

Influence of diffusion and induced π -bonds on the ultra-violet radiation-initiated crosslinking of polystyrene in solution

Z. Turzyński, K. Witkowski and L. Woliński

Institute of Experimental Physics, University of Gdańsk, 80-952 Gdańsk-Oliwa, Wita Stwosza 57, Poland

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An attempt has been undertaken to account for the mechanism of polystyrene crosslinking initiated by ultra-violet radiation with wavelengths of $\lambda \geq 270$ nm in outgassed solutions with CCl_4 and CHCl_3 . The investigations were carried out by the joint method of elastic and quasielastic light scattering, and by the use of absorption spectroscopy in the ultra-violet and visible spectral regions. From the experimental results obtained and the model and theoretical modifications introduced, the crosslinking of polystyrene macromolecules irradiated in solutions with CCl_4 and CHCl_3 is shown to be affected by both the diffusion properties of the macromolecules and the conjugated and isolated double $>\text{C}=\text{C}<$ bonds formed in polymer chains.

(Keywords: polymer crosslinking; polystyrene; chloride-containing solvents; light scattering; long wave u.v. radiation; polyene chromophores)

INTRODUCTION

As has already been reported in our previous papers¹⁻⁷, complex processes resulting in simultaneous polymer chain scission and crosslinking, as well as in the formation of conjugated and isolated chromophore $>\text{C}=\text{C}<$ groups, occur in polystyrene (PS) solutions with CCl_4 and CHCl_3 irradiated in the u.v. spectral region with wavelengths $\lambda \geq 270$ nm. When investigating the scission and crosslinking of polymer macromolecules, a joint method of elastic (ELS) and quasielastic (QLS) light scattering⁸ has been employed, which enables the molecular-mass distribution function $w(M)$ to be determined with high accuracy, in particular for polymer samples with high molecular masses. The method employed therefore provides insight into the details of polymer macromolecule crosslinking and branching.

The present paper reports the continuation of the investigations outlined above, with particular regard being paid to the mechanism of PS macromolecule crosslinking initiated with u.v. radiation in solutions with CCl_4 and CHCl_3 . When analysing the process of macromolecular crosslinking, apart from the variations in the mass distribution function $w(M)$ of the irradiated PS samples, the changes in the mean translational diffusion constant \bar{D}_{0z} of the macromolecules were also taken into account. The experimental investigations reported in this paper, as well as the model and theoretical modifications introduced taking into account the PS sample polydispersity, enable the effect of macromolecular dynamic properties in solution on the polymer chain crosslinking to be determined.

The investigations of the scattered light mentioned above together with the results obtained from absorption spectroscopy in the u.v.-vis. spectral region indicate a certain mechanism for the analysed crosslinking process occurring in irradiated PS macromolecules in the systems under study.

THEORY

The measurement of the scattered light by the joint methods of elastic (ELS) and quasielastic (QLS) light scattering for a series of monodisperse fractions of the polymer under study enables the dependence of the translational diffusion constant D_0 of the polymer macromolecules on the molecular mass M to be determined according to the relation⁹:

$$D_0(M) = K_D M^{-\gamma} \quad (1)$$

The values of constants K_D and γ depend on the type of polymer and solvent. By employment of the above relation, the molecular-mass distribution function $w(M)$ of the sample can be determined by measuring the autocorrelation function $C(q, t)$ for a polydisperse sample^{4,6,7,10}. Knowledge of the distribution function $w(M)$ affords, on the other hand, possibilities for determining the mean molecular masses \bar{M}_n , \bar{M}_w and \bar{M}_z , \bar{M}_n denoting the number-average mean value, \bar{M}_w the mean weight-average value and \bar{M}_z the mean molecular mass Z -average value of a given polydisperse sample. In the case under consideration, when the polymer samples investigated undergo simultaneous scission and crosslinking^{6,7}, the value of the mean molecular masses \bar{M}_n , \bar{M}_w and \bar{M}_z depend on the parameters describing the average number of scissions x and crosslinking bonds y attributed to a polymer macromolecule with an initial mass $\bar{M}_n(0)$. The values of parameters x and y can be determined based on the theoretical expressions obtained by Saito¹¹ and Inokuti^{12,13} for $\bar{M}_n(x, y)$, $\bar{M}_w(x, y)$ and $\bar{M}_z(x, y)$. The details of this procedure have been given in refs. 4, 6, 7 and 13.

As has already been mentioned, formula (1) can be applied for monodisperse samples. An analogous relation can be written for the mean values of the diffusion

constant and the mass in the case of polydisperse samples:

$$\bar{D}_{0Z} = K_D \bar{M}_D^{-\gamma} \quad (2)$$

where \bar{M}_D is the so-called 'mean diffusive molecular mass'¹⁴. The Z-average value of the translational diffusion constant \bar{D}_{0Z} can be determined by the method of quasielastic light scattering, when¹⁴:

$$\bar{D}_{0Z} = (1/\bar{M}_w) \int_0^\infty D_0(M) w(M) M \, dM \quad (3)$$

where D_0 is the value of the translational diffusion constant in the solution extrapolated to zero concentration according to the relation:

$$D_0 = \lim_{c \rightarrow 0} D(c)$$

In turn, \bar{M}_D can be determined by substituting formulae (1) and (3) into (2), to yield the following relation:

$$\bar{M}_D = \bar{M}_w^{1/\gamma} \left(\int_0^\infty M^{1-\gamma} w(M) \, dM \right)^{-1/\gamma} \quad (4)$$

Equation (4) describes the way of determining the mean value of \bar{M}_D , when the molecular-mass distribution function $w(M)$ of a polymer and the value of constant γ are known. Constants γ and K_D depend in general on the chemical composition, the macromolecular structure and the thermodynamic quality factor of the solvent, and can in most cases be determined experimentally. Theoretical values of γ are only known for some shapes of macromolecules at the θ -point. In a special case, a value of $\gamma=0.5$ is obtained at the θ -point for a great number of flexible polymers (including also crosslinked ones) that can be described by a Gaussian coil model¹⁵. Moderate crosslinking of the polymer does not alter the value of parameter γ ¹⁶ but it does however affect K_D and hence also the translational diffusion constant of macromolecules. The changes in the diffusion constant can most often be described by means of parameter h defined by the following relation¹⁷:

$$h = D_0/D_{0Z}^* \quad (5)$$

The quantity D_{0Z}^* in formula (5) refers to the crosslinked sample, whereas D_0 corresponds to the monodisperse uncrosslinked sample. The following equation should be satisfied for both types of samples:

$$\bar{M}_w^* = \bar{M}_w$$

In general, the magnitude of h depends on several factors, namely:

- (i) the crosslinking degree characterized by parameter y ;
- (ii) the molecular-mass distribution function $w(M)$;
- (iii) the distribution of the crosslinking bonds in the macromolecules, which in turn depends on the molecular-mass distribution function $w(M)$ of the initial sample (before crosslinking) and on the crosslinking mechanism; and
- (iv) thermodynamic quality factor of the solvent, since the swelling of the crosslinked and uncrosslinked samples is different.

Theoretical calculations of parameters h have so far been carried out for a few simple models^{15,18-20}:

(i) For the model of random crosslinking¹⁸ under the assumption that both the crosslinked and uncrosslinked samples are monodisperse fractions with the same mass,

then:

$$\frac{1}{h_0} = \frac{3\pi^{1/2}\Gamma(3y+1)}{4\Gamma(3y+\frac{5}{2})} \left(6y+1 + \frac{9}{2}y(y-1) \times \sum_{k=1}^{y-1} \frac{(2k+2)!(3y-k)!(y-2)!}{(k+1)!2^{k+1}(3y)!(y-k+1)!} 3^{k-1}(2k+4) \right) \quad (6)$$

(ii) For the model of random crosslinking¹⁵ under the assumption that the initial uncrosslinked sample is characterized by the 'most probable' mass distribution $w(M)$, where the condition $\bar{M}_Z : \bar{M}_w : \bar{M}_n = 3:2:1$ is satisfied, the value of parameter h is expressed by the relation:

$$h = 8/(3[2\pi(1+y)]^{1/2}) \quad (7)$$

In some recent papers^{21,22}, other models and methods of investigating the crosslinking of macromolecules were reported, thus evidencing the increasing interest in the research area under discussion and its further development.

EXPERIMENTAL

Description of the samples

Polydisperse atactic PS samples with a weight-average molecular mass $\bar{M}_w = 976\,000 \text{ g mol}^{-1}$ and a polydispersity index $\bar{M}_w/\bar{M}_n = 2.71$ were used for the investigations, the \bar{M}_w and \bar{M}_w/\bar{M}_n values given above being determined by light scattering³. The PS samples were irradiated in solutions with CCl_4 , CHCl_3 and 1,4-dioxane at $T = 294 \text{ K}$ ^{3,4}. Prior to irradiation the solutions were outgassed by the use of several freeze-thaw cycles at pressures $p < 0.1 \text{ Pa}$. Concentrations of the irradiated solutions were $c = 2.5 \text{ g dl}^{-1}$, which corresponds to a polystyrene monomeric unit concentration of 0.240 M. PS was recovered from the irradiated solutions by precipitation with methanol. The precipitated polymer was washed with methanol and dried using the method described elsewhere^{3,4}. The irradiated PS samples thus obtained were investigated by the joint method of elastic and quasielastic light scattering⁴, and by absorption spectroscopy in the u.v.-vis. spectral region. Further particulars concerning the characteristics and practical aspects of the preparation methods employed have been given in ref. 3.

Irradiation of the polymer solutions

The methods of irradiation of the polymer solutions have been described in detail elsewhere³⁻⁵. The PS solutions were irradiated with light wavelengths $\lambda \geq 270 \text{ nm}$ emitted by four high-pressure Hanau type Q 700 (FRG) mercury lamps. The detailed characteristics of this radiation have been given in our previous papers^{5,23}.

Measurement of polystyrene absorption spectra in the u.v.-vis. spectral region

As has already been mentioned, the PS samples irradiated in a given solvent were recovered for further investigations by precipitation with methanol and drying^{3,4}. Optical density A in the u.v.-vis. spectral region was determined for both the irradiated and non-irradiated polystyrene samples by preparing PS solutions of concentration 2.5 g dl^{-1} in 1,4-dioxane. The values of the optical density were measured by compensation techniques by means of a Specord u.v.-vis. (Carl Zeiss-Jena, GDR) spectrophotometer. The changes in the optical density A

of the PS samples dissolved in 1,4-dioxane, irradiated by the method described previously for time t in a given solvent or in two different solvents, were measured relative to non-irradiated PS dissolved in 1,4-dioxane. The absorption spectra of the PS samples investigated were recorded at room temperature.

Measurements of the mass distribution function $w(M)$ and translational diffusion constant \bar{D}_{OZ}

In the present paper, the results of the investigations on the changes in the molecular-mass distribution function $w(M)$ and the translational diffusion constant \bar{D}_{OZ} of irradiated PS samples relative to those prior to irradiation have been reported.

The changes in the function $w(M)$ and the constant \bar{D}_{OZ} resulted from the irradiation of PS for time t , ranging from 0 to 40 h, in deoxygenated solutions with CCl_4 , $CHCl_3$ and 1,4-dioxane. \bar{M}_w values were obtained from elastic light scattering by means of the conventional Zimm double extrapolation. Intensity autocorrelation functions obtained from QLS were converted to the molecular-mass distributions $w(M)$ using the experimentally determined $D(M)$ relation (equation (1)). A Provencher constrained regularization algorithm with further modifications^{4,23} was used for this purpose. Average diffusion coefficients \bar{D}_{OZ} were determined from QLS data by means of the method of cumulants^{8,24}.

ELS and QLS measurements were performed for all PS samples in three solvents: methyl ethyl ketone, chloroform and *trans*-decalin. In the above three solvents full agreement was obtained between the determined functions $w(M)$ for each of the PS samples investigated. The accuracy of the measurement of the distribution function $w(M)$ was about 4%, as estimated in ref. 10. The average molecular weights \bar{M}_n and \bar{M}_z were obtained based on distributions $w(M)$ determined experimentally with an accuracy of about 8% and \bar{M}_w with an accuracy of 5%. The methods employed to determine these quantities have been presented elsewhere^{3,8,10}.

RESULTS AND DISCUSSION

The results presented previously in refs. 1–7 together with further studies reported herein enabled an attempt to be undertaken to account for the mechanism of PS macromolecule chain crosslinking initiated by u.v. radiation in solutions with CCl_4 and $CHCl_3$. Since PS chain scission

and crosslinking in irradiated solutions occur simultaneously, it seems reasonable to summarize in *Table 1* the values of parameters x and y characteristic of both processes.

As regards this problem, it should be pointed out that the PS solutions were irradiated continuously in the same solvent (columns 1, 2, 7 and 8), and stepwise in the same (columns 3, 4, 9 and 10) or in two different solvents (columns 5 and 6). In the case of the stepwise irradiation, twice for 10 h, after the first 10 h irradiation of the solution, the irradiated PS was recovered and then irradiated for the next 10 h in the same solvent (columns 3 and 4) or in 1,4-dioxane (columns 5 and 6). The data shown in columns 9 and 10 of *Table 1* refer to PS irradiated eight times, each for 5 h ($8 \times 5 \text{ h} = 40 \text{ h}$), in the same solvent. In this case, after each step of the irradiation, the polymer was not recovered from the solution and was irradiated continuously. The following conclusions can be drawn based on the above investigations, with particular regard being paid to polymer crosslinking. Since the PS chain scission and crosslinking processes become detectable for irradiation times $t \geq 10 \text{ h}$, it can be inferred that they are due to the formation of photo-products, the concentration of which increases with irradiation time. A special equilibrium state is generated between these processes, characteristic of which is a constant ratio of parameters x and y , which, for PS irradiated in a given solvent, can be expressed approximately by the relation $x:y=6:1$, excluding the data given in columns 5 and 6 of *Table 1*, which will be explained in a later section of this paper. It can be assumed based on this relation that similar photo-products, including also transient species, are responsible for both processes. The crosslinking process is assumed to be due to long-lived polymer radicals^{25,26} P^\cdot with a lifetime $\tau = 750 \text{ ns}$ ²⁶, already formed during the first moments of irradiation. Bearing this in mind, the PS macromolecule crosslinking could in a given solvent proceed according to the following reaction scheme:

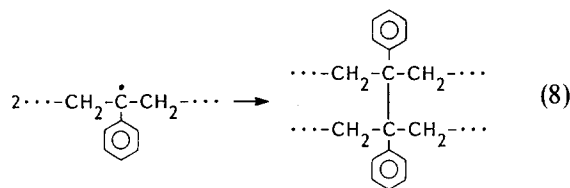


Table 1 Comparison of chain scission and crosslinking processes for PS chains irradiated in CCl_4 , $CHCl_3$ and 1,4-dioxane

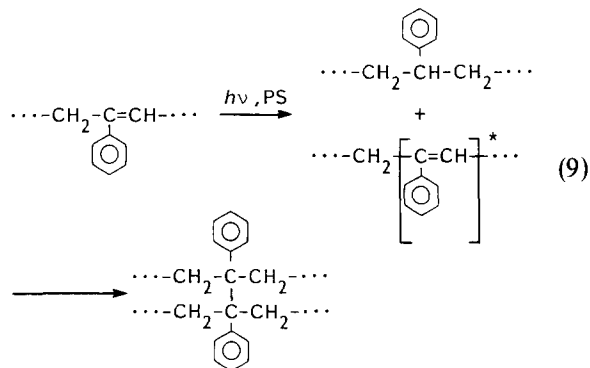
No.	Datum	Irradiation time for PS in solution									
		10 h in		10 h in		10 h in		20 h in		8 × 5 h = 40 h in	
		CCl_4	$CHCl_3$	CCl_4	$CHCl_3$	CCl_4	$CHCl_3$	CCl_4	$CHCl_3$	CCl_4	$CHCl_3$
		(1)	(2)	CCl_4	$CHCl_3$	1,4-dioxane	1,4-dioxane	(7)	(8)	(9)	(10)
1	x_k	0.51	0.24	1.45	0.80	0.50	0.25	2.43	1.22	6.75	3.30
2	y	0.08	0.04	0.24	0.12	0.11	0.06	0.40	0.20	1.16	0.60
3	$\frac{x_k}{y}$	6.37	6.00	6.04	6.67	4.54	4.16	6.07	6.10	5.82	5.50
4	$\frac{y(CCl_4)}{y(CHCl_3)}$	2.00		2.00		1.83		2.00		1.93	

Since, on the other hand, polymer crosslinking can be observed for the irradiation times $t \geq 10$ h, whereas the polymer macroradicals P^\cdot are already formed during the first moments of irradiation, this reaction is not considered likely. Such an experimental result gave rise to the assumption that the PS macromolecule crosslinking results from the formation of isolated and conjugated $>C=C<$ bonds in macromolecular chains during irradiation of the solutions. The identification, description and mechanism of formation of the polyene structures and isolated $>C=C<$ groups in the PS chains have been presented in our previous papers^{1,3}. The results reported therein indicate that in PS irradiated in CCl_4 or $CHCl_3$ similar polyene structures and isolated $>C=C<$ groups are formed, their number being greater in PS irradiated in CCl_4 than for the same time in $CHCl_3$ ^{1,3}. When comparing the above experimental results with the data in Table 1 determining the ratio of the numbers y of crosslinking bonds formed in the PS macromolecules irradiated in CCl_4 to that in $CHCl_3$, amounting to about 2:1, it can be assumed that there exists a certain correlation between the crosslinking of macromolecules and the number of π -bonds induced in polymer chains. The following experiment was carried out in order to verify this hypothesis. Following irradiation of the PS in CCl_4 or $CHCl_3$ for 10 h, a polymer was recovered which, as a result of the irradiation, exhibited the existence of induced isolated and conjugated π -bonds. PS thus prepared was dissolved in 1,4-dioxane and irradiated for a further 10 h. The resulting values of parameters x and y obtained for PS in this experiment are summarized in columns 5 and 6 of Table 1. As can be seen by comparing them with the results relevant to PS irradiated for 10 h in CCl_4 or $CHCl_3$ (columns 1 and 2), PS irradiated in the second 10 h step in 1,4-dioxane undergoes only the crosslinking process. Taking into account the results obtained previously^{2,5,27,28}, indicating that PS (with no π -bonds induced in the chain structure) irradiated in 1,4-dioxane undergoes neither polymer chain scission nor crosslinking, the experimental result presented above suggests the crosslinking process to be dependent on the π -bonds previously induced in the PS macromolecules. A convincing result confirming this conclusion was obtained by the authors when comparing the u.v.-vis. absorption spectra of PS irradiated for 10 h in 1,4-dioxane (after preceding irradiation for 10 h in CCl_4 or $CHCl_3$) with those obtained for PS irradiated for 10 h in CCl_4 or $CHCl_3$ only. In this regard, the percentage

changes in the absorption, expressed by:

$$I(A) = \int_{\nu_1}^{\nu_2} A \, d\nu$$

were analysed, where A is the absorbance and ν the frequency. The changes in the absorbance A due to the π -bonds induced in PS were observed in the frequency range from $\nu_1 = 16\,000 \text{ cm}^{-1}$ to $\nu_2 = 36\,000 \text{ cm}^{-1}$, which has been illustrated in Figure 1. By comparing the PS absorption spectra, after irradiation in 1,4-dioxane, a decrease in absorption $I(A)$ of the π -bonds induced in PS was observed, amounting to 20 and 30% for PS irradiated for 10 h in CCl_4 and $CHCl_3$, respectively. The absorption changes are in agreement with the tendency of the number of crosslinking bonds to increase in PS irradiated primarily for 10 h in CCl_4 or $CHCl_3$, and once more for 10 h in 1,4-dioxane (cf. the values of parameter y in columns 1, 2 and 5, 6 of Table 1). It can therefore be concluded that in PS with the π -bonds induced in the chain, irradiated in 1,4-dioxane, the number of crosslinking bonds increased at the cost of the decrease in the π -bond concentration. Hence, the crosslinking of macromolecules in the system considered might proceed according to the following reaction scheme:



In what follows we shall analyse the probability $P(M)$ of a macromolecule with mass M entering into the crosslinking reaction:

$$P(M) \sim n_\pi C_n \Delta \bar{R} \quad (10)$$

where n_π is the number of π -bonds in the macromolecular chain, C_n is the number of macromolecules in unit volume of the solution and $\Delta \bar{R}$ is the mean distance travelled in the solution during lifetime τ by a macroradical formed

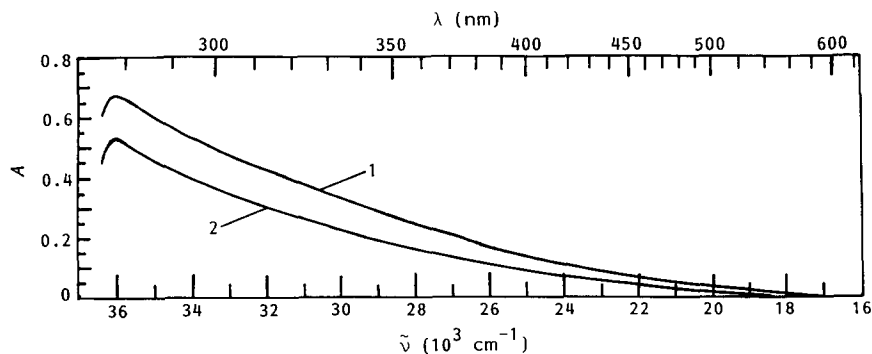


Figure 1 Absorbance changes for polystyrene irradiated for $t = 10$ h in $CHCl_3$ (curve 1) and $t = 10$ h in $CHCl_3$ and $t = 10$ h in 1,4-dioxane (curve 2) relative to non-irradiated polystyrene. Polystyrene absorption spectra were measured in 1,4-dioxane at the solution concentration of $c = 2.5 \text{ g dl}^{-1}$ at room temperature

in reaction (9). The first factor in formula (10) refers to the probability of macroradical formation, and the two remaining factors describe the probability of encounters between the macroradical and another macromolecule during the radical lifetime τ . For the solution irradiated for times $t < 10$ h, under the conditions described in the 'Experimental' section, $n_\pi \approx 0$, and hence $P(M) \approx 0$, which accounts for the lack of detectable crosslinking of the macromolecules in this range of irradiation times. For $t \geq 10$ h, when $n_\pi > 0$, changes in $P(M)$ can be observed. For polydisperse solutions of the PS samples with different molecular masses irradiated in a given solvent, i.e. in CCl_4 or CHCl_3 , at polymer mass concentrations $c = 2.5 \text{ g dl}^{-1}$, equal absorption values were observed resulting from the presence of induced $> \text{C}=\text{C} <$ groups. It can therefore be inferred that the number of π -bonds induced in unit volume of the PS solution is independent of the molecular mass of the solute polymer. Hence, it can be assumed that $n_\pi C_n = \text{const}$. Since the number of macromolecules in unit volume of the solution can be expressed by the relation $C_n = cN_A/M$, where N_A is the Avogadro number, $n_\pi \sim M$. The mean value of squared distance travelled by the macroradical $\langle \Delta R^2 \rangle$ during its lifetime τ is given by the relation²⁹:

$$\langle \Delta R^2 \rangle \sim D(c)\tau \quad (11)$$

where $D(c)$ is the translational diffusion coefficient of the macromolecules at concentration c . The relation between the diffusion coefficient and the molecular mass is given by equation (1); for the 'semidilute solutions' in which polystyrene was irradiated, the exponent γ should be substituted by the so-called 'effective exponent' γ_e taking into account the effect of macromolecular chain kinking³⁰. Upon substituting $\Delta \bar{R} \equiv \langle \Delta R^2 \rangle^{1/2}$ into formula (10) we obtain:

$$P(M) \sim M^{-\gamma_e/2} \quad (12)$$

Thus, for long irradiation times ($t \geq 10$ h), the effect of the molecular mass M of the macromolecules on their crosslinking is only manifested by the dependence of the macroradical mobility on M .

As has already been mentioned in the theoretical section of the present paper, the crosslinking process occurring in the system investigated can be described in more detail by using simultaneously the data from the measurements of the molecular-mass distribution function $w(M)$ and the values of the translational diffusion constant D_0 of the macromolecules. Based on formulae describing the dependence $h(y)$ for monodisperse samples, and on well known functions $w(M)$ of the samples investigated, models can be assumed describing the distribution of crosslinking number y in polydisperse samples.

As has been found for such models, different crosslinking rates can be taken into account depending on the molecular mass of macromolecules in the polymer sample. By comparison of relation $h(y)$ determined based on the model calculations (i.e. the dependence of the mean value of parameter h on the average number y of crosslinking processes per molecule) with that obtained experimentally for polydisperse PS samples enables the individual models to be verified, as well as essential conclusions to be drawn as to the crosslinking process and its dependence on the molecular mass of macromolecules.

By determining the mean diffusion constant \bar{D}_{0z}^* for a

crosslinked and polydisperse sample, the following relation is obtained based on formula (5):

$$\bar{D}_{0z}^* = (1/\bar{M}_w) \int_0^\infty [D_0(M)/h_0(M)]w(M)M \, dM \quad (13)$$

where $h_0(M)$ denotes the value of parameter h for a monodisperse sample with molecular mass M . The values of $h_0(M)$ are calculated below for certain crosslinking models. The expression for h for a polydisperse crosslinked sample is obtained from formulae (5) and (13) in the following form:

$$h = D_0(\bar{M}_w)\bar{M}_w \left(\int_0^\infty [D_0(M)/h_0(M)]w(M)M \, dM \right)^{-1} \quad (14)$$

Under such circumstances we shall consider two extreme cases, two reverse crosslinking models, by introducing different $h_0(M)$ into formula (14).

(i) It is assumed in the first model that each mer in every macromolecule in solution (irrespective of its size and mass M) is characterized by equal probability of entering into the crosslinking reaction. The value of parameter y is then proportional to the mass of the macromolecule $y \sim M$, so that the number z of crosslinking bonds per mer is constant, $z = \text{const}$, which means that quantity h_0 in formula (14) depends on M according to expression (6):

$$h = h(y)$$

where

$$y = y_0 M / \bar{M}_n \quad (15)$$

whereas y_0 denotes the mean value of y measured experimentally (summarized in Table 1). By the employment of formula (14), the following relation is obtained:

$$h = \bar{M}_w^{1-\gamma} \left(\int_0^\infty M^{1-\gamma} w(M) / h_0(y_0 M / \bar{M}_n) \, dM \right)^{-1} \quad (16)$$

Formula (16) enables the numerical values of h to be calculated for known molecular-mass distribution $w(M)$ of the irradiated PS sample, h_0 being determined by use of equation (6).

The model assumed, expressed by relation (16), is analogous to that represented by formula (7). The difference consists of the fact that formula (16) enables an arbitrary molecular-mass distribution in the irradiated polymer sample to be taken into account.

(ii) According to the assumptions of the second model, the average number of crosslinking bonds per polymer macromolecule is independent of the mass M of a macromolecule, which means that in smaller macromolecules the same number of crosslinking bonds exist, i.e. $y = \text{const}$, whereas $z \sim M^{-1}$. Such a model leads to the value of $h_0 = h_0(y_0)$ independent of M . The following relation can be now obtained from formula (14):

$$h = h_0(\bar{M}_w / \bar{M}_n)^{-\gamma} \quad (17)$$

Figure 2 shows the dependences $h(y)$ obtained: (a) from the calculations carried out based on the models presented, determined by formula (7) (curve 1), formula (16) (curve 2) and formula (17) (curve 3); and (b) based on the measurements of function $w(M)$ and on the determination of parameter y in CHCl_3 (curve 4) and *trans*-decalin (curve 5).

The experimental points in Figure 2 (curves 4 and 5)

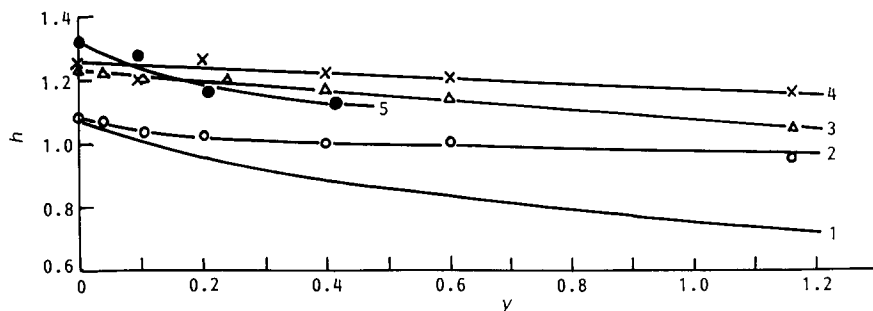


Figure 2 Dependence of parameter h on the number of crosslinking bonds y per PS molecule irradiated in CCl_4 and CHCl_3 : (a) determined from formula (7) (curve 1), formula (16) (curve 2) and formula (17) (curve 3); and (b) determined experimentally from the measurements of y and $w(M)$ by the joint ELS and QLS method in CHCl_3 (curve 4) and *trans*-decalin (curve 5)

refer to the PS samples irradiated both in CCl_4 and CHCl_3 . The effect of the solvent, in which the irradiation and crosslinking of the PS sample occur, upon the value of parameter h results from the values of parameter y determined experimentally for the samples and the function $w(M)$. Therefore the experimental relation $h(y)$ can be affected by the type of solvent in which the polymer macromolecules are crosslinked. However, since the experimental points $h(y)$ lie on one curve (curve 4) it can be assumed that the crosslinking of PS irradiated in CCl_4 and CHCl_3 proceeds according to similar mechanisms. The comparison of the experimental results (curves 4 and 5) with theoretical relations $h(y)$ enables the verification of the models assumed previously. Curves 2 and 3 shown in Figure 2 were obtained by the use of experimentally determined molecular-mass distributions $w(M)$, and mean values of y , whereas the diffusion constants \bar{D}_{0z}^* were calculated assuming two different models of $y(M)$. Curve 1 refers to an 'ideal' case, i.e. to 'the most probable' initial molecular-mass distribution, and to the use of solvent θ when measuring $w(M)$ and y , the character of the relation $y(M)$ in this case being the same as in the second model (curve 3). The investigation results shown in Figure 2 suggest the second model (formula (17)) to be accepted rather than the first. It should be taken into account that in the experimental dependence $h(y)$ obtained from the measurements in CHCl_3 (curve 4) an effect of the excluded volume has been revealed which has not been considered in the theoretical calculations. According to Orofino and Wenger³¹, this effect is responsible for the increase in $h(y)$ value by several per cent only. For the measurements in *trans*-decalin at the θ -point (curve 5), the function $h(y)$ actually assumes lower values, which, however, only differ slightly from those calculated according to the second model and from the experimental values obtained from measurements in CHCl_3 (curves 3 and 4). On the other hand, the course of curve 1 differs the most from the values of $h(y)$ determined according to both models and from the experimental results. This seems to result from the fact that the condition based on which formula (7) was derived has not been fulfilled. The condition concerns 'the most probable' molecular-mass distribution of the initial uncrosslinked polymer sample. As has been pointed out in our previous papers^{4,6,7}, such a molecular-mass distribution differs essentially from that applied in the investigations of the PS samples. The assumption of the second model (curve 3) leads to the conclusion that, in the system under study, the probability of a given bond of the vinyl chain, in the

initial non-irradiated PS sample, participating in the crosslinking reaction is greater for smaller macromolecules. It should be recalled that the translational diffusion constant of a macromolecule is a function of its molecular mass, which for monodisperse polymer samples is expressed by formula (1). This thus favours smaller macromolecules with greater mobility affording more frequent contact with other macromolecules, thus increasing the probability of their participation in the reactions resulting in polymer crosslinking. On the other hand, it must be borne in mind that, during the first 10 h step of irradiation of the PS solutions in CCl_4 and CHCl_3 , neither PS crosslinking nor its photodegradation were detected, which shows that these processes depend on the photo-product concentration. Thus, PS crosslinking is affected by both factors, the initiating and decisive role being played by the photo-products formed during the irradiation of solutions, including also transient individuals, the number of which is undoubtedly greater in PS solutions in CCl_4 than in CHCl_3 ^{1,3}, this being in accordance with the determined values of parameter y .

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