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STATISTICAL THEORIES OF MAIN CHAIN SCISSION AND CROSSLINKING OF POLYMERS—APPLICATION TO THE PHOTOLYSIS AND RADIOLYSIS OF POLYSTYRENE STUDIED BY GEL PERMEATION CHROMATOGRAPHY

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Abstract—The statistical theories of main chain scission and crosslinking resulting from either homogeneous or inhomogeneous energy dissipation in polymers are summarized. The molecular weight distributions of polystyrene samples subjected *in vacuo* to γ-rays (homogeneous energy dissipation) or to U.V. irradiation (inhomogeneous energy dissipation) have been measured by GPC for various absorbed doses. The results are discussed according to these theories.

INTRODUCTION

It is well known that, when a polymer is submitted to ionizing or u.v. radiation, chain scissions and crosslinking occur. The yields of these processes have been measured for the radiolysis of many polymers [1–4]. Determination of the soluble fraction of irradiated polymer as a function of dose has been often used. Other studies are based on the measurement of number or weight average molecular weight. The photolysis has been less extensively investigated quantitatively probably because of the experimental and theoretical difficulties brought about by the inhomogeneous absorption of u.v. radiation in most systems [5, 6].

The recent development of GPC affords a rather easy and rapid method to measure not only the average molecular weight but also the distribution; small variations in either the high or low molecular weight region can thus easily be detected. This method, although very promising, has not been often used yet in the field of polymer degradation.

The present work is concerned with the potentialities of GPC in that field. The main types of molecular weight distribution are first summarized. The various theories concerning the effect of degradation on molecular weight distribution and moment are then reviewed according to the initial molecular weight distribution and the type of energy dissipation, either homogeneous or inhomogeneous. Numerous theoretical papers concerning one or other aspect of this subject have been published, but a synthesis of these theories covering both photolysis and radiolysis and using unified symbolism was thought to be needed. The third part of this paper reports a study of the molecular weight distribution of polystyrene irradiated under *in vacuo* either with u.v. or γ-rays using GPC data analyzed according to these theories.

I. THE MOLECULAR WEIGHT DISTRIBUTION OF POLYMERS

The distribution functions generally used to characterize polymer molecular weight distribution are special cases of two generalized distributions, viz. the generalized exponential distribution and the logarithmic-normal distribution.

The generalized exponential distribution function $m(p, 0)$ is a function of three parameters m, k and a. It represents the fraction of the total number of molecules containing p monomeric units. The second index characterises degraded samples and will be used and defined in section II; an index 0 refers to non-degraded polymers. It is given by:

$$m(p, 0) = \frac{m\, a^{(k+1)/m} \cdot p^{k-1} \cdot e^{-ap^m}}{\Gamma\left(\frac{k+1}{m}\right)}. \qquad (1)$$

According to the value of the parameters m, k and a, the Schulz–Zimm, the random, the uniform or the Tung distribution can be obtained. These values are given in Table 1.

The generalized logarithmic normal distribution is a three-parameters function:

$$m(p, 0) = \frac{N^{-1} p^{n-1}}{\beta\sqrt{\pi}} \cdot \exp\left[-\frac{1}{\beta^2}\left(\ln\frac{p}{u_m}\right)^2\right] \qquad (2)$$

with

$$u_n = u_m \exp\left[(2n+1)\frac{\beta^2}{4}\right]$$

and

$$N = u_m^{n+1} \exp\left[(n+1)^2 \frac{\beta^2}{4}\right].$$

The Lansing–Kraemer and the Wesslau distributions are respectively obtained if $n = 0$ and $n = -1$. The parameter β defines the width of the distribution according to:

$$\frac{u_w}{u_n} = \frac{\bar{M}_w}{\bar{M}_n} = \exp\left(\frac{\beta^2}{2}\right)$$

Where u_n, u_w are respectively the number and weight average degrees of polymerization and u_m is the

Table 1. Value of the parameters m, k and a in Eqn. (1) for special distribution functions

Schulz–Zimm	Random	Uniform	Tung
$m = 1$ $k = \sigma$ $a = \sigma/u_n$	$m = 1$ $k = \sigma = 1$ $a = 1/u_n$	$m = 1$ $k = \sigma \to \infty$ $a \to \infty$	$m = \sigma$ $k = \sigma - 1$ $a = 1/(u_{n_0})^{\sigma}$ $u_{n_0} = u_n \Gamma(1 - 1/\sigma)$

medium value of the distribution defined as $u_m = (u_n \cdot u_w)^{1/2}$. These usual distribution functions will be given in the following section. Other size distribution functions can be used instead of $m(p, 0)$ and easily transformed into each other. There are: the number $n(p, 0)$ of molecules having p structural units and the weight fraction $w(p, 0)$. They are related by

$$w(p, 0) = pm(p, 0) \text{ with } \int_0^{\infty} pm(p, 0)\mathrm{d}p = 1$$
$$n(p, 0) = N \cdot m(p, 0)$$

where N is the total number of macromolecules.

Comprehensive reviews on the problem of the molecular weight distribution of polymers have been published recently [7, 8].

I.1. *The Schulz–Zimm distribution*

The general expression characterizing this distribution is:

$$m(p, 0) = \frac{\sigma^{\sigma}}{u_n p \Gamma(\sigma)} \cdot \left(\frac{p}{u_n}\right)^{\sigma} \cdot \exp\left(\frac{-\sigma p}{u_n}\right) \tag{3}$$

where $m(p, 0)$ is the fraction of molecules containing p monomeric units as defined previously and σ is a parameter that characterizes the width of the distribution:

$$\sigma = \frac{\overline{M}_n}{\overline{M}_w - \overline{M}_n} \tag{4}$$

u_n is the number average degree of polymerization
$\Gamma(\sigma)$ is the Gamma function.

This equation is the same as the generalized Poisson distribution used in statistics. Criteria can be used to verify if a given distribution belongs to the Schulz–Zimm distribution. They are:

$$\frac{\overline{M}_n + \overline{M}_z}{\overline{M}_w} = 2 \quad \text{and} \quad 1 < \frac{\overline{M}_z}{\overline{M}_w} < 2.$$

I.2. *The "most probable" or "random" distribution*

This distribution is obtained for condensation polymerisation but also for cationic and free radical polyadditions if disproportionation is responsible for chain termination. The expression for $m(p, 0)$ obtained from equation (1) or (3) and Table 1 is:

$$m(p, 0) = \frac{1}{u_n^2} \cdot \exp\left(-\frac{p}{u_n}\right). \tag{5}$$

The criteria to be verified for this distribution are:

$$\frac{\overline{M}_w}{\overline{M}_n} = 2 \quad \text{and} \quad \frac{\overline{M}_z}{\overline{M}_w} = 1,5.$$

I.3. *The "uniform" distribution*

This is an ideal case where all the macromolecules have the same size with $\overline{M}_n = \overline{M}_w = \overline{M}_z$ and k or $\sigma \to \infty$ as given in Table 1. This gives:

$$m(p, 0) = 1/p\, \delta(p - u_n) \tag{6}$$

where δ is the Dirac function defined by

$$\delta(x) = 0 \text{ for } x \neq 0$$

and

$$\int_{-\infty}^{+\infty} \delta(x)\, \mathrm{d}x = 1.$$

Distribution close to this type can be obtained by anionic polymerization or by fractionation.

I.4. *The Tung distribution*

This distribution is given by:

$$m(p, 0) = \frac{\sigma p^{\sigma - 2}}{u_{n_0}^{\sigma}} \cdot \exp\left[\left(\frac{-p}{u_{n_0}}\right)^{\sigma}\right]. \tag{7}$$

The parameter u_{n_0} is equal to

$$u_n \Gamma\left(\frac{\sigma - 1}{\sigma}\right).$$

The Tung distribution applies to narrow molecular weight distributions

$$\left(\frac{\overline{M}_w}{\overline{M}_n} \leqslant 2\right).$$

Indeed, when σ, defined as

$$\frac{\overline{M}_n}{\overline{M}_w - \overline{M}_n},$$

is less than unity, $m(p, 0)$ becomes infinite at $p = 0$ and this distribution loses its meaning.

I.5. *The Wesslau distribution*

The usual expression obtained from (2) is:

$$m(p, 0) = \frac{1}{\beta\sqrt{\pi}\, p^2} \exp\left(-\frac{1}{\beta^2}\left(\ln \frac{p}{u_m}\right)^2\right). \tag{8}$$

Here β defines the width of the distribution according to:

$$\frac{\overline{M}_w}{\overline{M}_n} = \exp\left(\frac{\beta^2}{2}\right) \tag{9}$$

and

$$u_m = u_n \exp\left(\frac{\beta^2}{4}\right). \tag{10}$$

It applies to polymers with a broad distribution tailing on the high molecular weight side. Such a distribution is obtained if

$$\frac{\bar{M}_n \cdot \bar{M}_z}{\bar{M}_w^2} = 1 \quad \text{and} \quad 1 < \frac{\bar{M}_z}{\bar{M}_w} < \infty. \tag{11}$$

The parameters $\beta/\sqrt{2}$ and u_m can be obtained by plotting the cumulative weight fraction of the polymer as a function of ln p on "probability paper". Obtaining a linear relation is a test for this type of distribution.

II. EFFECT OF DEGRADATION ON THE MOLECULAR WEIGHT DISTRIBUTION AND AVERAGE MOLECULAR WEIGHTS OF POLYMERS

The changes of molecular weight distribution and average molecular weight of degraded polymers result from main chain scissions and/or from the formation of crosslinks between macromolecules. When this last effect is the most important, the molecular weight increases and finally insolubility appears, the fraction of insoluble polymer becoming more important with increasing radiation dose. The yield of crosslinking and chain scission in polymers developing insolubility can be determined by measuring the gel fraction as a function of absorbed doses. These methods have been reviewed [1–4], and will not be considered here. They usually require high irradiation doses and give less information than the study of the changes of molecular weight distribution as a function of absorbed dose before insolubility appears.

In any case, the mode of energy dissipation in the polymer has to be considered. The absorbed energy on irradiation varies in the sample according to:

$$R_x = R_0 \, e^{-kx} \tag{12}$$

where k is the absorption coefficient in cm^{-1}, R_0 and R_x are the energies absorbed at incident surface and at depth x in photons$\cdot g^{-1}$. It is thus inhomogeneous.

When the term kx is very small, the fraction of incident energy absorbed is low and the approximation $R_x \approx R_0$ can be used. Energy dissipation is then homogeneous. Solid polymers undergoing ^{60}Co irradiation and thin films with small absorption coefficient irradiated with u.v. light belong to this category.

In this section, the effect of main chain scission, crosslinking and simultaneous main chain scission and crosslinking on molecular weight distribution and average molecular weight will be considered for different initial molecular weight distributions and the two modes of energy dissipation.

To make it easy to understand this chapter, the following symbols will be used for the average molecular weights and degrees of polymerization:

$\bar{M}_{n_0}$, $\bar{M}_{w_0}$, u_n and u_w for nondegraded polymers
$\bar{M}_n$, $\bar{M}_w$, p_n and p_w for degraded polymers.

II.1. *Theory of main chain scissions*

II.1.1. *Uniform energy dissipation.* If energy is homogeneously absorbed, any polymer of initial molecular weight distribution function $m(p, 0)$ must satisfy the general equation [9–11].

$$\frac{\partial m(p, y)}{\partial y} = -pm(p, y) + 2 \int_p^\infty m(l, y) \, dl \tag{13}$$

where y, the number of scissions per structural unit, is given by:

$$y = p_0 r$$

p_0 is the probability of scission per unit absorbed dose, r is the absorbed dose.

The parameter y is used to calculate the radiochemical yield G_S and the quantum yield ϕ_S given by:

$$G_S = \frac{100 N_A y}{R} \tag{14a} \qquad \phi_S = \frac{N_A y}{R} \tag{14b}$$

where N_A is Avogadro's number and the radiation dose R absorbed in one mole of structural units is expressed in eV (14a) or in Einstein (14b).

Equation (13) gives the variation in the number of molecules having p structural units during the irradiation. The first term of the right hand side corresponds to the decrease of the number of molecules having p structural units owing to chain scission. The second term corresponds to the increase of the number of molecules having p structural units owing to the scission of larger molecules (l initial structural units).

The solution is given by:

$$m(p, y) = e^{-yp}\left[m(p, 0) + y \int_p^\infty (2 + yl - yp) \, m(l, 0) \, dl \right] \tag{15}$$

where $m(p, 0)$ and $m(l, 0)$ depend on the initial distribution. Replacing these parameters by their value for an initial Schulz–Zimm distribution and rearranging give the distribution for the degraded polymer. The number and weight average molecular weights are then easily obtained by integration. Since the random and uniform distribution can be considered as limiting cases of the Schulz–Zimm distribution (see Table 1), the distribution and average molecular weight can then easily be derived for degraded polymers characterized by these initial distributions.

(a) *Initial Schulz–Zimm distribution*

Introducing (3) in (15) gives according to [9]:

$$m(\eta, \rho) = \frac{1}{u_n \eta}\left\{ 2\rho\eta + (1 - \eta)\eta\rho^2 + \frac{1}{\Gamma(\sigma)} \times \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} (\sigma\eta)^{\sigma+k} \cdot C_k \right\} \cdot e^{-\eta\rho} \tag{16}$$

with

$$\eta = \frac{p}{u_n}, \quad \rho = u_n y \tag{17}$$

and

$$C_k = \frac{(\sigma + k)\cdot(\sigma + k + 1) - 2(\sigma + k + 1)\eta\rho + (\eta\rho)^2}{(\sigma + k)\cdot(\sigma + k + 1)}. \tag{18}$$

This gives

$$\bar{M}_n = \frac{\bar{M}_{n_0}}{1 + u_n y} \tag{19}$$

$$\bar{M}_w = \bar{M}_{w_0}\left(u_n y - 1 + \left(1 + \frac{u_n y}{\sigma}\right)^{-\sigma}\right) \times \frac{2\sigma}{(1+\sigma)(u_n y)^2} \tag{20}$$

where $\bar{M}_{n_0}$ and $\bar{M}_{w_0}$ refer to the initial undegraded polymer.

(b) *Initial random distribution*

This initial distribution is characterized by $\sigma = 1$. Introducing this value in (16) gives according to [10]:

$$m(p, y) = \left(\frac{1}{u_n} + y\right)^2 \exp\left[-\left(\frac{1}{u_n} + y\right)p\right] \tag{21}$$

and

$$\bar{M}_n = \frac{\bar{M}_{n_0}}{1 + u_n y} \tag{22}$$

$$\bar{M}_w = \frac{\bar{M}_{w_0}}{1 + u_n y}. \tag{23}$$

(c) *Initial uniform distribution*

Integration of equation (15) gives the following distribution and average molecular weight [9]:

$$m(p, y) = \left(\frac{y}{u_n}\right)\cdot[2 + (u_n - p)y] \times \exp(-py) \quad p < u_n \tag{24}$$

$$= \exp(-u_n y) \quad p = u_n \tag{25}$$

$$= 0 \quad p > u_n \tag{26}$$

$$\bar{M}_n = \frac{\bar{M}_{n_0}}{1 + u_n y} \tag{27}$$

$$\bar{M}_w = 2\,\frac{\bar{M}_{w_0}(e^{-u_n y} - 1 + u_n y)}{(u_n y)^2}. \tag{28}$$

The equations given in Section II.1.1 (a, b and c) show that, *in the case of homogeneous dissipation of energy and random main chain scission, the number average molecular weights depends only on the initial number average molecular weight and on the number of chain scission but not on the initial distribution.* This is however not true for the weight average molecular weight. Radiochemical and quantum yields of scission can thus be obtained by measurement of $\bar{M}_n$ for the degraded polymer without knowing the distribution.

It can also be shown, by introducing different values of σ and different values of $u_n y$ ranging from 1 to 10, that, after 4 to 5 scissions per chain, $\bar{M}_w/\bar{M}_n$ tends to 2 for any initial distribution.

II.1.2. *Non-uniform energy dissipation.* Only the cases of initially random and uniform distributions have been treated.

(a) *Initial random distribution*

In this case, Shultz [12] expresses the distribution as:

$$m(M, y) = \frac{1}{M}\left\{Z\,e^{-Z} + (\ln D)^{-1} Z\,e^{-Z}\left(\sum_{n=1}^{\infty}(-1)^n\frac{(BDZ)^n}{n\cdot n!} - \sum_{n=1}^{\infty}(-1)^n\frac{(BZ)^n}{n\cdot n!}\right) + 2e^{-Z}(\ln D)^{-1}(e^{-BZ} - e^{-BDZ}) + \frac{e^{-Z}}{Z}(\ln D)^{-1} \times [(BZ+1)e^{-BZ} - (BDZ+1)e^{-BDZ}]\right\} \tag{29}$$

where M is the molecular weight of a polymer molecule,

$$Z = \frac{M}{\bar{M}_{n_0}} = \frac{p}{u_n}$$

is the reduced molecular weight,

$$D = e^{-kL}$$

$$B = \phi_S R_0 \bar{M}_{n_0} N_A^{-1}$$

is the number of scissions per chain at the surface of the sample,

$$R_0 = k\,v\,I_0\,t$$

is the absorbed energy at the surface of the film in photons$\cdot$g^{-1},

N_A = Avogadro's number
t = irradiation time,
v = specific volume of the polymer,
k = absorption coefficient (cm^{-1}),
I_0 = incident intensity (photons$\cdot$cm^{-2}, sec^{-1}),
L = film thickness,
ϕ_S = quantum yield of scission.

The average molecular weights of the degraded polymer are:

$$\bar{M}_n = \frac{\bar{M}_{n_0}}{1 + (\ln D)^{-1} B(D-1)} \tag{30}$$

$$\bar{M}_w = \bar{M}_{w_0}\left[1 - (\ln D)^{-1}\ln\left(\frac{1+BD}{1+B}\right)\right]. \tag{31}$$

If the fraction of incident energy absorbed in the sample is low, $kx \ll 1$ in (12) and (30) becomes:

$$\bar{M}_n = \frac{\bar{M}_{n_0}}{1+B} = \frac{\bar{M}_{n_0}}{1 + \phi_S R_0 \bar{M}_{n_0} N_A^{-1}}. \tag{32}$$

This equation is identical to that given for homogeneous energy dissipation.

In the same way, at low optical density, $\bar{M}_w$ reduces to

$$\bar{M}_w = \frac{\bar{M}_{w_0}}{1+B} \tag{33}$$

which is identical to (23).

(b) *Initial uniform distribution*

Jellinek [13] has solved the problem of molecular weight distribution:

$$m(p, y) = -\frac{1}{N_A k L u_n}\left[(u_n - p)\left\{\frac{(1-\alpha)^{p+1}}{p+1} - \frac{(1-\alpha_0)^{p+1}}{p+1} - \frac{(1-\alpha)^p}{p} + \frac{(1-\alpha_0)^p}{p}\right\} - \frac{2}{p}\{(1-\alpha)^p - (1-\alpha_0)^p\}\right] \quad (34)$$

with

$$\alpha = \alpha_0 \, e^{-kL}$$

$$\alpha_0 = \frac{\phi_S \cdot t \, I_0 k}{\mu}$$

μ = the number of monomeric units per cm^3.

The other parameters have been defined in the preceding sections.

The number average molecular weight is in this case:

$$\frac{1}{p_n} = \frac{1}{u_n} + \frac{\phi_S I_0 t}{\mu L}(1 - e^{-kL}) \quad (35)$$

where p_n is the number average degree of polymerization of the degraded polymer.

Rearrangement of this equation yields Eqn. (30). It can be concluded from Section II.1.2 (a and b) that *the number average molecular weight and the yield of main chain scission resulting from the absorption of a given number of quanta are independent of the initial molecular weight distribution but depend on the mode of energy dissipation.*

II.2. *Theory of crosslinking*

II.2.1. *Uniform energy dissipation.* Every distribution must satisfy the following general equation [9, 13]:

$$\frac{\partial m(p, x)}{\partial x} = -2pm(p, x) + \int_0^p l(p - l) \times m(l, x)\, m(p - l, x)\, dl. \quad (36)$$

where $x = \frac{1}{2} q_0 r$ is the number of crosslinks per structural unit formed by absorption of a dose r, q_0 is the probability of formation of one crosslinked unit per unit absorbed dose, r is the absorbed dose.

The first term of the right hand term expresses the decrease, due to crosslinking, in the number of molecules having initially p structural units in their chain. The second term gives the increase in the number of such molecules owing to crosslink formation between molecules having l and $p - l$ units in their chain.

The parameter x is used to calculate the radiochemical yield G_{CL} and the quantum yield ϕ_{CL} for the formation of crosslinks. These are given by:

$$G_{CL} = \frac{100 N_A x}{R} \text{ (a)} \quad \phi_{CL} = \frac{N_A x}{R} \text{ (b)}$$

where N_A is Avogadro's number and the radiation dose R absorbed in one mole of structural units is expressed in eV (a) or in Einstein (b). The solution of this equation has been given by Kimura [15] and Guillet [18]:

$$m(p, x) = \sum_{k=1}^{\infty} \frac{a_k(t)}{(k-1)!} p^{k-1} e^{-(2x+\theta)p} \quad (37)$$

where θ is a parameter to be determined from the initial molecular size distribution, the coefficients $a_k(t)$ being defined by:

$$\frac{d a_k}{dt} = 0 \quad \text{for } k = 1, 2, 3$$

$$= \sum_{i=1}^{k-3} (k - 2 - i)\, a_i a_{k-2-i} \quad \text{for } k \geqslant 4. \quad (38)$$

Equation (37) has been applied to different initial molecular weight distributions. The resulting functions are given below.

(a) *Initial Schulz–Zimm distribution* [15]

$$m(\eta, \xi) = \frac{1}{u_n^2 \eta}\left\{\frac{\sigma^{\sigma+1}}{\sigma!}\eta^{\sigma} + \frac{\sigma^{2\sigma+4}}{(\sigma!)^2} \times \frac{\eta^{2\sigma+2}\xi}{(2\sigma+1)!}\right\} \cdot e^{-\eta(\sigma+2\xi)} \quad (39)$$

with

$$\eta = \frac{p}{u_n} \quad \text{and} \quad \xi = x u_n$$

$$\overline{M}_n = \frac{\overline{M}_{n_0}}{1 - u_n x} \quad (40)$$

$$\overline{M}_w = \frac{\overline{M}_{w_0}}{1 - 2 u_w x}. \quad (41)$$

(b) *Initial random distribution* [15]

The distribution function is obtained by introducing $\sigma = 1$ in Eqn. (39).

$$m(\eta, \xi) = \frac{1}{u_n^2}\left(1 + \frac{1}{3!}\eta^3 \xi\right) \cdot e^{-\eta(1+2\xi)} \quad (42)$$

$\overline{M}_w$ and $\overline{M}_n$ are given by (40) (41).

(c) *Initial uniform distribution* [9, 23]

The distribution of the crosslinked polymer has been derived [23]:

$$m(p, x) = \frac{1}{p}(2px)^{p-1} \frac{e^{-2px}}{p!}. \quad (43)$$

In this case, the degree of polymerization characterized by p is actually p times the initial degree of polymerization. $\overline{M}_w$ and $\overline{M}_n$ are given by (40) (41). The equations given in Section II.2.1 (a, b and c) show that *the values of* $\overline{M}_n$ *and* $\overline{M}_w$ *resulting from crosslinking are independent of the initial molecular weight distribution.*

II.2.2. *Non-uniform energy dissipation.* Only the number and weight average molecular weights for the

initial random distribution have been reported [16]:

$$\overline{M}_n = \frac{\overline{M}_{n_0}}{1 - (\ln D)^{-1} B(D-1)} \tag{44}$$

$$\overline{M}_w = \overline{M}_{w_0} \cdot \left[1 - (\ln D)^{-1} \ln\left(\frac{1 - 4BD}{1 - 4B} \right) \right] \tag{45}$$

with

$$B = \tfrac{1}{2} \phi_C \overline{M}_{w_0} R_0 N_A^{-1}$$

where ϕ_C is the quantum yield for the formation of crosslinked units.

The parameter ϕ_C must not be confused with ϕ_{CL}, the quantum yield for the formation of crosslinks. Both parameters are used in the literature and are related by $\phi_{CL} = \frac{1}{2}\phi_C$.

Equations (44) and (45) reduce to (40) and (41) if $kx \ll 1$ in (12).

II.3. *Theory of simultaneous crosslinking and chain scission*

In this section, we consider the changes in distribution and average molecular weight in systems where crosslinking and chain scission occur at random, independently but both being proportional to radiation dose. These problems are solved by considering that chain scission and crosslinking occur consecutively rather than simultaneously.

II.3.1. *Uniform energy dissipation.*

(a) *Initial Schulz–Zimm distribution*

The distribution is given by Kimura [15]:

$$m(\eta, \xi, y) = \frac{1}{u_n^2 \eta} \left[\frac{\sigma^{\sigma+1}}{\sigma!} \eta^\sigma + \xi \left\{ \frac{\sigma^{2\sigma+4}}{(\sigma!)^2 (2\sigma+1)!} \eta^{2\sigma+2} + 2\lambda \sum_{k=0}^{\infty} \frac{\sigma^{\sigma-k-1}}{(\sigma-k-1)!} \eta^{\sigma-k} \right\} \right] e^{-\eta(\sigma+(\lambda+2)\xi)} \tag{46}$$

with

$$\lambda = \frac{p_0}{q_0} \quad \text{and} \quad \begin{aligned} p_0 &= y/r \\ q_0 &= 2x/r \end{aligned}$$

η and ξ have been defined previously. The number and weight average molecular weights are given by:

$$\overline{M}_n = \frac{\overline{M}_{n_0}}{1 + u_n(y - x)} \tag{47}$$

$$\overline{M}_w = \frac{2\overline{M}_{n_0} \left(u_n y - 1 + \left(1 + \frac{u_n y}{\sigma} \right)^{-\sigma} \right)}{(u_n y)^2 - 4 \left(u_n y - 1 + \left(1 + \frac{u_n y}{\sigma} \right)^{-\sigma} \right) u_n x}. \tag{48}$$

(b) *Initial random distribution*

Introducing $\sigma = 1$ in (46) gives according to [15]:

$$m(\eta, \xi, y) = \frac{1}{u_n^2} \left\{ 1 + \left(2\lambda + \frac{\eta^3}{3!} \right) \xi \right\} \times \exp[-\eta(1 + (\lambda + 2)\xi)] \tag{49}$$

provided y^2 is sufficiently small to be neglected. This gives in any case:

$$\overline{M}_w = \frac{\overline{M}_{w_0}}{1 + u_n(y - 4x)} \tag{50}$$

while $\overline{M}_n$ is given by (47).

(c) *Initial uniform distribution*

In this case

$$\overline{M}_w = \frac{2\overline{M}_{w_0}(e^{-u_n y} + u_n y - 1)}{(u_n y)^2 - 4u_n x(e^{-u_n y} + u_n y - 1)}. \tag{51}$$

The expression of $\overline{M}_n$ is (47) while $m(\eta, \xi, y)$ has not been derived.

It can thus be concluded from section II.3.1 (a, b and c) that the values of $\overline{M}_n$ *resulting from simultaneous crosslinking and chain scission is independent of the initial molecular weight distribution while* $\overline{M}_w$ *depends on it.*

II.3.2. *Non-uniform energy dissipation.* Only $\overline{M}_n$ and $\overline{M}_w$ have been derived in the case of initially random distribution [16]:

$$\overline{M}_n = \frac{\overline{M}_{n_0}}{1 + (\ln D)^{-1} B(D-1)} \tag{52}$$

$$\overline{M}_w = \overline{M}_{w_0} \left\{ 1 - (\ln D)^{-1} \ln\left(\frac{1 + B^* D}{1 + B^*} \right) \right\} \tag{53}$$

with

$$D = e^{-kL}$$
$$B = (\phi_S - \tfrac{1}{2}\phi_C)\overline{M}_{n_0} R_0 N_A^{-1}$$
$$B^* = (\tfrac{1}{2}\phi_S - \phi_C)\overline{M}_{w_0} R_0 N_A^{-1}$$

R_0 is the absorbed energy at the surface of the film in photons $\cdot g^{-1}$.

Equations (52) and (53) allows ϕ_S and ϕ_C to be determined. They reduce to (47) and (50) if $kx \ll 1$ in (12).

II.4. *Conclusion*

When main chain scissions only are involved, $\overline{M}_n$ is independent of the initial molecular weight distribution. If molecular weight changes are due to crosslinking only, both $\overline{M}_n$ and $\overline{M}_w$ are independent of the initial distribution. As a consequence, when chain scission and crosslinking occur, only $\overline{M}_n$ is independent of the initial distribution. In all cases, the law of energy dissipation has to be taken into account. According to this, the yield of crosslinking or chain scission can thus be determined without knowing the initial distribution provided only one of these processes occurs. If both effects occur, the initial distribution has to be known to obtain these parameters. It is also important to realize that in the case of inhomogeneous energy dissipation the relative variations in $\overline{M}_n$ or $\overline{M}_w$ are smaller than in the homogeneous case for a given average number of scissions or crosslinks per chain.

Indeed, according to the optical density of the film, its superficial part is mainly affected by scissions and crosslinks while the remainder of the sample is almost unaffected by the radiation.

III. EXPERIMENTAL RESULTS

Some of the equations developed in the preceding Section will be applied to the radiolysis and photolysis of polystyrene *in vacuo*.

In the radiolysis, energy dissipation is homogeneous when ^{60}Co is used as source of γ-rays. The radiochemical yields for crosslinking and chain scission have been determined by various methods [1–4]. Some involve molecular weight measurements by sedimentation or light scattering for absorbed doses lower than the gelling dose; others are based on the measurement of the gel fraction. In the photolysis, energy dissipation is often inhomogeneous; fewer quantitative data on scission and crosslinking are available [5].

In the present work, radiochemical yields for the degradation of polystyrene are determined using number and weight average molecular weights obtained by GPC to test the applicability of this method, by comparison with published results. Also, the molecular weight distribution of the initial polymer is compared with the theoretical relations given in Section II. The molecular weight distributions and average molecular weights are then determined for thin films of polystyrene irradiated with light of 253.7 nm. Energy dissipation is inhomogeneous in this case. To our knowledge, this system has not been studied by other methods either below or above the gel point.

III.1. *Non-degraded polystyrene*

Polystyrene was obtained by free radical polymerization initiated by AIBN at 60° of carefully purified and outgassed monomer, with conversion limited to 50%. The polymer was purified by successive dissolutions in benzene and precipitations in methanol followed by drying at 60°C in vacuo to constant weight. The GPC experiments were done using a Waters 200 apparatus fitted with $3.10^6 - 5.10^5 - 10^5 - 2.5\ 10^4$ and 10^3 Å Styragel columns operating at 80° with toluene as solvent. Careful calibration of this system was carried out using 11 polystyrene standards of molecular weight ranging from 2.10^3 to $5.9\ 10^6$ supplied by Waters. Reproducibility was excellent when the same polymer was analyzed using the same column set and calibration curve. The values of $\overline{M}_n$ and $\overline{M}_w$ obtained for the same polymer using different temperatures and sets of columns are very good (Table 2). The average molecular weights were calculated using a CDC 6400 computer. Correction for dispersion in the columns does not significantly affect the yields of crosslinking and chain scission and the distribution. The experimental distribution of the non-degraded initial polymer is compared with the theoretical random. Schulz–Zimm and Wesslau distributions in Fig. 1. Departure from random and Schulz–Zimm distribution is not very important. For free radical polymerization of styrene limited to very low conversion, the theoretical value of $\overline{M}_w/\overline{M}_n$ is 1.5 and the distribution of the Schulz–Zimm type. In the present case however, the conversion is rather high (50%) and the purification procedure has altered the molecular weight distribution. This justifies the small departure from the theoretical distributions reported in Fig. 1. Since the experimental initial distribution does not fit exactly any of these distributions, the experimental results will be analyzed according to the equation derived for an initial random distribution.

III.2. *Radiolysis of polystyrene*

Polystyrene powder was irradiated in sealed bulbs *in vacuo* with a Gammacell 200 at a dose rate of 0.57 Mrad hr^{-1}. The molecular weight distributions obtained for typical samples are given in Table 3 and Fig. 2. These normalized curves clearly indicate an important increase in the high molecular weight fraction and, at low dose, some increase in the low molecular weight fraction. The ratios $\overline{M}_{n_0}/\overline{M}_n$ and $\overline{M}_{w_0}/\overline{M}_w$ plotted as a function of dose according to Eqns. (47) and (50) are given in Fig. 3 a and b. Linearity predicted by these equations is verified for $\overline{M}_{w_0}/\overline{M}_w$ but not for $\overline{M}_{n_0}/\overline{M}_n$.

Extrapolation of $\overline{M}_{w_0}/\overline{M}_w$ to zero value gives the gelling dose. The slope of Fig. 3b gives $(y - 4x)$ according to (50), but simultaneous verification of (47) is necessary to obtain x and y. The departure from linearity of $\overline{M}_{n_0}/\overline{M}_n$ can reasonably be assigned to a change in the relative importance of crosslinking and chain scission as a function of dose. Chain scissions are indeed only apparent at low dose in the distribution curve (Fig. 2). They can be due to preferential breaking of weak links, perhaps peroxy groups incorporated in the chain during the polymerization owing to the presence of minute quantities of oxygen. In any case, the number of these weak links is very low since 0.1 breaking per chain are counted if Eqns. (47) and (50) are applied to the average molecular weights of a sample that has absorbed 32.6 Mrad. If the least square straight line (excluding the point for 32.6 Mrad) is considered in Fig. 3 a and used to calculate x and y in conjunction with Fig. 3 b, values of

Table 2. Average molecular weights of the initial polymer obtained with different sets of columns

Experimental conditions	Columns	T°C	$\overline{M}_n \cdot 10^{-5}$	$\overline{M}_w \cdot 10^{-5}$	$\overline{M}_w/\overline{M}_n$
1	$3\cdot10^6 - 5\cdot10^5 - 10^5$ $2.5\cdot10^4 - 10^3$	78	1.74	3.30	1.90
2	$3\cdot10^6 - 5\cdot10^5 - 10^5$ $2.5\cdot10^4 - 10^3$	60	1.75	3.33	1.91
3	$3\cdot10^6 - 5\cdot10^5 - 10^5$ $3\cdot10^4 - 10^4$	80	1.73	3.31	1.90
4	$3\cdot10^6 - 5\cdot10^5 - 10^5$ $2.5\cdot10^4$	80	1.77	3.36	1.90

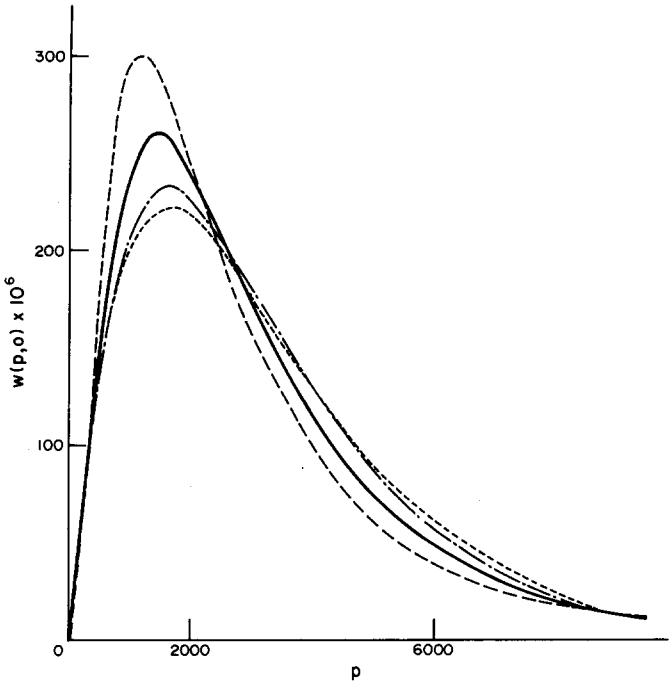

Fig. 1. —— Experimental weight distribution of non-degraded polystyrene—$\overline{M}_n$ = 173,000, $\overline{M}_w$ = 331,000; ------- Theoretical random distribution for the same $\overline{M}_n$; -·-·-·-·- Theoretical Schulz–Zimm distribution for the same $\overline{M}_n$ and σ = 1.1; ----- Theoretical Wesslau distribution for the same $\overline{M}_n$ and $\overline{M}_w$ (normalized curves).

0.0174 and 0.0012 are respectively obtained for the yields of crosslinks G_{CL} and of chain scission G_S. These values agree excellently with those obtained by light scattering [17] and sedimentation [18] methods. In the present case however, the molecular weight of crosslinked molecules is an apparent molecular

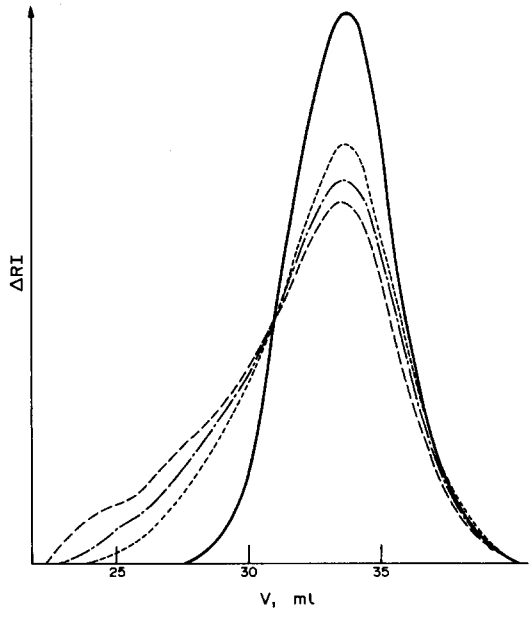

Fig. 2. Elution curves of γ irradiated polystyrene (normalized curves) —— initial polymer*; ------ 32.6 Mrad; -·-·-· 41.8 Mrad; ----- 50.9 Mrad; ΔRI = differential refractive index. * Refers to Table 3.

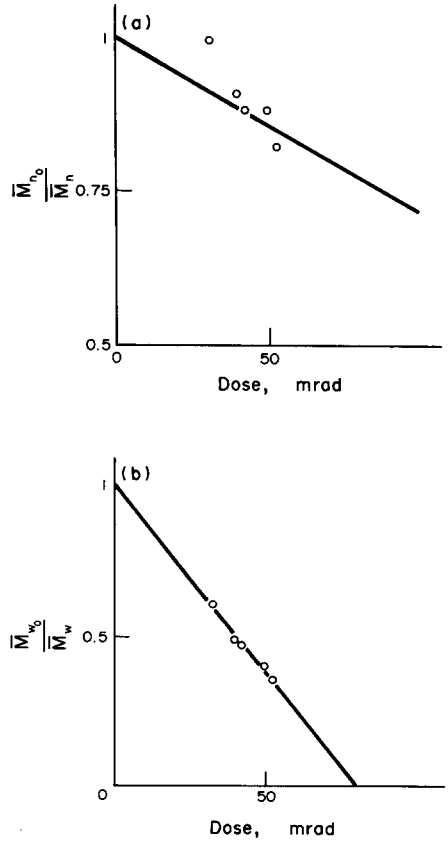

Fig. 3. Variation of the average molecular weight of γ irradiated polystyrene as a function of absorbed dose.

Table 3. Radiolysis of polystyrene

Absorbed dose Mrad	32.6	39.5	41.8	49.7	50.9
$\overline{M}_n \cdot 10^{-5}$	1.78	1.95	2.01	2.01	2.15
$\overline{M}_w \cdot 10^{-5}$	5.47	6.91	7.10	8.65	9.35
$\overline{M}_w/\overline{M}_n$	3.08	3.54	3.54	4.30	4.38

* Experimental conditions 4 in Table 2—$\overline{M}_{n_0} = 177{,}000$ $\overline{M}_{w_0} = 336{,}000$.

weight, deduced from GPC calibration curves obtained with linear macromolecules whereas sedimentation and light scattering take branching into account. The present result proves that $\overline{M}_n$ and $\overline{M}_w$ obtained from GPC, although underestimating crosslinking, does not significantly alter the results at low dose (i.e. corresponding to less than 0.6 crosslinked units per weight average molecule) in agreement with the theoretical treatment of Shultz [19]. This author has calculated correction factors for $\overline{M}_w$ and $\overline{M}_n$ to take crosslinking into account. If the exponent of the Mark–Houwink equation is 0.74 for polystyrene in toluene at 80° [24] and the absorbed dose corresponds to 0.6 crosslinked unit per chain, the data of Shultz [19] give:

$$\frac{\overline{M}_n}{\overline{M}_{n\,real}} = 1.04 \quad \text{and} \quad \frac{\overline{M}_w}{\overline{M}_{w\,real}} = 1.24$$

If the yield of crosslinks G_{CL} is calculated by introducing $\overline{M}_{n\,real}$ and $\overline{M}_{w\,real}$ in equations (47) and (50), the value obtained is 0.015 whereas it is 0.017 without correction.

III.3. *Photolysis of polystyrene at 253.7 nm*

In this case, energy dissipation is inhomogeneous and consequently the variation in the molecular weight distribution with the number of crosslinks per average molecule is much lower than in the case of homogeneous energy dissipation except in the neighbourhood of the gelling dose. Figure 4 and Table 4 demonstrate the presence of chain scissions at low doses while crosslinks only are formed for irradiation times larger than 15 min. An insoluble gel fraction finally appears.

The experimental values of $\overline{M}_n$ and $\overline{M}_w$ are given in Table 4. $\overline{M}_{n_0}/\overline{M}_n$ and $\overline{M}_{w_0}/\overline{M}_w$ must satisfy Eqns. (52) and (53) and consequently decreases with irradiation time for systems with predominant crosslinking. However, an increase in $\overline{M}_{n_0}/\overline{M}_n$ is observed at low doses, indicating that Eqn. (52) is not verified. Concerning Eqn. (53), the values of B^* calculated for the different irradiation times are not constant although $\overline{M}_{w_0}/\overline{M}_w$ decreases. This means that the ratio of chain scission to crosslinking changes as a function of dose, scission being more important at low doses. As in the preceding case, these scissions can be assigned to rupture of weak peroxide links. It has been shown independently that energy transfer to hydroperoxides and thus also probably to peroxides is very efficient in polystyrene [20]. Furthermore, selective breaking of weak links has also been reported in the thermal degradation of polystyrene [21].

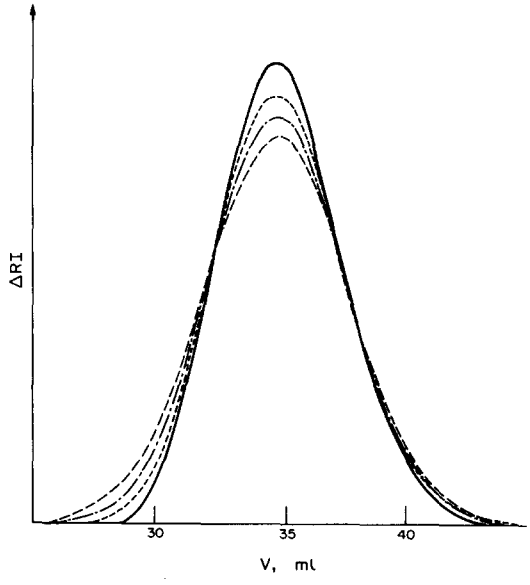

Fig. 4. Elution curves of u.v. irradiated polystyrene (normalized curves) —— initial polymer; ------ 30 min.*; —·— 60 min.*; – – – 112 min.*. *Refers to Table 4.

Table 4. Photolysis of polystyrene at 253.7 nm*

Irradiation time	7′ 30″†	15′†	15′‡	30′‡	60′‡	112′†	112′‡
absorbed dose $E \cdot g^{-1} \cdot 10^6$	4.1	9.2	11.2	22.4	43.7	85.6	78.0
$\overline{M}_n \cdot 10^{-5}$	1.57	1.48	1.44	1.53	1.63	1.72	1.71
$\overline{M}_w \cdot 10^{-5}$	3.16	3.01	3.00	3.36	3.69	3.90	3.97
$\overline{M}_w/\overline{M}_n$	2.01	2.03	2.08	2.19	2.26	2.27	2.32

* A low pressure Philips TUV 15 W tube was used. Incident intensity at 5 cm: $4.44\ 10^{-7}$ $E \cdot min.^{-1} \cdot cm^{-2}$.

† Experimental conditions 2 in Table 2—$\overline{M}_{n_0} = 175{,}000$, $\overline{M}_{w_0} = 333{,}000$.

‡ Experimental conditions 3 in Table 2—$\overline{M}_{n_0} = 173{,}000$, $\overline{M}_{w_0} = 331{,}000$.

These results show that GPC is very useful to demonstrate qualitatively a variation in the mechanism of photolysis of a polymer even for very inhomogeneous degradation.

In this last case indeed, the relative variation of $\overline{M}_n$ and $\overline{M}_w$ corresponding to a given average number of crosslinks per chain is much less important than for homogeneous energy dissipation except in the vicinity of the gel point. An estimation of the order of magnitude of the quantum yield of photocrosslinks of polystyrene can be obtained from the $\overline{M}_w$ values corresponding to 30, 60 and 112 min assuming that chain scissions are negligible. This gives $\phi_{CL} = 1 \cdot 10^{-5}$ in agreement with the low yield of H_2 formation [22].

IV. CONCLUSION

Gel permeation chromatography is the most powerful method to demonstrate the occurrence of one or various mechanism of molecular weight changes due to polymer degradation even in superficially degraded samples. Accurate quantitative determination of the yields of these transformations is, however, difficult if more than one mechanism is involved in the alteration of the molecular weight distribution. Indeed, if crosslinking and chain scission occur as concurrent processes, the equations to be used to calculate the yields depend on the initial molecular weight distribution and this does not often correspond for commercial polymers to the usual random, uniform, Schulz–Zimm or Wesslau distributions.

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Résumé—Les théories statistiques de la réticulation et des ruptures de chaînes résultant d'absorption d'énergie soit homogène, soit inhomogène sont résumées. La distribution des masses moléculaires de polystyrène dégradé sous vide au moyen de rayonnement γ (absorption homogène) ou u.v. (absorption inhomogène) a été mesurée par GPC en fonction de la dose absorbée. Les résultats sont discutés en fonction de ces théories.