Eur. Polym. J. Vol. 25, No. 9, pp. 917–924, 1989
Printed in Great Britain

0014-3057/89 $3.00 + 0.00
Pergamon Press plc

CHARACTERIZATION BY LIGHT SCATTERING OF SIMULTANEOUS POLYMER CHAIN SCISSION AND CROSS-LINKING PROCESSES

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(*Received* 13 *May* 1988; *in revised form* 7 *November* 1988)

Abstract—The results of investigations on the changes in molecular parameters, viz. the average molecular weights, $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_z$; the poly-dispersities $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$; and the translational diffusion coefficient, $\bar{D}_{0z}$, are presented for a polymer sample undergoing simultaneous chain scission and cross-linking. The calculations were carried out within the framework of the model of Saito and Inokuti. The values of $\bar{D}_{0z}$ were calculated by the use of the cascade substitution technique. The results of calculations were compared with the experimental results obtained by the light scattering method for polystyrene samples exposed to u.v. radiation with wavelength $\geqslant 270$ nm in degassed solutions containing CCl_4 and $CHCl_3$. Analysis of the results leads to conclusions about the usefulness of the measurement of individual molecular parameters for the detection and characterization of simultaneous chain scission and cross-linking.

INTRODUCTION

During the past decade, the development of theoretical methods such as the cascade substitution technique [1, 2] or the renormalization group methods [3, 4] have allowed calculation of a series of molecular parameters characteristic of a macromolecule in solution for various macromolecular models [2, 5–8]. In some cases, these calculations make it possible to determine the model of the macromolecule in solution specific for a given sample (e.g. a rigid, cross-linked, variously branched macromolecule) if the measurement yields the values of the average molecular parameters [2, 8].

In investigations of polymer photodegradation, a single molecular parameter is frequently measured, e.g. the number-average molecular weight, $\bar{M}_n$, determined by osmometry [9], the weight-average molecular weight, $\bar{M}_w$, obtained by light scattering [10, 11], or the viscosity average molecular weight, $\bar{M}_v$, obtained from viscometric measurements [12]. In certain cases, methods enabling the determination of the molecular weight distribution $w(M)$ of a degraded sample are employed [13, 14].

As shown in the present paper, it is improper to draw conclusions on the macromolecular structure or its changes based on measurement of one average molecular parameter. In our previous papers [15–17], investigations on polystyrene (PS) photodegradation in degassed solutions containing carbon tetrachloride and chloroform were reported. As has been shown [17], the simultaneous processes of chain scission and cross-linking or branching of polystyrene macromolecules take place in these solutions. It has been found that, for a given ratio of the rates of these processes (scission and cross-linking), some average molecular parameters are practically constant despite considerable changes in the molecular weight distribution function $w(M)$. Thus, investigation on the changes in macromolecular structure in such systems is not reliable unless the full molecular weight distribution function is determined experimentally. The functions $w(M)$ given in the present paper were determined by use of the joint methods of elastic and quasi-elastic light scattering (ELS and QLS) already described in detail [15, 18].

THEORETICAL SECTION

Use of the joint ELS and QLS methods in investigations of polymer solutions offers the possibility of determining a number of molecular parameters enabling the macromolecules to be characterized. These parameters include:

$\bar{M}_n$—number-average molecular weight,
$\bar{M}_w$—weight-average molecular weight,
$\bar{M}_z$—z-average molecular weight,
$w(M)$—molecular weight distribution function

and

$\bar{D}_{0z}$—average value of the translational diffusion constant of a macromolecule related strictly to the diffusion average molecular weight $\bar{M}_D$.

For a polydisperse polymer sample, the average values, $\bar{X}_m$, of molecular parameters are used. The average values $\bar{X}_m$ of any parameter $X(M)$ depending on the molecular weight, M, are defined using the weight molecular weight distribution function $w(M)$, when $w(M)\,dM$ is the weight fraction of molecules with molecular weight between M and $(M + dM)$. The following normalization condition results from the above definition of the function $w(M)$:

$$\int_0^{\infty} w(M)\,\mathrm{d}M = 1. \tag{1}$$

Then, the average value $\bar{X}_{\mathrm{m}}$ can be defined as an $(m-1)$-normalized moment of parameter $X(M)$ relative to the distribution function $w(M)$ [19]:

$$\bar{X}_{\mathrm{m}} = \frac{\int_0^{\infty} M^{m-1}X(M)w(M)\,\mathrm{d}M}{\int_0^{\infty} M^{m-1}w(M)\,\mathrm{d}M} \tag{2}$$

in particular, the average values of molecular weight are termed as follows: $\bar{M}_{\mathrm{n}}$, for $m = 0$; $\bar{M}_{\mathrm{w}}$, for $m = 1$; and $\bar{M}_z$, for $m = 2$.

When the macromolecules undergo the process of random chain scission (without cross-linking); the distribution function $w(M, x_k)$ can be represented by the following formula due to Saito [20]:

$$w(M, x_k) = \exp\left(\frac{-Mx_k}{\bar{M}_{\mathrm{n}}(0)}\right) \times \left[w_0(M) + \frac{2x_k}{\bar{M}_{\mathrm{n}}(0)} \times \int_M^{\infty} w_0(M)\,\mathrm{d}M + \left(\frac{x_k}{\bar{M}_{\mathrm{n}}(0)}\right)^2 \times \int_M^{\infty}\int_{M_1}^{\infty} w_0\,\mathrm{d}M_1\,\mathrm{d}M_2\right], \tag{3}$$

where

x_k = the average number of polymer chain scissions per initial macromolecule of an undegraded polymer with weight $\bar{M}_{\mathrm{n}}(0)$

and

$w_0(M)$ = the initial molecular weight distribution of an undegraded sample.

When simultaneous chain scission and cross-linking occur under the assumption that:

(a) the initial weight distribution $w_0(M)$ is described by the Schulz–Zimm equation [21],

$$w(M) = \frac{bp^p}{\Gamma(p+1)}(t\,\mathrm{e}^{-t})^p, \tag{4}$$

where

$t = M/\bar{M}_{\mathrm{n}}$,

$\Gamma(x)$ = the Euler gamma function

and

b, p = the parameters related to the average molecular weights by $\bar{M}_{\mathrm{n}} = p/b$, $\bar{M}_{\mathrm{w}} = (1+p)/b$, $\bar{M}_z = (2+p)/b$;

(b) the ratio of the rates of chain scission and cross-linking remains constant, the following equations describing the changes in $\bar{M}_{\mathrm{m}}$ and the polymerization degrees, $\bar{N}_{\mathrm{m}}$, as functions of parameters x_k and y are obtained [22]:

$$\frac{\bar{N}_{\mathrm{n}}(x_k, y)}{\bar{N}_{\mathrm{n}}(0)} = \frac{\bar{M}_{\mathrm{n}}(x_k, y)}{\bar{M}_{\mathrm{n}}(0)} = \frac{1}{1 + x_k - y}, \tag{5}$$

$$\frac{\bar{N}_{\mathrm{w}}(x_k, y)}{\bar{N}_{\mathrm{w}}(0)} = \frac{\bar{M}_{\mathrm{w}}(x_k, y)}{\bar{M}_{\mathrm{w}}(0)} = \frac{pf_2(x_k)}{(p+1)[1 - 2yf_2(x_k)]} \tag{6}$$

and

$$\frac{\bar{N}_z(x_k, y)}{\bar{N}_z(0)} = \frac{\bar{M}_z(x_k, y)}{\bar{M}_z(0)} = \frac{pf_3(x_k)}{(p+2)[1 - 2yf_2(x_k)]^2 f_2(x_k)}, \tag{7}$$

where

$$f_2(x_k) = \frac{2}{x_k}\left\{1 - \frac{1}{x_k}\left[1 - \left(1 + \frac{x_k}{p}\right)^{-p}\right]\right\} \tag{8}$$

and

$$f_3(x_k) = \frac{6}{x_k^2}\left\{1 + \left(1 + \frac{x_k}{p}\right)^{-(p+1)} - \frac{2}{x_k}\left[1 - \left(1 + \frac{x_k}{p}\right)^{-p}\right]\right\}. \tag{9}$$

In these equations, the parameters x_k and y denote the number of polymer chain scissions and cross-links, respectively, per initial macromolecule with weight $\bar{M}_{\mathrm{n}}(0)$.

The following relation between the average translational diffusion constant, $\bar{D}_{0z}$, of a macromolecule and the average diffusive molecular weight, $\bar{M}_{\mathrm{D}}$, apply to a polydisperse polymer sample [19]:

$$\bar{D}_{0z} = K_{\mathrm{D}}\bar{M}_{\mathrm{D}}^{-\gamma}. \tag{10}$$

The constants K_{D} and γ in this formula depend on a defined polymer–solvent system and can be determined experimentally by measuring the translational diffusion constant D_0 for a number of monodisperse polymer samples in a given solvent [19, 23, 24]. Given the value of the parameter γ and the molecular weight distribution $w(M)$ for a polydisperse polymer sample, the average diffusive molecular weight, $\bar{M}_{\mathrm{D}}$, can be calculated employing the following equation:

$$\bar{M}_{\mathrm{D}} = \left(\bar{M}_{\mathrm{w}} \Big/ \int_0^{\infty} M^{1-\gamma}w(M)\,\mathrm{d}M\right)^{1/\gamma} \tag{11}$$

Equation (10) is analogous to the Mark–Houwink–Sakurada equation [19] describing the relation between the intrinsic viscosity $[\eta]$ and the viscosity average molecular weight, $\bar{M}_\eta$, of a polymer in solution:

$$[\eta] = K_\eta \bar{M}_\eta^{\alpha}. \tag{12}$$

The exponents γ and α in equations (10)–(12) are related by the so-called Scheraga–Mandelkern equation [25]:

$$\gamma = (\alpha + 1)/3. \tag{13}$$

The constants K_η and α depend on the chemical composition and structure of the macromolecules, as well as on the thermodynamic quality of the solvent for a given polymer, and are most frequently determined by experiment.

The present paper gives an analysis of the theoretical values of relative changes in the diffusion constant, $\bar{D}_{0z}$, relating to PS macromolecules undergoing chain scission and cross-linking $[\bar{D}_{0z}(x_k, y)]$, as well as to the macromolecules of the initial polymer sample $[\bar{D}_{0z}(0)]$. The values of $\bar{D}_{0z}(x_k, y)/\bar{D}_{0z}(0)$ were calculated with the additional assumption that the macromolecues were built of flexible chains and the average distance between two segments could be approximated by the Gaussian function. The latter assumption can be roughly satisfied for a "theta" solution [2]. According to the above assumptions, the values of $\bar{D}_{0z}$ of the macromolecules can be given by the following equation [2]:

$$\bar{D}_{0z} = \frac{kT \int_0^{\infty} \bar{P}_z(q, x_k, y)\, dq}{3\pi^2 \eta_0}, \qquad (14)$$

where

$q = \frac{4\pi\tilde{n}}{\lambda_0} \sin\frac{\theta}{2}$,

$\tilde{n}$ = the refractive index of the solvent,
λ_0 = the wavelength of the incident light,
θ = the angle of light scattering,
k = the Boltzmann constant,
T = temperature,
η_0 = the solvent viscosity

and

$\bar{P}_z(q, x_k, y)$ = the z-average of the scattering function for a given polymer sample.

The average value $\bar{P}_z(q, x_k, y)$ for a polymer subjected to chain scission and cross-linking can, according to the results of the cascade substitution procedure [2], be determined from the following equation:

$$\bar{P}_z(q, x_k, y) = \frac{(1 + \beta\phi)\bar{N}_w(x_k)\bar{P}_z(q, x_k)}{\bar{N}_w(x_k, y)\{1 - \beta[\bar{N}_w(x_k)\bar{P}_z(q, x_k,) - 1]\}}, \qquad (15)$$

where

$\beta = y/\bar{N}_n(x_k)$,

$\phi = \exp(-a^2q^2/6)$.

$\bar{N}_w(x_k)$, $\bar{N}_n(x_k)$ = average (weight and number) polymerization degree of a polymer sample determined from formulae (5)–(9) when only chain scission is taken into account,
$\bar{N}_w(x_k, y)$ = weight-average polymerization degree determined by equation (6), taking into account both chain scission and cross-linking

and

a = the length of the Kuhn segment.

Quantity $\bar{P}_z(q, x_k)$ in equation (15) is the z-average scattering function in which cross-linking has not been taken into account, i.e. refers to the polymer sample with molecular weight distribution, $w(N, x_k)$, which was determined from equation (3). $\bar{P}_z(q, x_k)$ can be expressed thus:

$$\bar{P}_z(q, x_k) = \frac{1}{\bar{N}_w(x_k)} \int_0^{\infty} P(q)\bar{N}_w(N, x_k)\, dN, \qquad (16)$$

where

$$P(q) = \frac{2}{u^2}(e^{-u} + u - 1)$$

is the Debye scattering function and $u = a^2q^2N/6$; N is the number of segments in the macromolecular chain with weight M and the weight M_s of the segment so that $N = M/M_s$.

Finally, the values of the changes in $\bar{D}_{0z}$ were determined for the samples under investigation from the following equation:

$$\frac{\bar{D}_{0z}(x_k, y)}{\bar{D}_{0z}(0)} = \frac{\int_0^{\infty} \bar{P}_z(q, x_k, y)\, dq}{\bar{N}_w(x_k, y) \int_0^{\infty} \bar{P}_z(q)\, dq}, \qquad (17)$$

where

$\bar{P}_z(q, x_k, y)$ was found according to (15),
$\bar{P}_z(q)$ from equation (16) with $x_k = 0$

and

$\frac{\bar{N}_w(x_k, y)}{\bar{N}_w(0)}$ from equation (6).

EXPERIMENTAL PROCEDURES

Characteristics of the samples investigated

A polydisperse atactic PS sample with $\bar{M}_w = 976{,}000$ g/mol and $\bar{M}_w/\bar{M}_n = 2.71$ was used. The PS samples were irradiated in degassed solutions containing CCl_4 and $CHCl_3$, at 294 K [15, 16]. The concentration of the irradiated solutions was 0.025 kg/l corresponding to a PS mer concentration of 0.240 mol/l. Prior to irradiation, the solutions were degassed by freezing [16] by means of apparatus enabling a pressure of $p < 10^{-3}$ Tr to be attained. PS was recovered from the irradiated solutions by precipitation with methanol. The precipitate was washed with methanol, and dried as already described in [15, 16]. The irradiated PS samples thus obtained were investigated by the joint method of integral and dynamic light scattering [15]. The particulars of the characteristics and preparation of the PS samples and solutions have been reported [16].

Method of the irradiation of polymer solutions

The method of irradiation of the polymer solutions has been described [15, 16, 26]. The PS solutions were irradiated with wavelengths of $\lambda_0 \geq 270$ nm emitted by four high-pressure Q700 type Hg lamps (Hanau, F.R.G.). The detailed characteristics of this radiation have been given [26, 27].

Measurement of the weight distribution function

The results of investigations on the changes in $w(M)$ and $\bar{D}_{0z}$ of the irradiated PS samples relative to those of the initial polymer are reported. The changes in $w(M)$ and constant $\bar{D}_{0z}$ result from the irradiation of PS for times ranging from 0 to 40 hr in degassed solutions with CCl_4 and $CHCl_3$. The $w(M)$ and $\bar{D}_{0z}$ were determined for all the PS samples by the joint ELS and QLS method [16, 28–30] in three solvents, viz. methyl ethyl ketone (MEK), chloroform and *trans*-decalin. Full agreement of the functions $w(M)$ determined experimentally was obtained for these solvents. The accuracy of the measurement of $w(M)$ has been discussed [18]. The measure of this accuracy can be represented by the mean-square error which, for the polymer samples with values of $\bar{M}_w/\bar{M}_n$ close to those of the PS sample, is estimated to be about 4%. The functions $w(M)$ were obtained experimentally with an accuracy of about 8% for $\bar{M}_n$ and 5% for $\bar{M}_w$. The procedures for measurements and calculations of these quantities have been described in detail [16, 18, 29].

RESULTS AND DISCUSSION

The investigations of $w(M)$ of the polymer samples are fundamental in determining the changes in the macromolecular structure. The accuracy of the determination of parameters K_D and γ ocurring in equation (10) is of essential importance in these

Table 1. Relative changes in the average molecular quantities of the polystyrene samples as functions of the irradiation time in solutions containing CCl_4 and $CHCl_3$

Irradiated sample	Irradiation time t [h]	$\frac{\bar{M}_n(t)}{\bar{M}_n(t=0)}$ 1	$\frac{\bar{M}_w(t)}{\bar{M}_w(t=0)}$ 2	$\frac{\bar{M}_z(t)}{\bar{M}_z(t=0)}$ 3	$\frac{\bar{D}_{0z}(t)}{\bar{D}_{0z}(t=0)}$ 4	$\frac{\bar{M}_D(t)}{\bar{M}_D(t=0)}$ 5	$\frac{\bar{M}_w(t)}{\bar{M}_n(t)}$ 6	$\frac{\bar{M}_z(t)}{\bar{M}_w(t)}$ 7
PS in CCl_4	0	1.00	1.00	1.00	1.00	1.00	2.71	1.63
	5	0.99	0.99	1.02	1.00	0.99	2.73	1.67
	10	0.70	0.77	0.98	1.16	0.95	2.97	2.08
	20	0.45	0.57	0.94	1.20	0.78	3.41	2.67
	40	0.15	0.25	0.57	1.88	0.44	4.41	3.77
PS in $CHCl_3$	0	1.00	1.00	1.00	1.00	1.00	2.71	1.63
	5	0.99	0.99	1.02	0.99	0.99	2.73	1.67
	10	0.81	0.76	0.79	1.16	0.75	2.55	1.70
	20	0.49	0.64	0.85	1.20	0.73	2.95	2.16
	40	0.27	0.42	0.94	1.45	0.65	4.25	3.62

The values of the average molecular quantities for the initial non-irradiated polystyrene sample are: $\bar{M}_n(t=0) = 3.60 \times 10^5$ g/mol; $\bar{M}_w(t=0) = 9.76 \times 10^5$ g/mol; $\bar{M}_z(t=0) = 15.90 \times 10^5$ g/mol; $\bar{D}_{0z}(t=0) = 1.107 \times 10^{-7}$ cm^2/sec.

studies. As is already known [23], the change in the geometry of macromolecules, with fixed chemical composition, does not affect the value of parameter γ, whereas it can influence the value of K_D [equation (10)]. The values of K_D for the irradiated PS samples indicate, however, slight changes within experimental error [15]. Also the weight distribution functions, identical within experimental error, obtained from the measurements for the irradiated and non-irradiated PS samples in three solvents (*trans*-decalin, MEK, $CHCl_3$) confirm that the assumed values of K_D are correct [15, 17].

The values of $\bar{D}_{0z}$, measured for the PS samples, were compared with those calculated from equation (10), where $\bar{M}_D$ was found from equation (11) using the measured molecular weight distribution functions $w(M)$. The experimental values of $\bar{D}_{0z}$ agree with those calculated from equation (10) with an accuracy better than 5%, which confirms the correctness of the measurement of the weight distribution functions

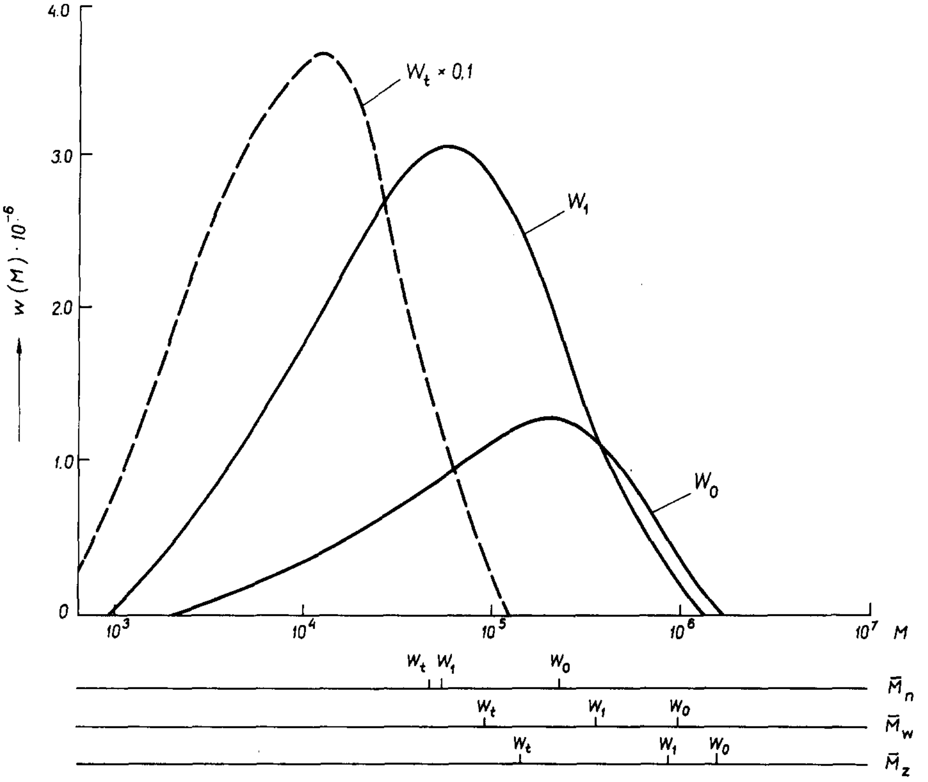

Fig. 1. Weight molecular weight distribution functions $w(M)$ determined experimentally [$w_0(M)$—for non-irradiated PS sample; $w_1(M)$—for PS irradiated in CCl_4 for 40 hr] and the distribution function $w_t(M)$ calculated for polystyrene irradiated for 40 hr in CCl_4 without considering cross-linking. The values of $w_t(M)$ are decreased ten-fold in the figure, $w_t(M) \times 0.1$. At the bottom of the figure, the values of $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_z$, determined from the respective molecular weight distribution functions, w_0, w_1 and w_t, have been marked.

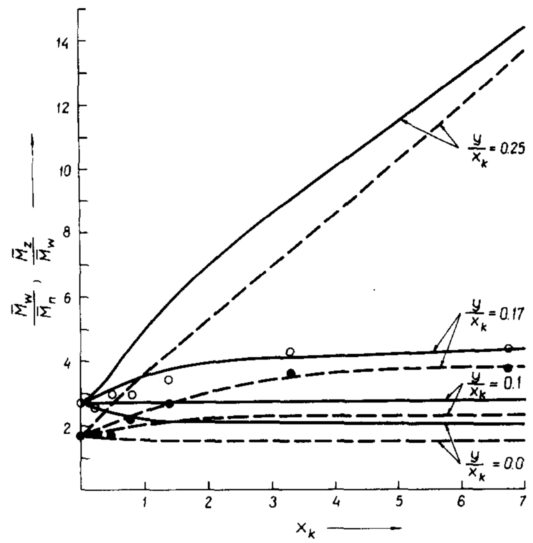

Fig. 2. Theoretical changes in the polydispersity, $\bar{M}_w/\bar{M}_n$ (——) and $\bar{M}_z/\bar{M}_w$ (----), as functions of the average number, x_k, of chain scissions, calculated for different levels of polymer cross-linking. The cross-linking is characterized by the given values of y/x_k. The values of the polydispersity obtained experimentally for the PS samples investigated have also been marked in the plot: $\bar{M}_w/\bar{M}_n$ is denoted by ○; and $\bar{M}_z/\bar{M}_w$ by ●.

$w(M)$ and the estimation of the values of K_D and the changes in the average molecular quantities such as $\bar{D}_{0z}$, $\bar{M}_D$, $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$, determined experimentally for the PS samples irradiated in CCl_4 or $CHCl_3$ are given in Table 1, relative to the same quantities for the initial non-irradiated PS sample. Noting that the PS macromolecules were subjected to simultaneous chain scission and cross-linking to different degrees, depending on the irradiation time [17], the effect of both these processes upon the changes in the average molecular quantities of the polymer investigated can be analyzed based on the data summarized in Table 1.

In general, the quantities given in Table 1 indicate the occurrence of photodegradation during irradiation. This is shown by the systematic decrease in the relative average values of $\bar{M}_m$ with increasing irradiation time, and by the increase of $\bar{D}_{0z}$. By comparing the relative changes in these quantities, it can be concluded that the higher the moment $\bar{M}_m$ of the molecular weight distribution function $w(M)$, the slighter the changes observed. A problem arises as to the reason for the differences in the observed changes in the average molecular quantities, $\bar{M}_m$ and $\bar{D}_{0z}$, and whether the analysis of the changes in one of these quantities yields sufficiently reliable information on structural changes in macromolecules. In order to solve this problem, an attempt was made to analyze the experimental and theoretical data on the PS samples. The results of the analysis are presented in Figs 1–3. Figure 1 illustrates the changes in $w(M)$ due to the irradiation of the PS sample. The distribution functions $w_0(M)$ and $w_1(M)$ were determined experimentally by the QLS and ELS methods [15, 17, 18] whereas the function $w_t(M)$ was obtained theoretically [20].

The molecular weight distribution $w_0(M)$ refers to the initial PS sample before irradiation whereas the weight distribution $w_1(M)$ characterizes this sample after irradiation for 40 hr in CCl_4. The values of the average number of scissions in the main chain and the average number of cross-linking bonds per PS molecule [equations (5)–(9)], calculated from the changes in the average molecular weights, are in this case $x_k = 6.75$ and $y = 1.16$, respectively. The theoretical molecular weight distribution, $w_1(M)$, shown in Fig. 1 was determined from equation (3). $w_t(M)$ was determined assuming that the initial molecular weight distribution of the PS sample investigated was represented by the distribution $w_0(M)$ which can be described with high accuracy by the Schulz–Zimm equation (4) [21]. It was also assumed that the value $x_k = 6.75$ determined from equations (5)–(9) for the function $w_1(M)$ is the same as for the distribution function $w_t(M)$, the changes in $w_t(M)$ relative to $w_0(M)$ resulting only from chain scission, i.e. when $y = 0$.

The function $w(M)$ shown in Fig. 1 was normalized according to equation (1). The apparent differences between the magnitudes of the areas under the individual curves $w(M)$ in the figure are due to the use of a logarithmic scale on the axis of the independent variable M. Moreover, the values of the function $w_t(M)$ were decreased ten-fold in order to show them together with the functions $w_0(M)$ and $w_1(M)$. In the lower section of the plot, the changes in $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_z$, determined from the respective functions $w(M)$, are shown. As can be inferred from the theoretical relations [31, 32], when chain scission is the only process, i.e. $y = 0$, $x_k \rightarrow \infty$, the function $w(M)$ approaches the Flory–Schulz distribution described by equation (4) for $p = 1$, and the heterogeneity of the molecular weight distribution, $U = \bar{M}_w/\bar{M}_n - 1$, approaches unity. In other words, the value of heterogeneity U is decreased as illustrated by the plots of the function $w(M)$ in Fig. 1. In this case, the distribution function $w_t(M)$ shifts rapidly towards lower molecular weights, as do all the average values of the molecular weights. Comparison of the function $w_1(M)$ obtained experimentally with the theoretical function $w_t(M)$ suggests that the observed difference between them can be accounted for by the occurrence of simultaneous chain scission and cross-linking. Thus, based on the above observations together with the experimental results summarized in Table 1 and determining the changes in $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$, it can be suggested that the chains of the irradiated PS samples were indeed subjected to both processes, as shown by the polydispersity of the PS samples increasing systematically with irradiation time, and hence, by the heterogeneity U of the molecular weight distribution. Thus, it can be concluded that, when chain scission is accompanied by cross-linking, the effect of the latter upon the molecular weight distribution function is shown by the broadening of the range of the function $w_1(M)$, the increase in the heterogeneity, U, of the molecular weight distribution, and the increase of the average molecular weight, $\bar{M}_m$, relative to those determined based on $w_t(M)$. Although for all the irradiated PS samples [17] the ratio of parameters x_k and y is $y/x_k \approx 0.17$, it can be seen in Fig. 1 that the cross-linking process causes a distinct decrease in the rate of the shifting of the function $w(M)$ and the average molecular weight values, $\bar{M}_m$, towards lower molecular weights. When analysing the changes in average molecular weight, it should be noted that the effect of chain scission (the changes in w_t relative to w_o) on $\bar{M}_n$ is most pronounced, whereas that the cross-linking (observed as variations of w_l relative to w_0) is most clearly indicated by the change in $\bar{M}_z$. This results from the definition of the respective average molecular weights, $\bar{M}_m$, i.e. the share of the molecules with low molecular weight in the average $\bar{M}_n$ is relatively the greatest. The effect of the macromolecules with high molecular weight originating during the cross-linking is most pronounced for $\bar{M}_z$. These conclusions confirm the experimental results summarized in Table 1. The observed effect of cross-linking upon the change in the z-average translational diffusion constant, $\bar{D}_{0z}$, of the macromolecules can be similarly accounted for. The changes in $\bar{D}_{0z}$ listed in Table 1 should be explained by the effect of two simultaneous and opposite in this respect processes (i.e. chain scission leading to increase in the mobility and cross-linking diminishing macromolecular mobility) upon the mobility of the macromolecules in solution. For example, the PS irradiated for 40 hr in CCl_4, more than a six-fold lowering of $\bar{M}_n$ has been observed, when the value of $\bar{D}_{0z}$ increases 1.88 times. Despite the fact that the relation $y/x_k \approx 0.17$ holds, the contribution of big macromolecules, formed as a result of cross-linking, to the z-average of constant $\bar{D}_{0z}$ is once more considerably higher than the effect of smaller molecules formed by chain scission. This results from the influence of the factor $M \cdot w(M)$ in equations (10) and (11) upon $\bar{D}_{0z}$. Thus, estimate of the changes (or their lack) in the molecular weight distribution function

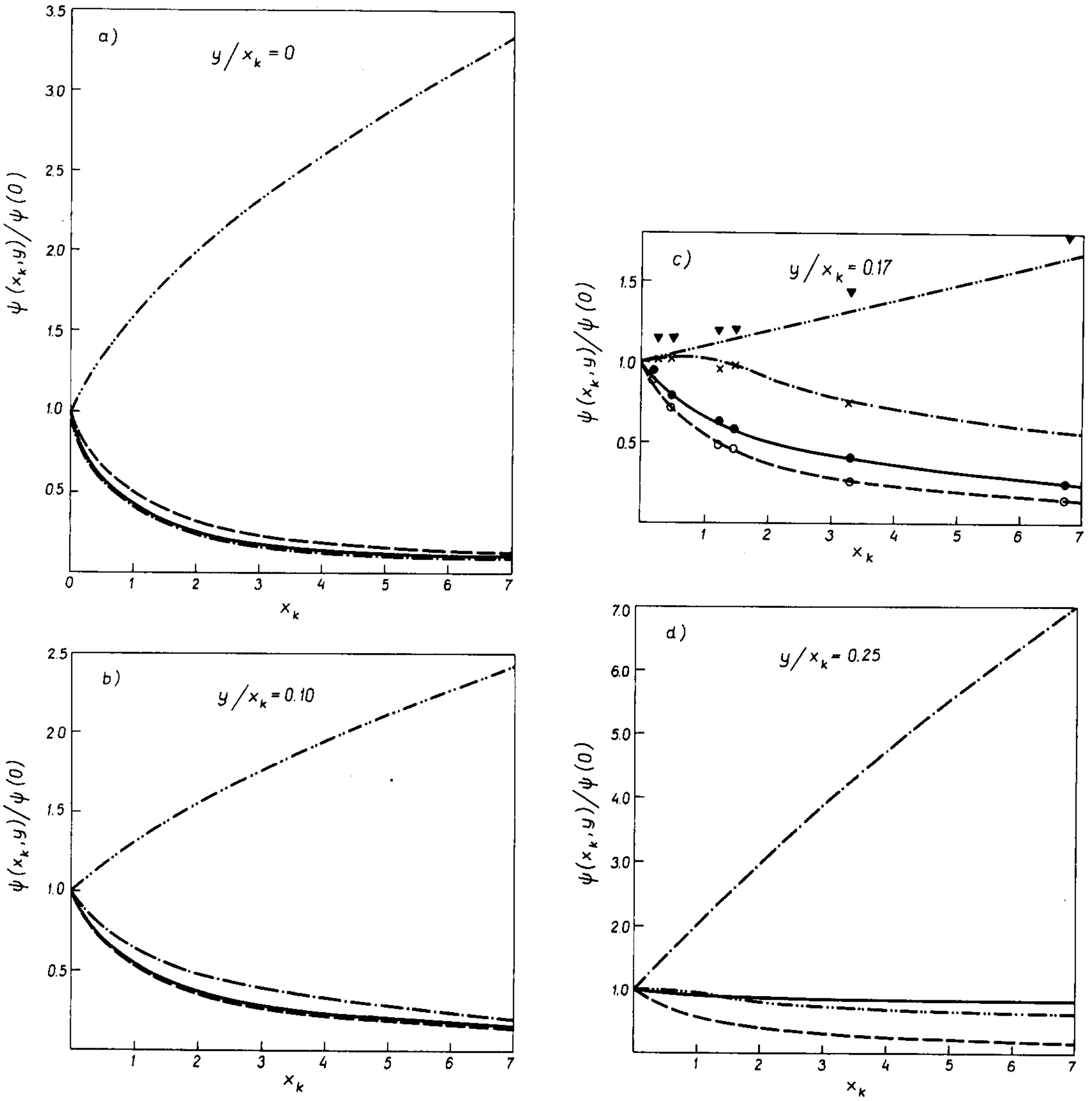

Fig. 3. The calculated relative changes, $\psi(x_k, y)]\psi(0)$, in $\bar{M}_n$, $\bar{M}_w$ and $\bar{M}_z$, and in the diffusion constant, $\bar{D}_{0z}$, as functions of the average number, x_k, of chain scissions. Plots (a)–(d) refer to different levels of cross-linking characterized by the given values of y/x_k. Figure 3c shows the same relations determined experimentally for the PS sample under investigation (points), with the following symbols: $\bar{M}_n(x_k, y)/\bar{M}_n(0)$ (– – –, ○); $\bar{M}_w(x_k, y)/\bar{M}_w(0)$ (——, ●); $\bar{M}_z(x_k, y)/\bar{M}_z(0)$ (-···-, ×); and $\bar{D}_{0z}(x_k, y)/\bar{D}_{0z}(0)$ (-··-, ▼).

based only on the determined values of $\bar{D}_{0z}$ can lead to false conclusions. Since analogous relations apply to the intrinsic viscosity $[\eta]$ [equations (12) and (13)], this comment refers also to the viscometric measurements.

According to the above considerations, it is essential to find whether simultaneous scission and cross-linking or only chain scission occur in the system under investigation. The polydispersity value of the polymer sample, $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$, is a very useful parameter which settles the above problem. This has already been suggested by the results shown in Fig. 1 and Table 1. The effect of cross-linking upon the polydispersity can be analyzed theoretically assuming the ratio y/x_k to be the measure of cross-linking. Figure 2 showing the changes in $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$, as a function of x_k can be the starting point for such considerations. Thus, when only scission occurs, i.e. $y/x_k = 0$, the molecular weight distribution, $w(M)$, tends to the Flory–Schulz distribution function, and the following limiting values are obtained for the polydispersity degrees:

$$\lim_{x_k \to \infty} (\bar{M}_w/\bar{M}_n) = 2$$

and

$$\lim_{x_k \to \infty} (\bar{M}_z/\bar{M}_w) = 1.5.$$

However, when considering relatively low levels of cross-linking, the values of the polydispersity degrees grow rapidly, and for $y/x_k = 0.25$, when the gelation of the polymer in solution starts [32], we obtain $\bar{M}_w/\bar{M}_n = \bar{M}_z/\bar{M}_w \to +\infty$. For moderate extents of cross-linking, e.g. when $y/x_k \approx 0.17$, the limiting values of the polydispersity are already attained for a number of chain scissions of $2 \leqslant x_k \leqslant 3$. This means in practice that when determining experimentally $\bar{M}_w/\bar{M}_n$ or $\bar{M}_z/\bar{M}_w$ at sufficiently high values of $x_k (x_k > 2)$, one can detect chain cross-linking occurring simultaneously with chain scission with considerable certainty, since under such conditions the following inequalities are satisfied:

$$\bar{M}_w/\bar{M}_n > 2$$

and

$$\bar{M}_z/\bar{M}_w > 1.5.$$

As is seen, the values of both polydispersities are quite sensitive to changes in y/x_k meaning that the parameter y/x_k can be determined from measurements of $\bar{M}_w/\bar{M}_n$ or $\bar{M}_z/\bar{M}_w$ with good accuracy. It can be inferred from Fig. 2 and the calculations that, for $x_k > 2$, the polydispersity values are independent of the parameter x_k except when gelation of the polymer occurs, i.e. when $y/x_k \approx 0.25$. Hence, the values of x_k cannot be determined with sufficient accuracy from the measurement of the polydispersity values only.

Figure 2 shows the experimental points referring to the irradiated PS samples in CCl_4 and $CHCl_3$. For low values of x_k, i.e. for $x_k \leqslant 1$, certain slight deviations of the experimental dependence of $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$ upon the parameter x_k from the theoretical curve for $y/x_k = 0.17$ can be seen. However, these deviations can be entirely accounted for by experimental errors. For $x_k > 1$, the agreement between the theoretical relations for this quantity with the experimental results is satisfactory, enabling the values of y/x_k to be determined with high accuracy.

We will now present and discuss the changes in $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$ and $\bar{D}_{0z}$ obtained theoretically from equations (5)–(11) and (14)–(17) as functions of the average number of chain scission, x_k, for different levels of cross-linking characterized, as previously, by the parameter y/x_k. The relevant results and conclusions agree with those formulated in the preceding sections of this paper. Thus, Fig. 3a implies that the rate of the changes in the all individual magnitudes for $y = 0$, or $y/x_k = 0$, is similar except that the values of $\bar{M}_n$ change somewhat more slowly than the other quantities. However, for low levels of cross-linking, i.e. for $y/x_k = 0.1$ (Fig. 3b), a distinct decrease in the rate of the changes in the individual quantities occurs compared to the case when $y/x_k = 0$, the changes in $\bar{M}_n$ being more rapid than those of the remaining quantities. For average levels of the cross-linking of macromolecules similar to those occurring in the PS samples investigated, i.e. for $y/x_k = 0.17$, the changes in $\bar{M}_z$ are the most sensitive to this process which is shown by slight increase followed by the decrease in the $\bar{M}_z$ values. Such a situation has been shown in Fig. 3c from which it can be concluded that, for $x_k > 2$, the values of $\bar{M}_z$ and $\bar{D}_{0z}$ change to a small extent and do not reflect considerable changes in the molecular weight distribution, $w(M)$, of the sample [15, 17] (see Fig. 1). It should be noted that the experimental points shown in Fig. 3c agree with the theoretical predictions. The only exception in this respect as the slight deviations of the experimental changes in $\bar{D}_{0z}$ from those determined theoretically from equations (14)–(17) which can be accounted for by the fact that the theoretical curves were obtained under theta conditions, whereas the experimental points were determined for the PS macromolecules in $CHCl_3$. Marked changes in $\bar{M}_z$ and small changes in $\bar{M}_w$ and $\bar{D}_{0z}$ have been observed for further increase in the cross-linking macromolecules reaching the point of gelation in solution, i.e. for $y/x_k \approx 0.25$. In this case, as previously, the values of $\bar{M}_n$ decrease monotonically with increase of x_k. This results in the rapid growth of $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$, confirmed by the experimental and theoretical results already presented.

The results suggest that, in order to detect degradation of a polymer sample in which cross-linking can also take place, it is best to study the changes in $\bar{M}_n$ from which the value of the apparent number of chain scissions, $x = x_k - y$, is obtained. The occurrence of cross-linking can in this case be confirmed by determining the changes in the higher moments of the molecular weight distribution functions, $\bar{M}_w$, $\bar{M}_z$ and $\bar{D}_z$, and, in particular, in the polydispersity and by comparison of these changes with the theoretical calculations.

Figure 3 implies that for $x_k \gtrsim 3$, the small changes in average molecular weight correspond to marked changes in x_k. Therefore, the determination of the parameters x_k and y for $x_k \gtrsim 3$ is not accurate.

Finally, it can be concluded that the measurements of the changes in single weight distribution function moment of low order, i.e. $\bar{M}_n$, enable chain scission to be detected, whereas measurements of the changes in the moment of higher order, i.e. $\bar{M}_z$, $\bar{D}_{0z}$, etc., can sometimes indicate, even with moderate levels of cross-linking, the lack of considerable changes in the distribution function $w(M)$. Hence, it can be inferred that, for simultaneous scission and cross-linking, more than one moment of the weight distribution function should be determined by different measuring methods, or such a measurement technique should be applied which allows the distribution function $w(M)$ to be determined. Such methods include improved gel chromatography [33], or the joint methods of ELS and QLS [15, 17, 18].

Acknowledgement—We gratefully acknowledge partial support of this research by the Polish Academy of Sciences, Research Project CPBP 01.12.8.

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