x_1} , can be evaluated from equation (9). If α_0 is known, \bar{s} , $\bar{\alpha}$ and P_t can be calculated and with it the quantum yield ϕ_s , which is given by,

$$\phi_s = \frac{m_t x_1 \bar{\alpha}}{I_0(1 - e^{-\alpha_{x_1}})t} = k \quad (10)$$

As already pointed out above, calculations for films which have an initial random distribution ($P_w:P_n = 2$) were carried out by Flynn⁵ and Shultz⁴, who also included crosslinking. The assumption of an initial random distribution simplifies the calculations very considerably.

The number average molecular weight for simultaneous random chain scission and crosslinking is, according to Shultz⁴,

$$\bar{M}_n = \bar{M}_{n_0} \left[\ln\left(\frac{R_0}{R_L}\right) \right] / \left[\ln\left(\frac{R_0}{R_L} - \frac{(2\phi_a - \phi_c)}{(2\phi_a - 4\phi_c)} \left(\frac{R_0}{R^x} - \frac{R_L}{R^x}\right)\right) \right] \quad (11)$$

If $\phi_a \geq 2\phi_c$, equation (11) is valid for all R_0 values; if $\phi_a < 2\phi_c$, equation (11) is valid for $R_0 \leq R^x$.

In equation (11) \bar{M}_n is the number average molecular weight, M_{n_0} the initial number average molecular weight, R_0 and R_L the amounts of energy absorbed in photons g^{-1} at the incident surface and opposite surface respectively, and L the film thickness. The Beer-Lambert law was assumed to hold; ϕ_a is the number of chain scissions for each absorbed photon (quantum yield for chain scission) and ϕ_c is the number of crosslinks for each photon absorbed (quantum yield for crosslinking). R^x is the radiation dose producing incipient gel formation in the polymer.

The weight average molecular weight \bar{M}_w is given by,

$$\bar{M}_w = M_{w_0} \left[1 + (kL)^{-1} \ln\left(\frac{A + (\phi_a - 1/4\phi_c)\bar{M}_{w_0}R_0e^{-kL}}{A + (\phi_a - 1/4\phi_c)\bar{M}_{w_0}R_0}\right) \right] \quad (12)$$

where k is an optical absorption coefficient and A is Avagadro's number.

In addition, Shultz⁴ evaluated the viscosity average molecular weight at different stages of the irradiation process, and gave expressions for the gel content, point of gelation and gel destruction by chain scissions.

The kinetics of various photodegradation mechanisms was elaborated by the author in his monograph¹.

Mechanisms pertaining to various polymers will be discussed in this paper when the particular polymer is being considered.

Photodegradation in solution

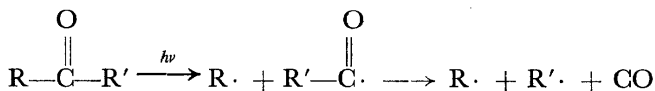
Investigation of photolysis in solutions has the advantage of an additional parameter, the polymer concentration. Thus it is to be expected that at low polymer concentrations the probability of crosslinking will be diminished and may become negligible; and so the chain scission reaction can be studied without any complicating effects.

Studies of degradation in solution were carried out by Guillet and Norrish⁶ on poly(methylvinylketone) in dioxan solutions using light of wavelength $\lambda = 3130 \text{ \AA}$.

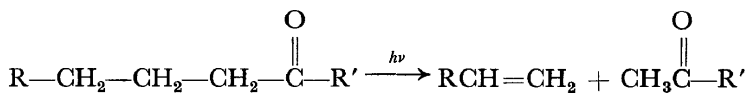
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It is known from experiments with ketones of small molecular weight that the primary reaction is due to absorption of light by the C=O group. Two types of reactions can be distinguished.

Type I:

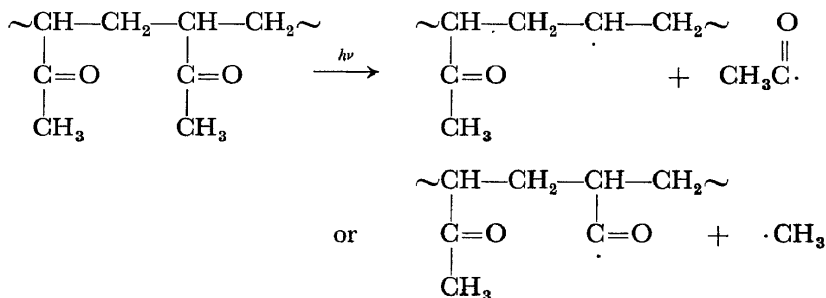


Type II consists of a scission of the C—C bond in $\alpha - \beta$ position to the carbonyl group. Radicals are not formed in this process:

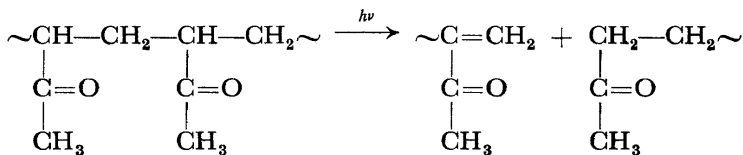


The equivalent reactions in poly(methylvinylketone) would be as follows:

Type I



Type II reaction leads to chain scission:



The effect of the type II reaction would be a decrease of chain length with irradiation time according to a random scission process. Actually

$\frac{[\eta]_0}{[\eta]_t} - 1$, which was shown by the authors to behave similar as

$\frac{P_0}{P_t} - 1$, is a linear function of the irradiation time during the initial stages

of the reaction; however, the reaction slows down rapidly in its later stages, indicating a process which opposes the chain scission reaction. These

reactions are not very temperature dependent in the range of temperatures from 80° to 250°. ϕ_{II} , the quantum yield for chain scission, can be estimated to be approximately 0.025. At the same time as the molecular

weight decreases, the optical density in the region from 2200 to 2300 Å

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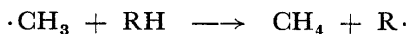
increases directly proportional to the light absorbed. This is in accordance with the assumption that double bonds are formed which are conjugate to the carbonyl groups. Gaseous products formed during the irradiation process are carbon monoxide, methane, and acetaldehyde. The quantum yields for these products are approximately; ϕ_{CO} from 0.0015–0.0103, ϕ_{CH_4} from 0.0006–0.0081 and $\phi_{\text{CH}_3\text{CHO}}$ from 0.038–0.012 over a range of temperatures from 25 to 80°.

The initial rate of decrease in chain length is directly proportional to the light intensity and polymer chain length, and independent of polymer concentration and type of solvent (dioxan or ethyl acetate).

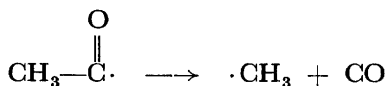
Acetaldehyde and methane could be formed by reactions of radicals formed during exposure,



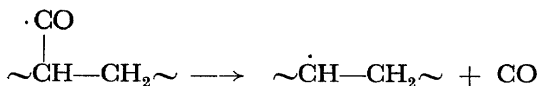
and



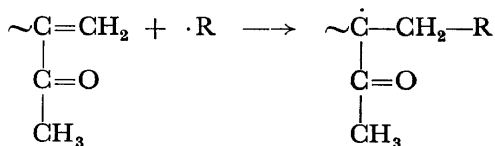
RH represents either solvent or polymer molecules. Carbon monoxide can be produced by,



or



The slowing down of the degradation process may be due to a "repolymerization" process,



R· could be a polymer radical or any other radical.

The authors have also given a kinetic scheme to account for the experimental results (compare Watson⁷). The over-all process is given by the following relationship,

$$D = \beta + \alpha - \gamma \quad (13)$$

where $D = \frac{c}{P_t}$, c is the polymer concentration in base mole/l. and P_t the

number average chain length at time t of the irradiation process. $\beta = \frac{c}{P_0}$

where P_0 is the initial number average chain length. α is the total number of polymer-polymer bonds broken per litre and γ the total number of polymer-polymer bonds reformed per litre at time t .

If the type II reaction is the only one responsible for the chain scission reaction, one has,

$$\frac{d\alpha}{dt} = \phi_{II} I_{\text{abs}} \quad (14)$$

where ϕ_{II} is the primary quantum yield for the type II reaction (chain scission) and I_{abs} the light absorbed in einsteins per litre per second. The opposing reaction or "repolymerization" reaction is due to the addition of polymer radicals to double bonds formed in the type II reaction; this gives,

$$\frac{dy}{dt} = pk_1 z [R] \quad (15)$$

where z is the concentration of double bonds, k_1 a rate constant, $[R]$ the concentration of radicals of all types and p the fraction of polymer radicals.

The steady state method is assumed to be applicable; this gives an expression for $[R]$,

$$k_2 [R]^2 = \phi_I I_{\text{abs}}$$

or

$$[R] = \left(\frac{\phi_I I_{\text{abs}}}{k_2} \right)^{1/2} \quad (16)$$

where ϕ_I is the quantum yield for the production of free radicals of all types. If it is assumed that the only double bonds which are effective are those produced in the type II reaction, one has,

$$\frac{dz}{dt} = \phi_{II} I_{\text{abs}} - k_1 \left(\frac{\phi_I I_{\text{abs}}}{k_2} \right)^{1/2} z = \phi_{II} I_{\text{abs}} - k' z \quad (17)$$

Equation (17) can be integrated,

$$z = \frac{\phi_{II} I_{\text{abs}}}{k'} (1 - e^{-k't}) \quad (18)$$

which results in,

$$\frac{dy}{dt} = p \phi_{II} I_{\text{abs}} (1 - e^{-k't}) \quad (19)$$

Since

$$\frac{dD}{dt} = \frac{d\alpha}{dt} - \frac{dy}{dt}$$

one obtains finally,

$$D = \beta + \phi_{II} I_{\text{abs}} (1 - p)t + p \frac{\phi_{II} I_{\text{abs}}}{k'} (1 - e^{-k't}) \quad (20)$$

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Experimental data can be satisfactorily fitted to equation (20). ϕ_{II} is obtained from the initial slope of experimental curves representing the degradation reaction; k' was found to be 10^{-3} and $p = 0.97$.

The kinetics and proposed reaction mechanisms are in agreement with the experimental facts—a random chain scission reaction opposed by “repolymerization”. The gaseous reaction products are accounted for by the proposed reaction mechanisms. Crosslinking apparently does not take place.

Preliminary experiments were also carried out by Guillet and Norrish⁸ on the preparation of graft polymers. As already pointed out, poly(methylvinylketone) irradiated with light of wavelength $\lambda = 3130\text{\AA}$ will photolyse according to the type I reaction, which consists in the formation of free radical sites along the polymer chains producing methyl and acetyl free radicals. If this irradiation is carried out in the presence of vinyl monomers, formation of branches starting at the radical sites is to be expected. Photopolymerization of the monomer itself is negligible under the experimental conditions used. Experiments were carried out with the polymer dissolved in acrylonitrile. After purification, the graft polymer contained 75 per cent acrylonitrile. Graft polymers were also obtained in the presence of methyl methacrylate and vinyl acetate.

The author and co-workers^{9, 10} studied the photodegradation of polyacrylonitrile in vacuum in ethyl carbonate-propylene carbonate solutions (80:20 by weight) at 25° , using light of wavelength $\lambda = 2537\text{ \AA}$. A rapid decrease of chain length with time took place, accompanied by appreciable changes in the ultra-violet absorption spectrum of polyacrylonitrile. The degradation could be represented by plotting $1/P_t$ against exposure time, giving approximately straight lines as expected from the relationship

$$\frac{1}{P_t} - \frac{1}{P_0} = kt$$

The degradation was shown to be independent of polymer concentration (0.1 per cent w/v to 0.4 per cent w/v) but the rate was dependent on the history of the sample. However, representing the experimental data by plotting $\frac{1}{[\eta]_t}$ against exposure time, straight lines were obtained whose slopes were independent of concentration, initial chain length and history of the polymer sample. The experimental rate constants increased linearly with the light intensity and the quantum yield was very small, about 10^{-4} main chain C—C bonds broken for each quantum absorbed. All the data is in agreement with the random theory of breaking links. The quantum yield was calculated from the relationship,

$$\frac{s}{P_0} = \frac{1}{P_t} - \frac{1}{P_0} = \phi_s \frac{2.303E}{n_0 I} I_0 t$$

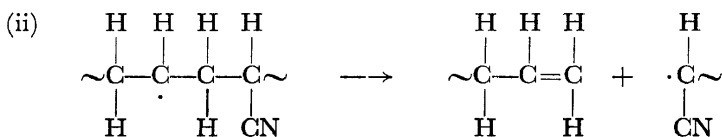
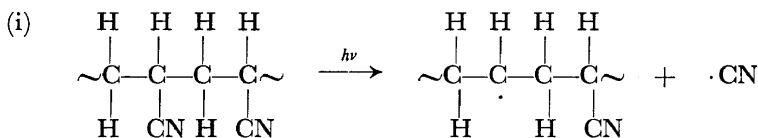
previously given (equation (5), p. 421). The light intensity was determined with uranyl oxalate as actinometer.

In addition to the chain scission reaction, reactions involving the nitrile group also took place, which led to modifications of these groups. This was

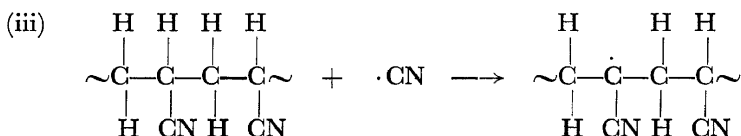
reflected in the ultra-violet spectra of polyacrylonitrile at various stages of the photolysis. Glutaronitrile, which was used as a model substance, showed similar changes in its spectrum on irradiation. Infra-red spectra did not show any changes under the conditions of the experiments. Polyacrylonitrile was also exposed in the form of films. In this instance, cross-linking took place. Low molecular weight compounds such as acrylonitrile and hydrogen cyanide are produced under certain conditions during the photolysis.

Tentative suggestions as to the reactions involved were elaborated by the authors.

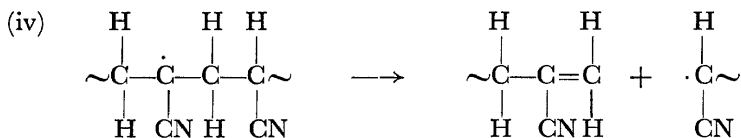
Chain scission may be caused by the following reactions:



The $\cdot\text{CN}$ radical can react with an α -hydrogen atom,

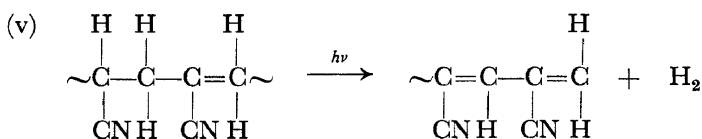


This may lead to another chain scission,

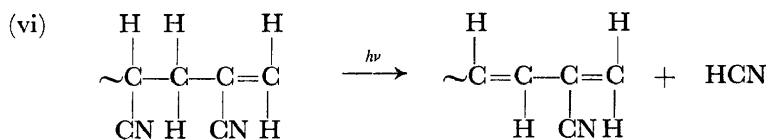


Such an isolated terminal double bond may increase the absorption at 2160 Å, which was found to be the case.

Small molecules may be produced by the following reactions,



and



Conjugated systems such as these may give rise to the absorption at 2950 Å, which develops markedly on exposure of the polymer solutions.

Preliminary experiments have been performed¹¹ on the photolysis of nylon 66 in formic acid (1 per cent w/v nylon in 98-100 per cent formic acid). The exposures were carried out in vacuum and with light from a high pressure mercury arc and it was found that degradation was more pronounced in air than under nitrogen in vacuum. Apparently a random chain scission reaction takes place. A slight decrease in absorption at 2900 Å occurs on exposure in air.

Some experiments on the photodegradation of polystyrene in benzene solutions exposed to light of wavelength $\lambda = 2537 \text{ \AA}$ were carried out by Shih-Wei Chen¹². This work has been discussed in the author's monograph¹. Apparently a random chain scission process with a small quantum yield (1.7×10^{-5}) takes place.

Voelker¹³ investigated the influence of daylight on poly(methacrylic acid) and poly(acrylic acid). A copolymer of 65 parts of methacrylic acid with 35 parts of methylmethacrylic ester, which is water soluble, was dissolved as the sodium salt and the pH adjusted to 6.2. One per cent solutions were exposed in glass bottles to daylight and the intrinsic viscosity measured every 24 hours. Chain scission took place, which seemed to be due to a random process and oxygen had no influence. Poly(acrylic acid) is also degraded under these conditions, but the process is sensitive to oxygen. Different metal salts of poly(methacrylic acid) degrade at different rates. This may have something to do with the configuration (coiling up) of the polymer molecules in solution. With shorter wavelengths degradation takes place over a wide range of pH values, even if the molecules can be assumed to be completely stretched out in solution.

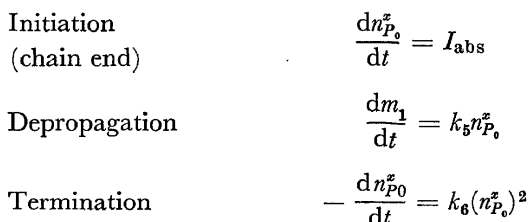
Photodegradation of polymers in bulk (polymer films)

The only case so far encountered which shows, on irradiation, a reverse polymerization process, *i.e.*, initiation at the chain ends with subsequent unzipping, is that of poly(methyl methacrylate) studied by Cowley and Melville¹⁴. However, there are indications that this is due to the high temperatures employed in the investigation. It seems that for exposure at low temperatures, a random chain scission reaction takes place, as has been the case for all other polymers so far investigated (unless crosslinking occurs). Poly(methyl methacrylate) has already been discussed in two monographs¹ and will be treated briefly here.

The authors studied the formation of monomer during the irradiation of thin layers of polymer in vacuum by means of a molecular still, the monomer concentration being determined with a Pirani gauge. The degradation

took place at 160° and higher temperatures, the polymer being in a highly viscous state. This high viscosity of the medium obscures to some extent the kinetics, especially the termination reaction which seems to be diffusion-controlled. The wavelength used was $\lambda = 2537 \text{ \AA}$. The main process consists of photo-initiation at the chain ends, which seem to be in a fairly high state of activation due to the high temperatures employed. This initiation reaction depends on the nature of the chain ends; those containing double bonds are more susceptible to initiation than other end groups. The quantum yield is larger than 200 monomer units formed for each quantum absorbed, which is a measure of the kinetic chain length of the depropagation reaction. From other data, this kinetic chain length can be estimated to be of the order of 10^3 to 2×10^3 monomer units/quantum. The rate of monomer formation during the initial stages of the photolysis is proportional to $I_{\text{abs}}^{1/2}$ for high molecular weight material. Rate constants for depropagation and termination were obtained by the rotating sector method. The rate constants for the depropagation reaction can be expressed by $k_5 = 8.9 \times 10^{11} e^{-18500/RT} \text{ sec}^{-1}$ and the rate constants for termination, which is a second-order reaction, at 167° is given by $k_6 = 4 \times 10^4 \text{ l.mole}^{-1} \text{ sec}^{-1}$. The energy of activation for the termination reaction (170 to 200°) is 21 kcal, indicating that it is diffusion-controlled. The mean lifetime of the depropagating chains at 167° for an initial rate of monomer formation of 3.66×10^{-3} moles of monomer/l. of polymer/sec is 4 seconds.

The initial stages of the photodegradation¹ can be represented by the following kinetic scheme,



The stationary state concentration of active chain ends is given by,

$$n_{P_0}^* = \frac{I_{\text{abs}}^{1/2}}{k_6^{1/2}}$$

or

$$\frac{dm_1}{dt} = \frac{k_5}{k_6^{1/2}} I_{\text{abs}}^{1/2}$$

where m_1 is the amount of monomer produced at time t , $n_{P_0}^*$ is the number of activated chain ends in the system, k_5 and k_6 are rate constants for depropagation and termination respectively.

Frolova and Riabov^{14a} exposed poly(methyl methacrylate) powder and films to ultra-violet light in a high vacuum. Gaseous products were evolved. The quantum yield for a wavelength range from 3030 to 3130 Å was 2.3×10^{-4} molecules of gas evolved for each quantum absorbed. No molecular weight measurements are reported.

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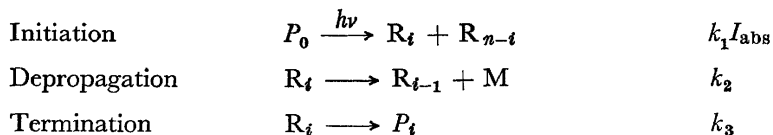
Stokes and Fox¹⁵ studied the photodegradation of poly(α -methylstyrene). This polymer presents a case of a random chain scission reaction with some unzipping at the newly formed chain ends producing monomer. Thin films (4.9 to 19 μ) were exposed to irradiation of the Hg lines 2804, 2753, 2654 and 2537 Å; longer wavelengths than these are not absorbed and consequently do not take part in the photolysis. Degradations in vacuum were studied at $27 \pm 2^\circ$ and $115 \pm 5^\circ$. The dark reaction at 115° was negligible for the times of irradiation employed. Up to a film thickness of 14 μ , the initial rate of monomer formation was found to be linearly dependent on the film thickness. Volatiles were analysed in a mass spectrometer, monomer in the films was determined optically and the decrease in chain length was followed by intrinsic viscosity measurements. An appreciable decrease in chain length took place on irradiation, which was accompanied by monomer formation. This monomer remained in the film whereas volatiles were trapped by liquid nitrogen. The following volatile products were found and determined quantitatively. Their quantum yields for experiments at 115° are given in parentheses: hydrogen (0.017), carbon dioxide (0.016), carbon monoxide (0.0068), acetylene (0.0028), ethylene (0.0024), isobutene (0.0020), methane (0.0012), ethane (0.0012), propene (0.0008), butanes (0.0008), branched pentanes (0.0004), benzene and toluene.

The quantum yields for monomer were 0.5 at 115° and 7×10^{-3} at 27° , and those for main chain scission were 1×10^{-3} at 27° and 2×10^{-2} at 115° .

The amount of monomer formed (g monomer/g polymer) is a linear function of the number of quanta absorbed at either temperature. The intensity exponent for monomer formation is one at both temperatures.

The function $\frac{P_{v_0}}{P_{v_t}} - 1$ plotted against the quanta absorbed for each gramme of polymer also shows a linear relationship; P_{v_0} and P_{v_t} are the viscosity average chain length at time $t = 0$ and t respectively. The relative viscosity average chain length $\frac{P_{v_t}}{P_{v_0}}$ decreases linearly with the amounts of monomer evolved. Results are given up to about 0.01 g monomer/g polymer; the relative viscosity average chain length decreased to about 0.6. A yellow colour developed during extended periods of exposure.

The degradation data can be interpreted by assuming a random chain scission process with production of monomer at the newly formed chain ends. The kinetics for such a process was given by the author¹,



where P_0 is an original polymer molecule, R stands for radicals and P_t for dead polymer molecules, I_{abs} is the rate of light absorption, k_1 , k_2 and k_3 are rate constants.

The rate of breaking main chain links is given by,

$$-\frac{dn}{dt} = k_1 I_{\text{abs}} \quad (21)$$

k_2 and k_3 are assumed to be independent of the radical size; under steady state conditions, one has,

$$\frac{dR}{dt} = 2k_1 I_{\text{abs}} - k_3 R = 0 \quad (22)$$

R is the total amount of radicals in the system. The rate of formation of monomer is then,

$$\frac{dm_1}{dt} = k_2 R = \frac{2k_2 k_1 I_{\text{abs}}}{k_3} \quad (23)$$

Equation (23) gives on integration,

$$m_1 = \frac{2k_2 k_1 I_{\text{abs}} t}{k_3} = \epsilon k I_{\text{abs}} t \quad (24)$$

where ϵ is the kinetic chain length for monomer formation or the average number of monomer molecules formed for each broken bond. Equation (24) can also be written in the form,

$$m_1 = \phi_{m_1} I_{\text{abs}} t \quad \text{molecules of monomer} \quad (25)$$

where ϕ_{m_1} is the monomer quantum yield and I_{abs} represents the quanta absorbed per second. The amount of monomer produced can also be given in g monomer/g polymer,

$$m_1 = \frac{\phi_{m_1} I_{\text{abs}} t M_1}{gA} \quad (26)$$

where A is Avagadro's number, g the sample weight in grams and M_1 the molecular weight of the monomer.

Equation (26) is well obeyed in the present case.

Integration of equation (21) and introducing $s = \frac{P_0}{P_t} - 1$ where s is the average number of main scissions for each original chain, gives,

$$n_0 - n_t = k I_{\text{abs}} t$$

$$\mathcal{N}s = \frac{n_0 s}{P_0} = \frac{n_0}{P_0} \left(\frac{P_0}{P_t} - 1 \right) = k_1 I_{\text{abs}} t = \phi_s I_{\text{abs}} t$$

or

$$\frac{1}{P_t} - \frac{1}{P_0} = \frac{\phi_s I_{\text{abs}} t}{n_0} \quad (27)$$

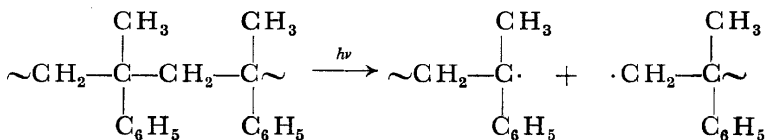
where \mathcal{N} is the number of original chains in the system, n_0 the total number of main chain links at $t = 0$ and ϕ_s the quantum yield for main chain scission. Approximate values for ϕ_s were given above (see also *Table I*,

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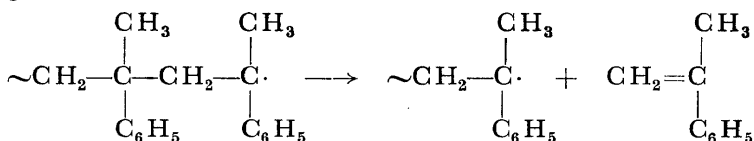
p. 446). Equation (27) is also satisfactorily obeyed by poly(α -methylstyrene). The number of monomers produced for each main chain scission can be obtained from $\frac{\phi_{m_1}}{\phi_s}$ and amounts to about 7 at 27° and 25 at 115°.

The reaction scheme proposed by the authors is as follows:

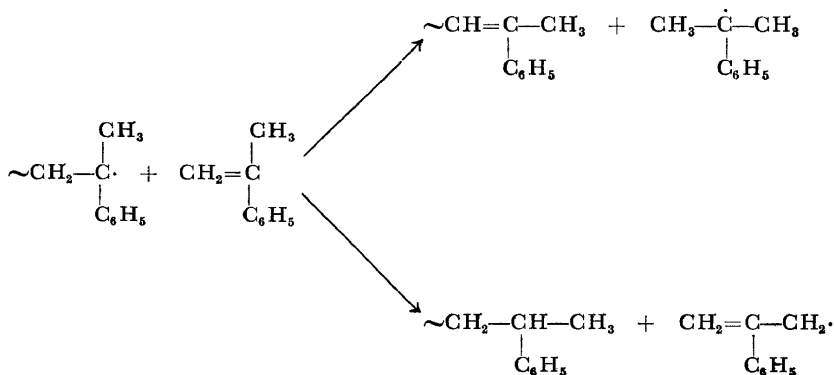
Initiation



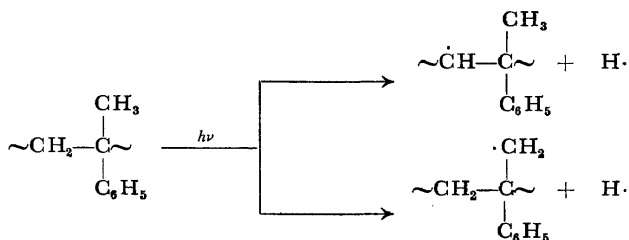
Depropagation



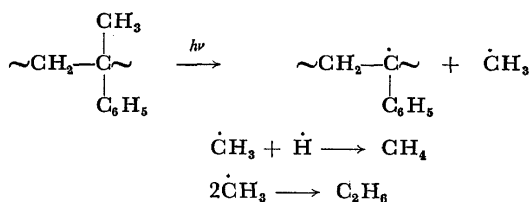
As the intensity exponent is one, the termination reaction should be of the first-order with respect to polymer radicals. Transfer to monomer molecules is a possible termination step,



The production of volatiles may be analogous to the reactions encountered during the photolysis of t-butylbenzene, which can be considered as a model substance of poly(α -methylstyrene)¹⁶ and may be represented by,



and



The other volatiles mentioned above do not occur in the photolysis of *t*-butylbenzene. The evolution of carbon monoxide and carbon dioxide may be due to oxygen atoms incorporated in the polymer molecules.

Kotliar¹⁷ studied the degradation of poly(α -methylstyrene) by ionizing radiation in vacuum at room temperature. He explained his experimental results by random chain scission with unzipping from the newly formed chain ends. A comparison of the photolysis and high energy degradation is given below (the quantum yield values were converted to *G* values),

	Chain scission (per 100 eV)	Monomer molecules (per 100 eV)	Zip length
Radiolysis (25°C)	0.25	25	100
Photolysis (27°C)	0.02	0.14	7

The photolyses of poly(methylvinylketone) and poly(methylisopropenylketone) in the form of films were investigated by Wissbrun¹⁸. Films of thickness 15.9 and 47.3 μ in the case of poly(methylvinylketone) and about 14.5 μ in the case of poly(methylisopropenylketone) were exposed to light of wavelength $\lambda = 3130 \text{ \AA}$ in vacuum.

Temperatures for the degradation of poly(methylvinylketone) were 28° and 80° respectively. The ratio $\frac{[\eta]_0}{[\eta]_t}$ as a function of the amount of radiation absorbed was found to be linear in the early stages of the process, but the reaction slowed down considerably during its later stages. This behaviour is similar to that observed by Guillet and Norrish⁶ for the photolysis of this polymer in dioxan solution. The linear portion of the reaction is independent of film thickness (16 and 47 μ) and temperature. In the non-linear region, the reaction is no longer independent of film thickness due to the non-uniform light intensity throughout the film.

The decrease in molecular weight is assumed to be solely due to the type II reaction discussed previously for the reaction in dioxan solution. The relationship,

$$\frac{P_0}{P_t} - 1 = \frac{M_0 \phi_s I_{\text{abs}} t}{g} \quad (28)$$

is obeyed, where M_0 is the initial number average molecular weight of the polymer, ϕ_s the quantum yield for main chain scission, I_{abs} the light absorbed

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in einsteins/sec, t the exposure time and g the sample weight. Equation (29) is equivalent to equation (27).

$$\frac{P_0}{P_t} - 1 = \frac{\phi_s I_{\text{abs}} t P_0}{n_0} = \frac{\phi_s I_{\text{abs}} t}{N} \quad (29)$$

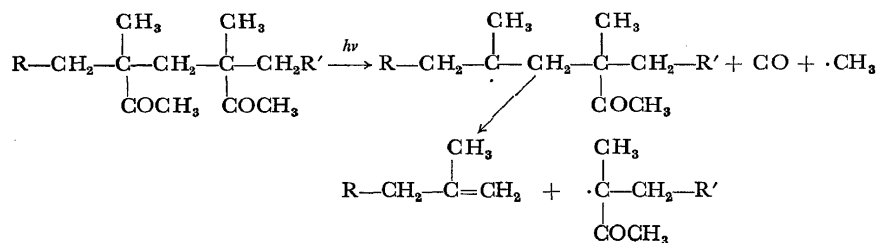
where I_{abs} is now the light absorbed in quanta/sec, n_0 the number of main chain links (or monomer units in the system) and N the number of original chains in the system. ϕ_s is approximately 0.02, which is very similar to the value 0.025 for the reaction in solution as found by Guillet and Norrish⁶.

The volatiles formed after irradiation for 16 hours at 80° were analysed in a mass spectrometer and were as follows (quantum yields are given in parentheses): acetaldehyde (0.06), carbon monoxide (0.003), methane (0.0006). The quantum yields for the degradation in dioxan solution were 0.01 for each of the compounds.

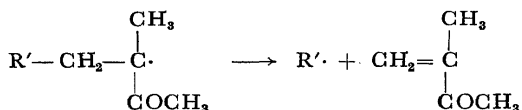
The reactions formulated by Wissbrun¹⁸ for the bulk degradation (films) are similar to those put forward for the degradation in dioxan solution. These were discussed above.

The photolysis of poly(methylisopropenylketone) is a random chain scission reaction with unzipping at the newly formed chain ends producing almost pure monomer. There is an induction period for monomer formation after which the rate becomes constant up to about 5 per cent conversion. Monomer continues to evolve after irradiation has ceased due to diffusion of monomer out of the film. The intensity exponent is 0.41 at 150° and 0.73 at 177° and the monomer quantum yield 0.46 at 150° and 4.8 at 177°. Percentage conversion was studied up to 20 per cent. Small amounts of methane and carbon monoxide are also produced.

The mechanism of degradation proposed by the author is as follows,



An unzipping reaction follows,



At low temperatures, the intensity exponent is 0.5, agreeing with a second-order termination reaction. The exponent increases with increasing temperature; this apparently is due to a change in the termination reaction from second to first order.

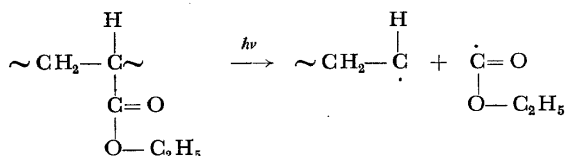
The photodegradation of poly(ethyl acrylate) in vacuum was investigated by Jacobs and Steele¹⁹. Polymer films approximately 10 mils thick were

irradiated with light of wavelength $\lambda = 2537 \text{ \AA}$. Swelling ratio, gel content and intrinsic viscosity (acetone soluble part) were determined. Apparently crosslinking takes place on irradiation, the exposed film being only partially soluble in good solvents after exposure. Solubility and swelling properties decrease with irradiation time. The intrinsic viscosity of the soluble part also decreases with exposure time indicating that, in addition to crosslinking, chain scission also takes place. The increase in crosslinkages for each original chain molecule was evaluated according to Charlesby's method²⁰. It was found that the extent of crosslinking changed very appreciably in the vicinity of the glass transition temperature. The extent of crosslinking is directly proportional to the amount of light absorbed by the system. The over-all amount of crosslinking diminishes appreciably with film thickness and increasing distance from the exposed polymer surface. This is to be expected according to the theories outlined in the theoretical section of this paper. The rate of crosslinking relative to the rate of chain scission is not affected by temperatures in the range from 30 to 50°.

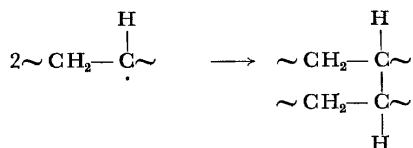
The films were also exposed at low temperatures (-196°). No crosslinking or gelation took place during those exposure times which bring about appreciable crosslinking at room temperature. Strong fluorescence was observed at the low temperatures after exposure. Apparently, radicals which lead to crosslinking are frozen in. A pronounced change in behaviour takes place near the glass temperature of the polymer (-17°). At -20° , for instance, no insoluble polymer is formed even after exposure for 7.5 hours; such exposure causes appreciable crosslinking at room temperature. The rate of chain scission depends only slightly on temperature, whereas crosslinking can be completely suppressed by decreasing the temperature.

Volatiles found by mass spectrometric analysis were: hydrogen, methane, carbon monoxide and carbon dioxide.

The mechanism proposed by the authors (taking into account that the bond strengths decrease in the following manner: $\text{C}=\text{O} > \text{C}-\text{H} > \text{C}-\text{O} > \text{C}-\text{C}$) consists of a primary process:



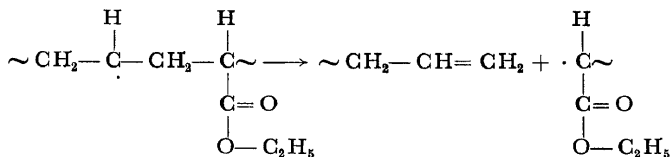
Carbon monoxide and carbon dioxide could be produced by reactions of the $\cdot\text{CO}_2\text{CH}_5$ radical. Crosslinking is brought about by,



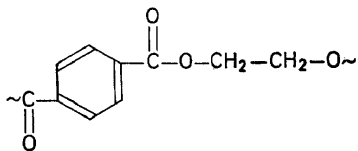
Below the glass temperature, the mobility of the polymer radicals becomes so small that crosslinking is negligible.

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The main chain scission reaction is assumed to be,



The photolysis of poly(ethylene terephthalate) was investigated by Osborn²¹. This polymer shows strong absorption in the near ultra-violet region, which is in accordance with its structure,



The relationship $\frac{1}{P_t} - \frac{1}{P_0} = kt$ is obeyed. The thickness of the exposed films was about 0.0025 cm and the light used ranged from 2800 to 4000 Å. The average rate of chain scission decreases with film thickness as expected from theoretical considerations. The intensity exponent was found to be one and the quantum yield for main chain scission was about $\phi_s = 5.0 \times 10^{-4}$. Presence of air and its relative humidity had little effect on the scission reaction and its quantum yield.

The random chain scission of poly(ethylene terephthalate) was also briefly investigated by Shultz and Leahy²². Films 0.00063 cm thick were arranged in a stack and irradiated. Beer-Lambert's law was assumed to be obeyed and an approximate evaluation of the wavelength causing scission was made by applying theories derived by Shultz⁴ already mentioned previously.

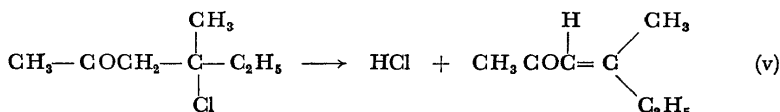
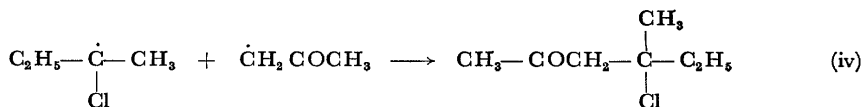
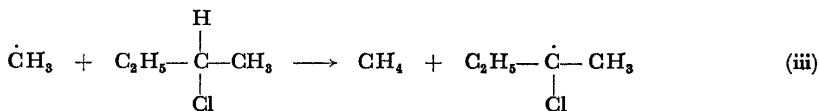
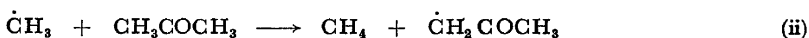
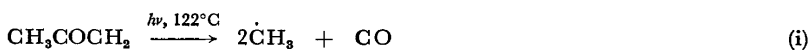
Polystyrene films were irradiated by Wall and Tyrone²³. They found that the light absorption in the 3400 Å region increased on exposure. This effect is believed due to decomposition of hydroperoxide groups.

The photodegradation of polyethylene was studied by Burgess²⁴. This paper has already been discussed in the author's monograph¹. The amounts of carbonyl, hydroxyl and vinyl groups increase on exposure to light in the region of 3130 Å. Oxygen uptake is linear with exposure time and approximately proportional to $I_{\text{abs}}^{1/2}$. The quantum yield for carbonyl formation is about 0.1.

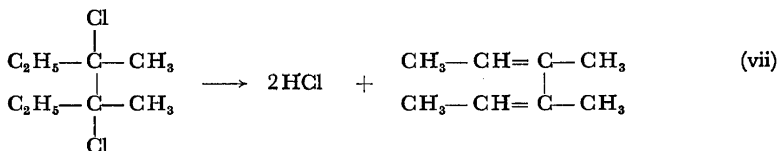
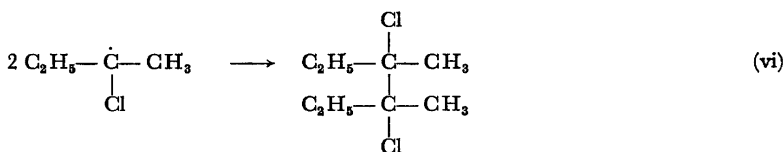
An interesting paper by Bateman²⁵ on the photolysis of rubber may be reviewed briefly here. Finely cut rubber was exposed to ultra-violet radiation. Immediate gas evolution took place which was linear with exposure time and had an intensity exponent of one and a quantum yield of 4×10^{-4} . Rates increased rapidly with decreasing wavelengths. An energy of activation of 1.5 kcal was found for the gas evolution reaction for a temperature range from 70 to 200°. The gaseous products consisted of 80 per cent hydrogen and 20 per cent simple hydrocarbons. Crosslinking took place during exposure. Between 150 to 200° isoprene was also evolved; this reaction has an energy of activation of 10 kcal.

Druessedow and Gibbs²⁶ studied the effect of ultra-violet light on poly(vinyl chloride). The photodegradation of this polymer is still very obscure. The exposure was carried out in the presence of oxygen. Hydrogen chloride evolution is small and oxygen is taken up by the polymer during exposure. The authors assume that free radicals are formed leading to formation of peroxide groups. These groups constitute weak spots for any subsequent thermal degradation.

Photodegradation of poly(vinyl chloride) powder was investigated by Kenyon²⁷. The powder was exposed to ultra-violet light under both nitrogen and oxygen. Hydrogen chloride evolution and oxygen uptake were measured. Hydrogen chloride is formed in the presence and absence of oxygen. The active wavelength was found to be in the neighbourhood of 3000 Å and shorter wavelengths. It is known that alkyl chlorides are very stable to light down to about 2300 Å. This indicates that the photolysis of poly(vinyl chloride) at longer wavelengths must be due to impurities or some double bonds in the polymer. During photodegradation in air, carbonyl groups are formed. It is believed that CO groups are initially present in the polymer, probably due to trace impurities which catalyse the photolysis in the absence of oxygen. This was shown to be likely by the addition of ketones to the polymer which increased the hydrogen chloride evolution appreciably. Also crosslinking was observed in the presence of nitrogen, whereas in the presence of oxygen, chain scission only was taking place. Discoloration which is less pronounced in the presence of oxygen than nitrogen, also occurs during exposure. More hydrogen chloride is evolved in the presence of oxygen than nitrogen. In addition some water is also formed. Butylchloride was studied as a model compound. No reaction takes place with the purified chloride when the light has a wavelength larger than 2700 Å; but, if an impurity is present in the form of a ketone, evolution of hydrogen chloride takes place. This reaction was studied in detail and a reaction scheme was proposed by the authors as follows:



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Reactions (v), (vi) and (vii) are thermal reactions. Similar reactions are believed to take place in the case of poly(vinyl chloride).

Boyer²⁸ has expressed doubts that the model compound gives a correct picture of the degradation process. A few hydrogen chloride molecules produced on exposure form sensitive sites which can give rise to further loss of hydrogen chloride forming large sequences of conjugated double bonds.

Scarborough, Kellner and Rizzo²⁹ exposed poly(vinyl chloride) discs to ultra-violet light in the presence and absence of oxygen. Ultra-violet absorption spectra were determined at different stages of the degradation process. Hydrogen chloride catalysed the reaction. The authors concluded that the presence of oxygen is not essential for the evolution of hydrogen chloride, but that oxygen takes part only in subsequent reactions of the degradation process. The initial oxidative attack depends on initial hydrogen chloride formation producing spots sensitive to oxidation. These

sites are allyl structures such as $\sim\underset{\text{H}}{\overset{\text{Cl}}{\text{C}}}-\underset{\text{H}}{\text{C}}=\underset{\text{H}}{\text{C}}\sim$. The Cl atom is particu-

larly reactive in such a system and conjugated bonds are believed to be formed by successive splitting-off of HCl, giving rise to discoloration. Oxygen counteracts the formation of these conjugated systems by reacting with double bonds, destroying the allyl structure. Thus, a bleaching action takes place.

Havens³⁰ exposed poly(vinyl chloride), copolymers of vinyl chloride and vinylidene chloride in a Fade-ometer. The light transmission at 4360 Å decreased to 0 per cent after 60 hours for poly(vinyl chloride) in nitrogen and in air, in oxygen, in presence of hydrogen chloride and hydrogen chloride plus oxygen. The copolymer and poly(vinylidene chloride) showed a higher transmission after exposure than poly(vinyl chloride) especially in the presence of oxygen. Crosslinking also took place.

Achhammer³¹ reported some observations on the effect of light and heat on poly(vinyl chloride). Gases evolved in vacuum at 45 and 100° were analysed in a mass spectrometer. At 45°, carbon monoxide, carbon dioxide and hydrogen were found but no hydrogen chloride. If the polymer is exposed longer than 100 hours, some hydrogen chloride is evolved.

Apparently the poly(vinyl chloride) contained some oxygen groups or some trace impurities containing oxygen. At 100°, water, carbon dioxide, hydrogen and carbon monoxide are evolved. Hydrogen chloride is formed and, once formed, its rate of evolution increases.

These results indicate that the initial step in the degradation may be due to residual oxygenated structures.

An extensive investigation of thermal and ultra-violet aging was carried out by Bersch, Harvey and Achhammer³². Numerous references of previous work are given, showing the complexity and lack of consistent knowledge concerning the degradation of this polymer. The work is a continuation of the one summarized above. The following gases were found by mass spectrometry for photolyses at 45° and 100° in powder form: hydrogen chloride, water vapour, carbon dioxide, carbon monoxide, benzene and hydrogen. Benzene and some of the carbon dioxide are due to catalyst fragments in the polymer. Discoloration also takes place. Infra-red spectra of exposed polymer were also determined. On exposure in vacuum only carbon monoxide formation took place.

Sobue, Tabota and Tajuma³³ exposed poly(vinyl chloride) films to radiation of wavelength $\lambda = 2537 \text{ \AA}$. The gel content increased with exposure time and decreased with increasing film thickness.

The whole mechanism of poly(vinyl chloride) photolysis still seems to be obscure and it would lead too far to discuss all observations in detail. Grassie's book¹ may also be of interest in this connection.

It may also be mentioned that Achhammer, Reinhart and Kline³⁴ studied the degradation of polyamide films. Nylon was exposed to ultra-violet light by Ford³⁵.

Straus and Wall^{35a} made some observations on the photo-induced degradation of poly(trifluorochloroethylene) and poly(tetrafluoroethylene) at temperatures about 100° below the normal thermal degradation temperatures. The first polymer gave an appreciable rate of volatilization on exposure mainly consisting of monomer. Appreciable post-irradiation decay periods persisted after turning off the light. These were of the second order as the reciprocal amounts of monomer produced plotted against time gave straight lines. Arrhenius plots indicated that a diffusion-controlled step becomes operative at lower temperatures. The authors suggest that photo-initiation takes place in a random fashion at the chlorine atoms forming radicals.

Poly(tetrafluoroethylene) was not very sensitive to the ultra-violet light used (medium pressure mercury lamp). Any effect is probably due to impurities.

For literature on the effect of ultra-violet light on cellulose and its derivatives, reference may be made to the book edited by Ott³⁶ and the monograph by Grassie¹. A few papers concerning cellulose and its acetate will be discussed here briefly.

Flynn, Wilson and Morrow³⁷ studied the photolysis of cellulose in a vacuum. Purified dried cotton sheets (0.0018 cm thick) were exposed to light of wavelength $\lambda = 2537 \text{ \AA}$. Composition and rate of evolution for gaseous products, changes in functional groups and chain scission were determined. All exposures were carried out at a temperature of 40°.

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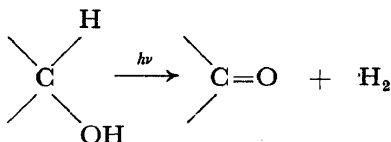
Gases found by mass spectrometric analysis were hydrogen, carbon monoxide and carbon dioxide. The square of the reciprocal rate of hydrogen production was found to be directly proportional to the amount of light absorbed by the system, which corresponds to the following rate law,

$$\frac{dx}{dt} = \frac{k}{1 + ax}$$

where $\frac{dx}{dt}$ is the rate of hydrogen evolution and k and a are constants (x in moles of hydrogen). The quantum yield for hydrogen evolution amounted to 10^{-2} ($k = \phi_{H_2} I_{\text{abs}}$), the quantum yield for carbon monoxide and dioxide combined was found to be $\phi_{CO+CO_2} = 10^{-3}$ and the quantum yield for chain scission $\phi_s \cong 10^{-3}$.

The number of aldehyde and carboxyl groups increased with irradiation time.

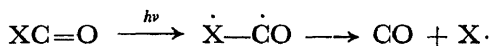
Hydrogen is believed to be produced by,



and



Additional carbon monoxide is produced by,



where X stands for the remaining cellulose chain.

The photodegradation in air at 40° was investigated by Launer and Wilson³⁸. Water vapour was found to retard the degradation of α -cellulose, cotton and wood cellulose if light of wavelength $\lambda = 2537 \text{ \AA}$ was used. Oxygen had no effect under these conditions. The reverse effect was observed when light of wavelengths $>3300 \text{ \AA}$ was used. In this case oxygen is needed for degradation to take place. The quantum yield for chain scission for a sheet of paper (0.008 cm thick) exposed to light of $\lambda = 2537 \text{ \AA}$ was *ca.* 10^{-3} .

Cellulose acetate powder was irradiated by Jortner³⁹ in the presence of air.

The relationship $\frac{1}{P_t} - \frac{1}{P_0} = kt$ was obeyed indicating a random chain scission process. The intensity exponent is one and the quantum yield $\phi_s = 2 \times 10^{-3}$, which compares well with the quantum yield $\phi_s = 7 \times 10^{-4}$ found by Launer and Wilson³⁸ for light of wavelength $\lambda = 2537 \text{ \AA}$. The degradation is independent of initial chain length. The reaction is inhibited by phenyl salicylate; however the relationship $\frac{1}{P_t} - \frac{1}{P_0} = kt$ is still obeyed but the rate constants are appreciably smaller than those for the uninhibited

reaction. The reaction is also inhibited by various anti-oxidants and metal oxides such as cupric oxide, ferric oxide and chromic oxide. Aromatic phenols and amines (*e.g.* phenylnaphthylamine) cause an induction period which lasts until the inhibitor is used up.

Sippel⁴⁰ reports a quantum yield of $\phi_s \cong 1$ for $\lambda = 2537 \text{ \AA}$ and $\phi_s \cong 10^{-4}$ at 3600 \AA for cellulose acetate.

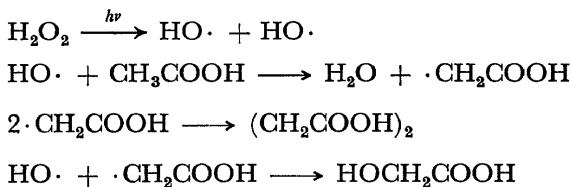
Photosensitized reactions

A number of photosensitized reactions may be discussed briefly without going into any great detail.

Grafting, crosslinking and rupturing bonds can be achieved with light of a wavelength which does not have enough energy to affect the polymer directly, provided that other substances are present which are broken down to produce radicals or other reactive species. These products then undergo secondary reactions with the polymer molecules.

Baxendale and Thomas⁴¹ carried out an extended investigation of the degradation of poly(methacrylic acid), in the presence of hydrogen peroxide as photosensitizer, in aqueous solutions with light of wavelength $\lambda = 2537 \text{ \AA}$.

Hydroxyl radicals photolytically produced from hydrogen peroxide are known to react with aliphatic acids as follows:

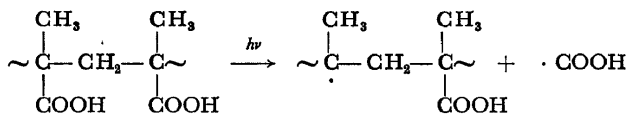


Poly(methacrylic acid) behaves similarly and undergoes degradation. The quantum yield for hydrogen peroxide decomposition in the presence of the polymer is 0.53 and apparently the polymer reacts with all the HO· radicals formed in the primary process up to concentrations of the acid of about 0.1 N; from there on the yield increases due to direct photolysis of the polymer. This direct photolysis of the polymer was also studied in aqueous solution. The number of chain scissions per litre of solution increases linearly with irradiation time, which is in accord with a random chain scission process; the degradation is also independent of initial chain length and polymer concentration. The quantum yield for chain scission is in the neighbourhood of $\phi_s \sim 0.023$ to 0.045. Presence of air decreases the efficiency of the process.

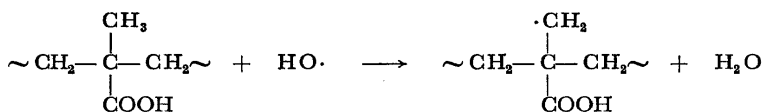
The rate of photolysis increases appreciably in the presence of hydrogen peroxide. The relationship between the number of chain breaks per litre of solution and irradiation time remains linear. The number of HO· radicals used for each chain rupture, corrected for the photolysis in absence of hydrogen peroxide, is 2.5 for the polymer acid and 1.4 for the half-neutralized polymer. These values remained constant over a five-fold variation in each of the variables involved, such as light intensity, polymer and peroxide concentrations. Presence of air also decreases the efficiency of the photosensitized reaction.

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The authors suggest that the photolysis of the acid polymer in the absence of peroxide is similar to that of aliphatic acids; the primary step is,

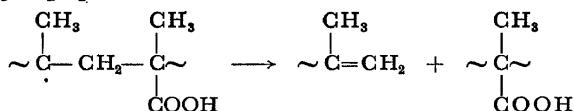


If peroxide is present, a hydrogen atom is abstracted from a methyl group and not from a methylene group because of steric hindrance,

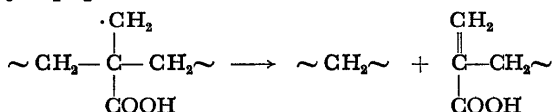


Rupture of the polymer chain can then take place in the following way:

In absence of H₂O₂:



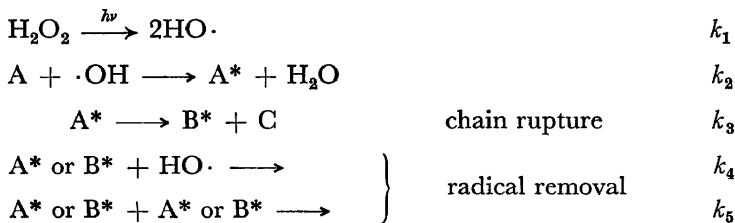
In presence of H₂O₂:



However, for chain rupture of the radicals to take place, this process must be sufficiently rapid to be able to compete with addition of radicals such as HO· or radical combination processes.

The chain rupture process can be decreased by the addition of oxygen to the radicals.

The kinetic scheme proposed by these authors is as follows:



where A stands for aliphatic acid and A* for an acid radical.

If radical removal is mainly accomplished by addition of HO· radicals and steady state conditions prevail, one has (where k_1 is the rate of HO· production),

$$k_1 = 2k_2[\text{A}] [\cdot\text{OH}]$$

For degradation to take place to any appreciable extent,

$$k_3[\text{A}^*] > k_4[\text{A}^*] [\cdot\text{OH}]$$

Hence,

$$k_3 > \frac{k_1 k_4}{2k_2[A]}$$

From numerical estimates it could be shown that the addition of oxygen to the radicals will be much faster than the chain rupture process, which is in agreement with the experimental observations.

Oster and co-workers⁴² found that benzophenone is an effective photosensitizer for polyethylene. This sensitizer can either be introduced during extrusion of the polymer or by soaking it in a benzophenone solution. Polyethylene films are easily crosslinked and their mechanical properties are improved. There are several advantages of this method over using ionizing radiation for thin polymer films. The radiation source is much cheaper and much less dangerous. The authors investigated a whole series of compounds for their suitability as sensitizers. Surface grafting can also be accomplished, changing the surface properties of polymers profoundly. For instance, a sensitized film of polyethylene containing 0.25 per cent of benzophenone was irradiated for one minute by ultra-violet light and was then stored for one week at room temperature. The sample was subsequently heated in styrene when grafting took place. A simpler method consists of the irradiation of the monomer in the presence of sensitized polymer film. The mechanism involved is believed to be due to the photolysis of the sensitizer into radicals, which then abstract hydrogen atoms from the polymer substrate (compare Guillet and Norrish's⁶ paper in this connection, which was discussed on pp. 423-4).

Charlesby⁴³ observed that a concentration of 0.2 per cent benzophenone, if fully utilized, has the same effect as 8 megarads of electron radiation in the case of Marlex 50 (high density) or Alkathene HD (intermediate density) or 4.3 megarads for Alkathene 2 (low density). For a quantitative treatment of crosslinking and degradation mechanisms due to atomic radiation, reference may be made to Charlesby's book⁴⁴.

In the case of ultra-violet radiation, plots of $s + s^{1/2}$ for values between 0.4 and 0.7 against c , the sensitizer concentration, give straight lines; s is the sol fraction in the irradiated sample. This is analogous to a relationship encountered for high energy radiation, where $s + s^{1/2}$ decreases linearly with the radiation dose. As crosslinking and chain scission take place simultaneously during high energy irradiation, this must also be the case for ultra-violet irradiation. Crosslinking during ultra-violet and high energy irradiation is due to secondary reactions in both cases.

Methyl methacrylate was grafted on to rubber by means of 1-chloro-anthraquinone as sensitizer by Cooper, Vaughan, Miller and Fieldhein⁴⁵. They formulated this reaction as follows:



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Grafts using cellulose and its derivatives were studied by Geacintov, Stannett, Abrahamson and Hermans⁴⁶. Vinyl monomers and anthraquinoid dye sensitizers were used. These authors propose a mechanism similar to one given by Bolland and Cooper⁴⁷ for phototendering of cellulose. Presence of oxygen increases the extent of grafting. The dye is activated by ultra-violet light and abstracts a hydrogen atom from cellulose; the cellulose radical then reacts with vinyl monomer, which is present in the system, producing a graft. However, in the absence of oxygen, homopolymer is produced to a large extent by reaction of an excited dye molecule with monomer. Oxygen prevents this reaction.

Experiments on crosslinking of thiol polymers with visible light, using dyes and crosslinking reactions due to metal ions such as Cr^{3+} , have been carried out by Oster and Oster⁴⁸.

Conclusions

Table 1 summarizes the main results for the photodegradation of polymers. The primary act is usually chain scission or the abstraction of a side group leading to chain scission. Further, chain scission, crosslinking, repolymerization, modification of side groups, monomer and gas formation are brought about by secondary reactions or photoreactions not directly involved in the scission reaction.

In contrast to thermal degradation at moderate temperatures, the chain scission reactions seem invariably to be of a random nature with small quantum yields for scission and large decreases in chain lengths. The random chain scission reaction may be followed by unzipping at the newly formed chain ends. Crosslinking may be suppressed by working in dilute solutions or at low temperatures (below the glass temperature of the respective polymer), thus decreasing the probability of recombination of polymer radicals. Whether crosslinking takes place is dependent to a large extent on the structure of the polymer. Thus, α -hydrogen atoms will promote crosslinking reactions by increasing the polymer radical concentration, whereas methyl groups in the α position have a stabilizing influence producing a tendency for unzipping.

Poly(methyl methacrylate) seems to be the only reaction which shows a reverse polymerization process, that is depolymerization with chain-end initiation. However, this seems to be mainly due to the high temperatures at which the photolysis of this polymer was studied (*ca.* 200°), which gives the chain ends activation needing only small support from the light quanta to trigger this reaction. However, a very recent paper by Shultz⁴⁹ indicates that at room temperature it also undergoes a random chain scission process with unzipping at the newly formed chain ends.

The secondary reactions are often of a similar nature as those found during high energy irradiation of polymers. However, the primary act is a specific one depending on the chemical nature of groups present in the polymer; this is to a large extent not the case with atomic irradiation. In addition high energy radiation has a far greater penetrating power than ultra-violet light radiation.

Table 1. Survey of photodegradation of polymers

Polymer	Structure	Temperature of degradation (°C) and state of polymer	Wavelength (Å)	Variables measured	Main reactions	Quantum yields	Reaction products	Intensity exponents for initial reaction and high molecular weights	Reference no.
Poly(methyl methacrylate)	$\sim\text{CH}_2-\text{C}(\text{CH}_3)(\text{COOCH}_3)-$	160-200 Bulk, thin layer Vacuum	2537	Osmotic pressure, monomer	End-group initiation, depropagation, termination (diffusion controlled); rates depending on nature of end groups	> 200 (monomer)	Monomer	1/2 (monomer)	14
Poly(methyl methacrylate)	See above	Films, 0.08-0.09 mm thick Vacuum	3030-3130	Viscosity	Random chain scission	0.23×10^{-3} (gases)			14a
Poly(methyl methacrylate)	See above	26 Films, 0.021-0.465 cm thick Air	2537	Viscosity	Random chain scission	2.3×10^{-3} (chain scission)			49
Poly(ethyl acrylate)	$\sim\text{CH}_2-\text{CH}(\text{COOC}_2\text{H}_5)-$	- 196 - 20 to 50 Films, ca. 10 mils thick Vacuum	2537	Viscosity, swelling, solubility, gases	Random chain scission and cross-linking; below -17°C (glass temperature) chain scission is predominant		$\text{H}_2, \text{CH}_4, \text{CO}, \text{CO}_2$		19
Poly(methacrylic acid)	$\sim\text{CH}_2-\text{C}(\text{COOH})-$	Aqueous solution Absence and presence of O_2	2537	Viscosity	Random chain scission	0.023-0.045			41
Poly(acrylic acid)	$\sim\text{CH}_2-\text{C}(\text{COOH})-\text{H}$ $\sim\text{CH}_2-\text{C}(\text{COOH})-$	Aqueous solution, pH 6.2 Absence and presence of O_2	Daylight	Viscosity	Random chain scission				13
Poly(methyl-isopropenyl-ketone)	$\sim\text{CH}_2-\text{CH}(\text{COCH}_3)-$	150-177 Films, 14.5 μ thick Vacuum	3130	Viscosity, monomer	Random chain scission followed by monomer formation at newly formed chain ends	5 (155°) 8 (177°) (monomer)	Monomer, CH_4 , CO	0.41 (155°) 0.73 (177°)	18
Poly(methyl-vinylketone)	$\sim\text{CH}_2-\text{CH}(\text{COCH}_3)-$ $\sim\text{CH}_2-\text{C}(\text{COCH}_3)-$	28-80 Films, ca. 15.9 and 47.3 μ thick Vacuum	3130	Viscosity	Random chain scission opposed by re-polymerization	0.02 (chain scission)	Acetaldehyde, CO, CH_4	1 (chain scission)	18
Poly(methyl-vinylketone)	See above	25-250 Dioxan solution	3130	Viscosity	As above	0.02 (chain scission)	As above	As above	6
Poly(α -methylstyrene)	$\sim\text{CH}_2-\text{C}(\text{CH}_3)(\text{C}_6\text{H}_5)-$	27 and 115 Films, 1.5 to 14 μ thick Vacuum	2537-2804	Viscosity, monomer	Random chain scission with monomer formation at newly formed chain ends	1×10^{-3} (27°) 2×10^{-2} (115°) (chain scission) 7×10^{-3} (27°) 0.5 (115°) (monomer)	Monomer, $\text{H}_2, \text{CO}, \text{CO}_2, \text{C}_2\text{H}_4, \text{C}_3\text{H}_4$, isobutane, methane, ethane, propene, butane, pentane, benzene, toluene	1 (chain scission and monomer)	15

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Polymer	Structures	Temperature of degradation (°C) and state of polymer	Wavelength (Å)	Variables measured	Main reactions	Quantum yields	Reaction products	Intensity experiments	Reference no.
Polystyrene	$\sim\text{CH}-\text{CH}_2\sim$ C_6H_5 See above	100-150 Films Air Benzene solution	2700 to 4000	Gases evolved	Random chain scission	ca. 1.7×10^{-6} (chain scission)	Various gases		50
Polystyrene	$\sim\text{CH}-\text{CH}_2\sim$ C_6H_5 See above	25 Ethylene carbonate-propylene carbonate (80 : 20 by weight) solutions Vacuum 25 Film Vacuum Powder Disks	2537	Viscosity ($M\eta$)	Random chain scission	10^{-4} (chain scission)		1 (chain scission)	12
Polyacrylonitrile	$\sim\text{CH}_2-\text{C}(\text{CN})\sim$	Air and vacuum Films in presence of oxygen (photo-oxidation)	2537	Spectra, gases evolved, gel content Spectra	Crosslinking (and chain scission)	1×10^{-1} (carbonyl formation)	$\text{HCl}, \text{H}_2\text{O}, \text{CO}_2, \text{CO}, \text{C}_2\text{H}_4, \text{H}_2$, etc.		9, 10
Polyacrylonitrile	See above	Vacuum 25 Film Vacuum Powder Disks	2537	Viscosity	Random chain scission and crosslinking	5×10^{-4} (chain scission)			10
Poly(vinyl chloride)	$\sim\text{CH}-\text{CH}_2\sim$ Cl	Air and vacuum Films in presence of oxygen (photo-oxidation)	2537	Spectra, gases evolved, gel content Spectra	Crosslinking (and chain scission)	1×10^{-1} (carbonyl formation)			26, 27, 28, 31
Polyethylene	$\sim\text{CH}_2-\text{CH}_2\sim$	Vacuum and air	2500-3500	Viscosity	Chain scission	5×10^{-4} (chain scission)		1/2 (oxygen uptake)	24
Poly(ethylene terephthalate)	$\sim\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$	Vacuum and air	2800-3600	Viscosity ($M\eta$)	Chain scission	5×10^{-4} (chain scission)			21
Poly(tetrafluoroethylene)	$\sim\text{CF}_2-\text{CF}_2\sim$	Vacuum Elevated temperatures	>2500	—	Impurities, otherwise stable				35a
Poly(chlorotrifluoroethylene)	$\sim\text{CF}_2-\text{CF}(\text{Cl})\sim$	Vacuum Elevated temperatures	>2500	Volatiles (monomer)	Chain scission (plus unzipping at newly formed chain ends)		Mainly monomer		35a
Rubber	$\sim\text{C}(\text{F})(\text{Cl})-\text{C}(\text{F})(\text{Cl})\sim$ $\sim\text{CH}_2-\text{C}(\text{CH}_3)=\text{C}-\text{CH}_2\sim$	70-200 Vacuum	2500-4000	Isoprene (gas evolved)	Chain scission	4×10^{-4} (gases)	80% monomer	1 (gases)	25
Cellulose	$\sim\text{CH}_2-\text{C}(\text{OH})(\text{H})-\text{O}-\text{C}(\text{OH})(\text{H})-\text{O}\sim$	40 Sheets of purified cotton Vacuum	2537	Viscosity gases evolved	Random chain scission, formation of groups on chains	10^{-4} (H_2) 10^{-4} ($\text{CO} + \text{CO}_2$) 10^{-4} (chain scission) 10^{-4} (chain scission)	$\text{H}_2, \text{CO}, \text{CO}_2$	1 (H_2)	37
Cellulose	$\sim\text{CH}_2-\text{C}(\text{OH})(\text{H})-\text{O}-\text{C}(\text{OH})(\text{H})-\text{O}\sim$	40 Sheets derived from cotton and wood	2537	Viscosity	Random chain scission	10^{-4} (H_2) 10^{-4} ($\text{CO} + \text{CO}_2$) 10^{-4} (chain scission) 10^{-4} (chain scission)	$\text{H}_2, \text{CO}, \text{CO}_2$	1 (H_2)	38
Cellulose acetate	—	25 Powder	2540-4340	Viscosity	Random chain scission	2.0×10^{-8} (chain scission)		1 (chain scission)	39
Cellulose acetate	—	Air	2537-3600	Viscosity	Random chain scission	$1 (2537 \text{ \AA})$ $10^{-4} (3600 \text{ \AA})$ (chain scission)			40

HIGH TEMPERATURE DEGRADATION

Introductory remarks

The study of degradation mechanisms at high temperatures is in its earliest stages (as far as published literature is concerned). Thermal degradation at relatively low and medium temperatures (up to *ca.* 450–500°) is quite well understood, though not in all details. Literature up to about 1955 can be found in two monographs¹ on the subject.

More recently, interest in the properties of polymers at high temperatures, 500–1000° or even higher, has increased very appreciably. At lower temperatures, the mechanisms of degradation can be divided into two extreme cases:

(a) the random chain scission process with or without subsequent formation of monomer from the newly formed chain ends, and

(b) the reverse polymerization process with chain end initiation, depropagation (monomer formation) and termination. There is, of course, a whole series of reactions covering the degradation spectrum from one extreme to the other. Chain transfer is a factor giving rise to such intermediate reaction mechanisms. The mode of breakdown is, to a large extent, conditioned by the structure of the polymer molecules. Thus, a general rule is that the presence of tertiary hydrogen atoms decreases the formation of monomer; substitution of tertiary hydrogen atoms by methyl groups, for instance, changes the mechanism leading to a reverse polymerization (depolymerization) process with almost 100 per cent monomer formation. Examples are poly(methyl acrylate) and poly(methyl methacrylate).

The importance of the reactive tertiary hydrogen atoms can be demonstrated by replacing them by deuterium atoms. This reduces transfer and enhances monomer formation. Substitution of methylenic β -hydrogen atoms has no marked effect.

Chlorine atoms in polymers are also fairly reactive and lead to transfer reactions decreasing monomer formation. Also the reactivity of radicals produced during degradation will have an effect on monomer formation, the more resonance stabilized or sterically inaccessible the radicals are the more will transfer be suppressed and monomer production be favoured. Higher degradation temperatures favour transfer reactions with consequent lower yields of monomer.

A survey of degradation characteristics for medium temperature ranges (structure, monomer yield, activation energy and rates of loss of weight at 350°) is given in a paper by Wall and Florin⁵¹.

Some characteristic values given by Wall⁵² in a more recent survey are given in *Table 2*.

Polytetrafluoroethylene is the most stable of the straight chain polymers⁵³. This is due to the strength of the C—F bond. Monomer is almost exclusively produced during degradation and breakdown becomes appreciable only at about 450°. If one of the fluorine atoms is replaced by a chlorine atom, however, the stability and mechanism of breakdown are appreciably altered, due to the reactivity of the chlorine atom.

DEGRADATION OF POLYMERS

Table 2. Activation energies and A-values from loss of weight measurements

(a) Hydrocarbon polymers	A (estimated) (sec ⁻¹)	E (kcal/mole)
Methyl methacrylate	10 ⁹ -10 ¹⁶	30-52 32-42 27-47 32-48
α-Methylstyrene	10 ²²	65
Styrene	10 ¹⁵	55
Isobutylene	10 ¹⁴	49
Propylene (linear)	10 ¹⁴	59
Ethylene (linear)	10 ¹⁸	72

(b) Fluorocarbon polymers	Rate at 350°C (% min ⁻¹)	A (estimated) (sec ⁻¹)	Total light volatiles (weight %)	E (kcal/mole)	Monomer and other products (weight %)
Tetrafluoroethylene	2 × 10 ⁻⁶	10 ¹⁹	100	81	97 monomer
α, β, β-Trifluoro- styrene	4.8	10 ¹⁹	74	64	73 monomer
Chlorotrifluoro- ethylene	0.2	10 ¹²	28	50	26 monomer
Trifluoroethylene	0.02	10 ¹²	13	53	7 HF
1, 1-Difluoroethy- lene	0.02	10 ¹⁰	25	48	13 HF
Monofluoroethy- lene	0.1	—	18	—	7.2 HF

A comparison of the stability, based on temperatures at which the rate of volatilization reaches 1 per cent per minute, was given by Wall⁵².

Table 3. Comparative stability of fluoro and hydrocarbon polymers; (temperatures are those at which rate of volatilization becomes 1 per cent per minute)

Polyfluorocarbons	Temperature (approx.) (°C)	Polyhydrocarbons	Temperature (approx.) (°C)
$\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ \sim\text{C}-\text{C}\sim \\ \quad \\ \text{F} \quad \text{F} \end{array}$	510	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \sim\text{C}-\text{C}\sim \\ \quad \\ \text{H} \quad \text{H} \end{array}$	410
$\begin{array}{c} \text{CF}_3 \quad \text{F} \\ \quad \\ \sim\text{C}-\text{C}\sim \\ \quad \\ \text{F} \quad \text{F} \end{array}$	310	$\begin{array}{c} \text{CH}_3 \quad \text{H} \\ \quad \\ \sim\text{C}-\text{C}\sim \\ \quad \\ \text{H} \quad \text{H} \end{array}$	370
$\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ \sim\text{C}-\text{C}\sim \\ \quad \\ \text{H} \quad \text{F} \end{array}$	330	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \sim\text{C}-\text{C}\sim \\ \quad \\ \text{H} \quad \text{H} \end{array}$	360

However, all the reactions mentioned above cannot be considered really high temperature degradation reactions. These start only in the neighbourhood of 500°. The choice of 500° is somewhat arbitrary; however, up to about this temperature, most conventional organic polymers behave in a way which has been investigated quite extensively and is fairly well understood.

Above 500°, however, changes in mechanisms of degradation are to be expected. Some progress has been made with the analysis of reaction products obtained at high temperatures with the help of mass spectrometry and chromatography. Appreciable research is in progress to find high temperature stable polymers. The latter work leads into the realm of semi-inorganic and inorganic polymers as well as highly crosslinked organic structures^{54, 55}. However, there are as yet no rate measurements for degradation processes at temperatures above 500°, though publications in this area may be expected very soon.

Mass spectrometric analysis

Winslow, Baker, Pape and Matreyek⁶ pyrolysed divinyl/ethylvinylbenzene copolymers up to 1000°. Gases were condensed in a liquid air trap and non-condensable gases were measured continuously with a Pirani gauge. Temperatures were increased at the rate of 100° per hour. The vacuum was of the order of 2 μ Hg. Condensable gases were evolved up to 350 to 400°. At the latter temperature the rate of loss of weight increased rapidly, tailing off at about 45 per cent loss of weight. Up to about 450° carbon monoxide, carbon dioxide, hydrogen and smaller hydrocarbons were produced; at higher temperatures mainly hydrogen, carbon monoxide, carbon dioxide and methane were evolved. Oxygen-pretreated polymers formed more carbon compounds than untreated ones. The initial spherical shape of the polymer particles was preserved during degradation; however, volume shrinkage took place.

Abrupt changes in the progress of polymer carbon formation occurred between 600 and 700°. The residue passed over into a rigid structure. Crosslinked graphite-like layers were formed of such heat stability that true graphitization did not take place at 2400°.

A series of crosslinked polystyrenes was pyrolysed by Winslow and Matreyek⁵⁷. Stability and the amount of residue increased with the degree of crosslinking (0 per cent residue for polystyrene at 440° for a temperature increase of 100° per hour and *ca.* 45 per cent residue at 550° for polytrivinylbenzene). At, or below, 400° most of the polymers or copolymers decomposed by a first-order reaction; however, at higher temperatures, a definite reaction order could not be recognized. At these higher temperatures the vinyl chain network is destroyed and the more stable aromatic groups condense into different structures. For instance, changes in the structure of poly(trivinylbenzene) were followed by X-ray analysis. Polymer samples were heated at 450°, 500°, 600°, 650° and 800° until volatilization practically ceased. The accumulated weight loss was 56 per cent. The original polymer skeleton persisted up to 450°; between 450 and 500° rapid breakdown of the structure took place and cokes were formed. At 650° a highly disordered carbon structure emerged. These structures, as already mentioned above, are very heat stable.

DEGRADATION OF POLYMERS

High temperature degradation of various polymers was studied by Madorsky and Straus⁵⁸. The apparatus consisted of a reaction tube into which a platinum boat containing the polymer sample was inserted; the reaction tube was connected to a high vacuum system, which allowed volatiles to be collected. The products were analysed in a mass spectrometer. Temperatures up to 850° were obtained by placing, very rapidly, a tube furnace over the reaction tube. Polymers were studied in vacuum or in different gaseous atmospheres. Polystyrene, poly(vinylidene fluoride), polyacrylonitrile and polytrivinylbenzene were investigated. Below 500°, the degradation followed patterns expected from previous experience. The process depended primarily on polymer structure. Crosslinked structures produced honeycombed carbonized residues.

Pyrolysis of polystyrene gave an increasing yield of small molecular weight fragments the higher the temperature and the higher the gas pressure (He) were during degradation. Some relevant data⁵⁸ obtained at 850° are given below.

Table 4. Pyrolysis of polystyrene in a vacuum and in He (1 atm)

<i>Experiment</i>	<i>Temperature</i> (°C)	<i>Heating time</i>	<i>Volatilization</i> (%)
1	362	1 h	83
2	850	35 sec	100
3	362	1 h	83
4	850	35 sec	98

Analysis of fractions of the gaseous products, which were volatile at room temperature, yielded in mole per cent:

<i>Component</i>	<i>Expt.</i>	1	2	3	4
Styrene		94.4	34.0	50.5	12.9
Toluene		5.6	5.5	5.6	14.9
Benzene		0	58.2	43.9	1.1
Propadiene		0	1.9	0	49.2
Ethylene		0	0	0	4.2
Ethane		0	0	0	—

Poly(vinylidene fluoride) and polyacrylonitrile tended to stabilize at higher temperatures yielding carbonaceous residues. Hydrogen fluoride, hydrogen and carbon monoxide were produced in the first instance; in the second instance hydrogen cyanide, acrylonitrile and vinylacetonitrile were formed.

The results for polytrivinylbenzene agree quite well with those of Winslow and Matreyek⁵⁷. Stabilization started at 500°, additional loss of weight between 500 and 800° was only 10 per cent. Slower rates of heating as used by Winslow and Matreyek produced less loss of weight than the sudden heating applied by Madorsky and Straus.

The rates of volatilization increase rapidly at about 450° in the case of the fluoride and trivinylbenzene; however, in the case of polyacrylonitrile, the rate of volatilization decreased gradually in the range of temperatures

from 240 to 800°. Rate measurements were only carried out at temperatures below 440°.

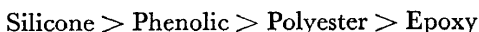
Further work on polydivinylbenzene, copolymers of styrene with divinylbenzene and trivinylbenzene was carried out by Straus and Madorsky⁵⁹. However, these experiments were performed in the medium temperature range up to about 450°. Polystyrene volatilizes completely within 30 minutes at 400° mainly forming monomer. This was not the case with polytrivinylbenzene under similar conditions. No appreciable amounts of styrene or trivinylbenzene were formed; however, saturated and unsaturated hydrocarbons having 1 to 11 C-atoms were produced and also larger fragments of an average molecular weight of 372 were formed. Copolymers with divinylbenzene take an intermediate position between polystyrene and polytrivinylbenzene. Unzipping becomes blocked by crosslinks.

Madorsky and Straus⁶⁰ also investigated a number of thermoset polymers. The degradation was followed up to 1200°. 10 to 15 mg samples were pyrolysed in the platinum boat; the vacuum was better than 10⁻⁴ mm Hg. The analysis was again carried out by mass spectrometry. Rate measurements were made only at temperatures up to 380°. Some results are comprised in *Table 5*.

Table 5. Pyrolysis of some thermoset polymers

	Pyrolysis temperature (°C)	Time (min)	Volatilization (%)
Polyester (Vibrin 136A)	360	60	28
	500	30	83
	800	5	89
	1200	5	93
Epoxy (Epon 1310)	360	60	38
	500	30	75
	800	5	86
	1200	5	87
Phenolic (CT-91-LD, Cincinnati Testing and Research Lab.)	360	60	11
	500	30	28
	800	5	44
	1200	5	48
Silicone (DC 2106)	360	60	2
	500	30	6
	800	5	13
	1200	5	17

The detailed results for the composition of the volatile products are given in the paper. Taking the residue as a measure of thermal stability, the following sequence was obtained:



The Si—O bonds are stronger than the Si—C bonds; hence there is a tendency of stripping of the side groups. The stability of phenolic is due to crosslinks and stability of the benzene ring. The lower stabilities of the polyester and epoxy are believed due to the smaller degree of crosslinking.

Chromatographic Analysis

Various authors employed chromatography for the analysis and identification of polymers, mixtures of polymers, and copolymers⁶¹. Such an analytical procedure has proved to be quite successful. The usual method is to pyrolyse a small sample of the polymer, preferably in the inlet system of the chromatograph. Reproducible and characteristic chromatograms are obtained under standardized conditions. Only two of the papers which are more relevant to the present topic will be discussed.

Barlow, Lehrle and Robb⁶² pyrolysed a number of polymers on a hot filament (poly(methyl methacrylate), poly(ethyl metacrylate), polymethacrylate, polystyrene, polytetrafluoroethylene, poly(vinyl chloride), poly(vinyl acetate), 50 per cent methyl methacrylate-50 per cent styrene copolymer and various other copolymers and polymer mixtures). The products were swept directly into the chromatograph by means of a carrier gas. Another method for the pyrolysis of the polymer by electric discharge of high energy was not so successful.

The polymer sample (< 2 mg) was placed on the filament; the polymer melted and coated the filament before degradation took place. Instead of the solid polymer, a drop of polymer solution can be placed on the filament and the solvent can be evaporated before firing.

Two methods were used:

(a) the temperature chosen was so high that all the polymer pyrolyses in a short period during one firing;

(b) pyrolysis was started at a low temperature and subsequently increased in steps, such that a series of characteristic chromatograms was obtained over a range of temperatures; this method illustrates very vividly the change in degradation mechanism going from low to high temperatures.

Temperatures up to 1000° could be obtained by pre-set voltages. Pyrolysis was completed within 10 to 15 seconds or even faster. Secondary reactions could be minimized by increasing the flow rate of the carrier gas. Nine temperature settings were chosen covering the temperature range from 150 to 950°.

At the highest temperatures acetylene was the main product whereas, in the medium range of temperatures, monomer was formed by many polymers, indicating an unzipping reaction.

Some polymers such as poly(vinyl chloride) and poly(vinyl acetate) indicated stripping of side groups (hydrogen chloride and acetic acid, respectively, were produced) forming more stable polyacetylene chains, which at the highest temperatures formed acetylene and other small unsaturated molecules. Polytetrafluoroethylene again proved the most stable straight chain polymer (*ca.* 450°).

Polymer mixtures and copolymers often gave similar chromatograms; however, degradation over a range of temperatures permitted one to distinguish the mixtures from the copolymers. Also block and random copolymers could be distinguished. The random copolymers showed less unzipping than the block copolymers. No rate measurements have been as yet reported, though the authors pointed out that they are engaged in such research.

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The other paper of interest in this connection is one by Lehmann, Forziati and Brauer⁶³. These authors also used a filament technique. The polymer sample was contained in a small Vycor vessel surrounded by the heating coil, which was situated directly in the inlet system of the chromatograph. Helium was used as carrier gas. 2 to 3 mg samples of polystyrene and poly(methyl methacrylate) were pyrolysed at a number of temperatures. The main results are shown in *Tables 6 and 7*.

Table 6. Composition of pyrolysates of polystyrene at various temperatures in weight per cent

	Temperature (°C)					
	400	500	600	700	850	1000
Carbon dioxide	—	—	—	—	—	Trace
Ethylene	—	—	—	Trace	4.4	7.2
Acetylene	—	—	—	Trace	4.4	7.2
Benzene	—	—	—	Trace	8.2	14.0
Toluene	—	—	—	} 1	2.7	5.8
Ethylbenzene	—	—	—			
Styrene	100	100	100	98	79.7	65.6
Residue	Nil	Nil	Nil	Nil	Nil	Nil

Styrene monomer was the main product up to about 700°.

The amounts of secondary products obtained in this work were consistently smaller than those reported by Madorsky and Straus⁵⁸. This is probably due to the fact that the products in the latter case were kept longer at elevated temperatures.

Monomer formation in the case of poly(methyl methacrylate) decreased rapidly at temperatures above 600 to 700°. Probably this monomer is not as thermally stable as styrene, since it seems likely that the monomer is the primary product. Some pertinent results are given in *Table 7*.

Table 7. Composition of pyrolysates of poly(methyl methacrylate) at various temperatures in weight per cent

	Temperature (°C)					
	400	500	600	700	800	1000
Gaseous Components*	Trace	3.6	4.2	18.2	60.3	76.3
Methanol	—	—	Trace	Trace	Trace	Trace
Ethanol	—	—	Trace	Trace	0.6	0.4
Methylacrylate	—	Trace	Trace	Trace	Trace	Trace
Methylpropionate	Trace	Trace	0.4	0.5	0.7	0.3
Methylisobutyrate	Trace	Trace	0.4	0.5	0.8	3.0
Methylmethacrylate	99.4	96.2	94.7	80.6	37.4	19.9
Residue	Nil	Nil	Nil	Nil	Nil	Nil

*CH₄, CO, C₂H₆, CO₂, C₂H₄, C₃H₄

Between 800 and 1000° quantities of carbon monoxide, methane and ethane decreased rapidly, whereas carbon dioxide and ethylene increased. The percentage production of monomer is dependent on the rate of the carrier gas flow.

Miscellaneous experimental methods

An interesting type of degradation was studied by Chaiken, Anderson, Barsh, Mishuk, Moe, and Schultz⁶⁴. A hot plate was pressed against a polymer surface over a range of temperatures from 550 to 910°K. The rate of movement of the hot plate into the polymer under constant load was measured.

Linear and crosslinked poly(methyl methacrylates) were investigated. The mechanism at high temperatures differed from that of the bulk degradation at lower temperatures. It is suggested by these authors that desorption (or vaporization) from the hot interface is the rate-determining step at high temperatures. A liquid layer of monomer is assumed to be present in the interface. At temperatures lower than about 800°K, diffusion of monomer through the polymer is believed to be rate-determining. At high temperatures the energy of activation was found to be 11.2 ± 0.6 kcal/mole, which is similar to the heat of vaporization of 9.2 kcal/mole for the monomer at 100°C. Both linear and crosslinked polymers (ethylenediacylate) have the same overall energy of activation supporting the view that vaporization from the interface is rate-determining.

High intensity light flashes can initiate thermal reactions in polymers, according to Nelson and Lundberg⁶⁵. The conditions for such reactions to take place are as follows:

- (a) a very intense light source is needed, and
- (b) dark material in the form of particles, filaments or foil must be present in the transparent polymer, which is also a poor heat conductor. Temperatures up to 2000 or even 5000° are obtained at the sites where the black material is located. If these foreign bodies are absent, thermal degradation does not take place. Gases, fluorescent material and carbon were formed. Polyethylene which had black tungsten wire embedded was flashed. The total number of moles of volatiles for each gram of polyethylene was nearly proportional to the square of the number of flashes.

Differential thermal analysis will also become a useful tool for the investigation of thermal degradation at high temperatures⁶⁶. Various fibre and fabric samples were investigated by Schwenker and Beck⁶⁷, using D.T.A. up to 550°. A number of reactions such as rearrangements, crosslinking and depolymerization can be detected by this method. Endothermic and exothermic reactions can be distinguished and quantitative information on heats of reactions can be obtained.

Conclusion

The study of thermal degradation of polymers at high temperatures is still in its very beginning. There are, as yet, no rate measurements available in temperature ranges above 500°. This is due to the experimental difficulties encountered, such as the high rate of these reactions. This requires new methods for very rapid heating of polymers to high temperatures and methods for measuring useful variables, such as amount of volatiles produced during the short time intervals, which may be of the duration of a fraction of a second to several minutes.

However, there are methods available for the identification and analysis of various polymers, polymer mixtures and copolymers, which in principle

seem to be suitable for rate measurements. These methods are chromatography, where small amounts of polymer are pyrolysed on hot filaments directly located in the inlet system of the apparatus, the gaseous products being swept into the chromatograph by a carrier gas, and mass spectrometry where again a filament method could in principle be used similar to that employed for chromatography and the peak of a single product could be observed as a function of time.

Differential thermal analysis may also be useful in this connection, discovering the extent of the exothermic or endothermic nature of the reactions.

The thermal behaviour of conventional polymers in the medium range temperatures is quite well understood in principle. However, at higher temperatures ($> 500^\circ$), profound changes in degradation mechanisms may take place. Whether these are due to primary reactions or secondary reactions is not known. Thus, whereas for many polymers monomer is the main product, this is not any more the case at higher temperatures (*ca.* 1000°). This may be due to a complete change in the character of the reaction or due to a secondary breakdown of the monomer initially produced. Investigations of the thermal stability of monomers will have to be included in the investigation of high temperature degradation of polymers.

Any appreciable thermal stability of conventional polymers is not to be expected at these high temperatures; however, they may be sufficiently stable for short periods of time and the reactions sufficiently endothermic to be useful for many purposes.

Also the residues of pyrolysed polymers, especially those of highly cross-linked polymers, which show graphite-like structures, may be valuable in virtue of their high thermal stability.

Polymers stable at these high temperatures will be of the semi-inorganic and inorganic type. Intensive research is being pursued in these areas.

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