Pergamon

PII: S0014-3057(97)00042-6

Eur. Polym. J. Vol. 34, No. 1, pp. 113-115, 1998

Printed in Great Britain
0014-3057/97 $17.00 + 0.00

POLYMER DEGRADATION WITH SIMULTANEOUS SCISSION AND CROSSLINKING. WEIGHT-AVERAGE MOLECULAR WEIGHT CHANGES IN THE CASE WHERE CROSSLINKING RATE SURPASSES SCISSION RATE

A. V. SHYICHUK
Mykolaichuka St. 7/48, Ivano-Frankivsk, 284006 Ukraine

(Received 3 July 1996; accepted in final form 30 October 1996)

Abstract—When the ratio of scissions and crosslinks numbers is less than unity ($n_s/n_x < 1$), gel starts to form at an effective crosslinking index equal to 0.25. The weight-average MW diverges in the vicinity of the gel-point: $M_w/M_{wo} = (1 - CI_{eff}/0.25)^{-S}$. The scaling exponent, S, has been found as the function of the ratio of scission and crosslinking rates: $S = (1 - n_s/n_x)^{-1}$. © 1997 Elsevier Science Ltd

INTRODUCTION

The changes in average molecular weight before the gel-point are of great interest in order to be able to determine the crosslink and scission yields at a low conversion degree. The classical approach to the theory of crosslinking with scission of macromolecules supposes that the crosslinks occur consecutively after all scissions have taken place. The predictions obtained within the framework of that consecutive approach have been described in fundamental books [1, 2]. On the other hand, computer models have been developed which simulate crosslinking of macromolecules and chain scission by means of random numbers [3–5]. Monte Carlo simulations of crosslinking with simultaneous scission have been recently advanced [6–8]. In ref. [6] the ratio of scission and crosslinking rates under the oxidation of low molecular weight polyethylene are evaluated with the computer simulation of the MWD changes. Work [7] has been devoted to the maximum ratio of scission and crosslink numbers which allows gel formation. This quantity has been evaluated to be 1, while the classic theory predicts that value to be equal to 4. Considering the above facts, there is a need to develop and to verify a new theory of macromolecules crosslinking and scission. The present paper deals with that problem: here the changes of weight-average molecular weight have been quantitatively investigated. The simple correlations obtained will be of help to researchers in the fields of polymer degradation and polymer modification.

EXPERIMENTAL AND DEFINITIONS OF TERMS

The Monte Carlo simulations and treatment of results obtained were performed with a PC/AT 386. The algorithm of the simulation has been described in detail [6]. The initial molecular weight distribution was the Flory–Schulz one with $M_n = 100{,}000$.

The scission and crosslink numbers are denoted by n_s and n_x, respectively. The ratio of rates of scission and crosslinking is designated by λ:

$$\lambda = n_s/n_x \tag{1}$$

The parameter absolute crosslinking index, CI_{abs}, is equal to the average number of crosslinks per initial number-average macromolecule:

$$CI_{abs} = n_x/n_o$$

Here n_o is the initial number of macromolecules. As crosslinks and scissions occur simultaneously, one can also define the effective (or apparent) number of crosslinks:

$$n_{x.eff} = n_x - n_s$$

and, respectively, the effective crosslinking index:

$$CI_{eff} = (n_x - n_s)/n_o$$

Considering equation (1), the two different crosslinking indexes may be correlated by the following expression:

$$CI_{eff} = CI_{abs}(1 - \lambda) \tag{2}$$

The value of CI_{eff} is measurable through the changes of number-average molecular weight:

$$CI_{eff} = (M_n - M_{no})/M_{no} \tag{3}$$

RESULTS

The relative changes of weight-average MW at different values of λ are shown in Fig. 1. When crosslinking of macromolecules is the only process ($\lambda = 0$), then the value of weight-average MW increases with the increasing rate and diverges near $CI_{abs} = 0.25$ (see Fig. 1). The dependence of M_w on CI_{abs} is expressed by the following power formula:

$$M_w/M_{wo} = (1 - CI_{abs}/0.25)^{-1} \tag{4}$$

in complete agreement with the classical theory of macromolecules crosslinking [1].

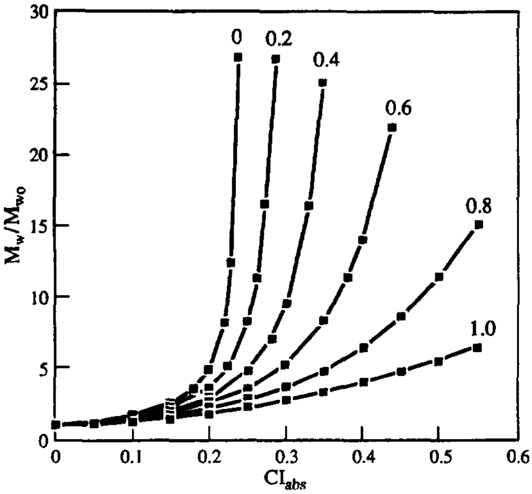

Fig. 1. Relative changes of weight-average MW vs absolute crosslinking index at indicated values of λ.

When crosslinking of macromolecules is accompanied by chain scission, the increase of weight-average MW is slowed down. The greater the parameter λ is the greater the slowdown is (see Fig. 1). That phenomenon is clear because chain scissions lead to the decrease of all average molecular weights, including the weight-average one. The values of weight-average MW plotted in Fig. 1 vs CI_{abs} are also plotted vs the effective crosslinking index in Fig. 2. Here an opposite order of the curves is observed: the greater parameter λ the greater the dependence of the weight-average MW on CI_{eff} is. This phenomenon may be explained by considering that effective crosslinking index decreases with increasing λ, according to equation (2). At $\lambda = 1$ the value of CI_{eff} is zero at any values of absolute crosslinking index. As the value of weight-average MW increases at $\lambda = 1$ (see Fig. 1), the dependence of M_w on CI_{eff} is strongly vertical. This is illustrated in Fig. 2.

In order to obtain some quantitative correlations, it is necessary to take into account the divergence of

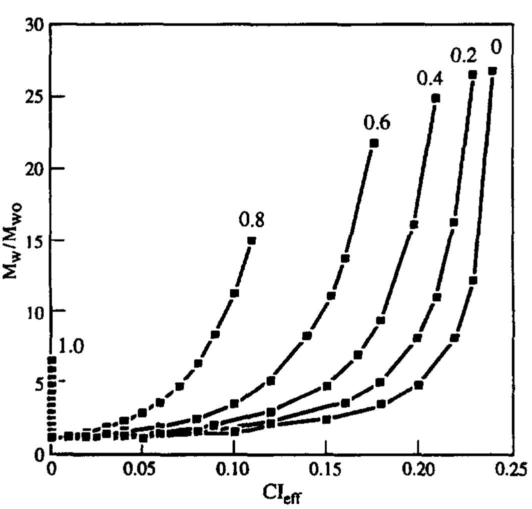

Fig. 2. The same data vs effective crosslinking index.

Table 1. Values of both crosslinking indexes at the gel-point

λ	0	0.2	0.4	0.6	0.8
$CI_{g.abs}$	0.25	0.32	0.42	0.63	1.22
$CI_{g.eff}$	0.25	0.256	0.252	0.252	0.244

the weight-average MW value and the gel incipiency at a specific value of CI_{abs}. Considering the above regularities, it has been assumed that all the dependences in Fig. 1 are similar to the one at $\lambda = 0$, when only crosslinking occurs. Thus, the assumed correlation looks like equation (4):

$$M_w/M_{wo} = (1 - CI_{abs}/CI_{g.abs})^{-S} \quad (5)$$

with $CI_{g.abs}$ being the absolute crosslinking index needed for the gel incipiency and S being a coefficient. At $\lambda = 0$ these quantities are: $CI_{g.abs} = 0.25$; $S = 1$ and, respectively, equation (5) becomes equation (4). At other values of λ the quantities $CI_{g.abs}$ and S are unknown. In order to verify equation (5) and to determine the values of $CI_{g.abs}$ and S, the graphical method was used. According to equation (5), plots of $\ln(M_w/M_{wo})$ vs $\ln(1 - CI_{abs}/CI_{g.abs})$ are expected to be rectilinear. The data for M_w and CI_{abs} are known from computer experiments, and the parameter $CI_{g.abs}$ has been found from the screening. For all investigated values of λ many different values of $CI_{g.abs}$ were tested. The plots of $\ln(M_w/M_n)$ vs $\ln(1 - CI_{g.abs})$ initially produced curve lines and suitable values of $CI_{g.abs}$ where found to produce reasonable linear plots. The values of the absolute crosslinking index, $CI_{g.abs}$, obtained in this way are listed in Table 1. The table also shows the values of the effective crosslinking index required for the gel incipiency calculated from equation (2). It can be seen that the values in the last line of Table 1 are close to quantity 0.25, which corresponds to the gel-point at $\lambda = 0$. For this reason, the value of $CI_{g.eff}$ has been accepted to be constant for all the cases studied:

$$CI_{g.eff} = 0.25 \quad (6)$$

With this assumption equation (5) is transformed to:

$$M_w/M_{wo} = (1 - CI_{eff}/0.25)^{-S} \quad (7)$$

The plots in the corresponding coordinates are fairly linear (Fig. 3). The values of the exponent S have been found as slopes of the plots in Fig. 3 and are shown in Fig. 4. The data may be described reasonably by the following relation:

$$S = 1/(1 - \lambda) \quad (8)$$

which is plotted by the broken line in Fig. 4.

The value of the absolute crosslinking index corresponding to the gel-point at any value of λ may be calculated by combining equations (2) and (6). The data predicted in this way have been plotted by line A in Fig. 5. It can be seen that the gel-point moves off to infinity when λ approaches unity. That is clear because at $\lambda = 1$ the weight-average MW value increases with an almost constant rate (see Fig. 1) and, consequently, the infinite crosslinking index is required to reach the gel-point. Thus, the maximum ratio of scission and crosslink numbers allowing the gel-formation has been found to be equal to unity. That inference is in complete agreement with the quantity evaluated in ref. [7]. On the other hand, the

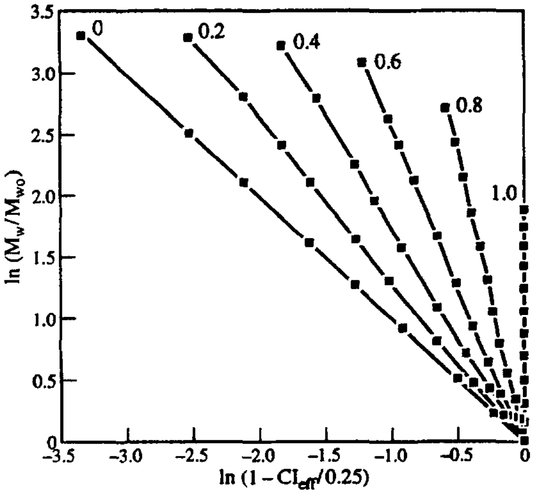

Fig. 3. The same data transformed according to equation (7).

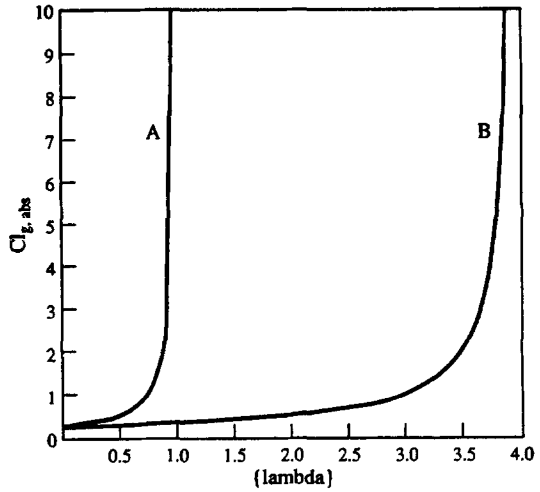

Fig. 5. Absolute crosslinking index at the gel-point vs the ratio of scission and crosslink numbers.

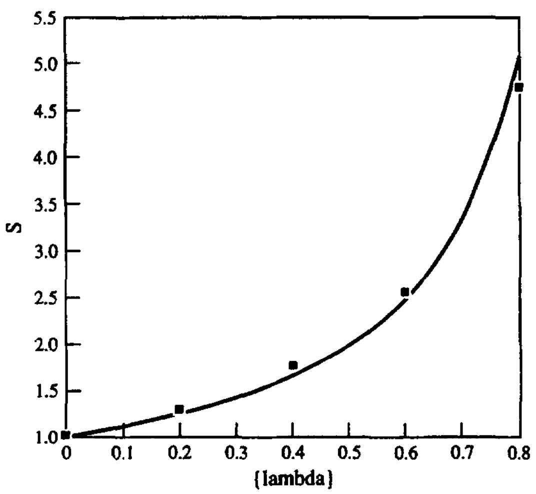

Fig. 4. Exponent S vs the ratio of scission and crosslink numbers: empirical values (quadrates) and equation (8) data (broken line).

classic theory predicts the maximum ratio of scission and crosslinking rates for the allowance of the gel-formation to be equal to 4 [1, 2] (line B in Fig. 5).

CONCLUSION

The expressions (7) and (8) together make it possible to determine the ratio of rates of scission and crosslinking from the measurements of weight- and number-average molecular weights: first the value of CI_{eff} should be determined according to equation (3). Then the value of the scaling exponent should be calculated as:

$$S = -\ln(M_w/M_{wo})/\ln(1 - CI_{eff}/0.25)$$

The last step is to calculate:

$$\lambda = 1 - 1/S$$

In order to diminish experimental inaccuracy, a number of measurements of CI_{eff} and corresponding values of M_w can be determined. In that case the value of the exponent S may be obtained as the slope of plot of $\ln(M_w/M_{wo})$ vs $\ln(1 - CI_{eff}/0.25)$ by means of the least squares linear fit.

REFERENCES

1. Charlesby, A., *Atomic Radiation and Polymers*. Pergamon Press, Oxford, 1960.
2. Saito, O., in *The Radiation Chemistry of Macromolecules*, ed. M. Dole. Academic Press, New York, 1972.
3. Van der Hoff, B. M. E. and Gall, C. E., *J. Macromol. Sci., Chem.*, 1977, **A11**, 1739.
4. Chiantore, O. and Guaita, M., *J. Appl. Polym. Sci., Appl. Polym. Symp.*, 1993, **52**, 1.
5. Kotliar, A. M. and Podgor, S., *J. Polym. Sci.*, 1961, **55**, 423.
6. Shyichuk, A. V., *Eur. Polym. J.*, 1995, **31**, 631.
7. Shyichuk, A. V., *Eur. Polym. J.*, 1997, **33**, 1267.