

A New Method for Treatment of Sol-Gel Data in Irradiated Polymers

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ABSTRACT: A log-log plot of sol fraction versus dose has been found to be an effective graphical technique to treat sol-gel analysis data. The treatment procedure is described in detail with an example of radiation crosslinking of linear low-density polyethylene. Radiation chemical yields both for crosslinking and scission of macromolecules were determined using Monte Carlo simulation. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2621–2625, 2001

Key words: sol-gel analysis; gel-point; radiation yield

INTRODUCTION

The radiation-induced crosslinking of macromolecules is a useful tool for modification of polymer properties. The changes in the characteristics of a polymer are caused by crosslinks and main chain scissions due to radical reactions in the polymer matter. The crosslinking kinetics are usually observed by measuring the insoluble fraction (gel) content. To treat the gel fraction data, a few different methods have been developed. The most well-known method is the Charlesby-Pinner (CP) equation¹:

$$s + s^{1/2} = \frac{p_0}{q_0} + \frac{2}{q_0 \cdot u_{2,0} \cdot D} \quad (1)$$

where p_0 is the degradation density, average number of main chain scission per monomer unit and per unit dose; q_0 is crosslinking density, proportion of monomer units crosslinked per unit dose; and $u_{2,0}$ is initial weight-average degree of polymerization. The CP equation is simple to use,

and for that reason is widely disseminated in radiation chemistry of polymers. At the same time, the CP equation was derived concerning initial molecular weight distribution (MWD) of a certain type—so called most probable distribution with polydispersity index, M_w/M_n , which is equal two. Because many industrial polymer samples have MWDs different from the most probable distribution, the CP coordinates ($s + s^{1/2}$ vs. $1/D$) produce curvilinear dependencies and for that reason are inapplicable in many cases.

Numerical solutions of gel formation kinetics^{2,3} concern initial distributions of Schulz-Zimm and Wesslau types. However, the results are rarely used due to their inconvenient presentation as cumbersome tables. In addition, MWDs of real polymer samples frequently differ from the generalized types. In order to extend the applicability of the CP equation to specimens with different distributions, many studies have been performed. It has been proposed⁴ that an experimental polymer specimen be considered as a specimen having initially the most probable distribution but exposed to a virtual dose, D_v , causing some changes in MWD. The virtual dose value is chosen by computer until the closest approximation to a straight line in modified coordinates $s + s^{1/2}$

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versus $1/(D + D_v)$ is reached. The modified CP equation has been shown to be relevant for various crosslinked polymers.⁴

Researchers have proposed a modification of the CP equation assuming the crosslink and scission densities are power functions of an irradiation dose with the exponent depending on structural features of an irradiated polymer.^{5,6} Accurate selected values of the exponent provide very fine curve-fits for experimental data.^{6,7} However, such an approach cannot be considered as fully correct because it does not take initial MWD shape into account at all. As a matter of fact, initial MWD has a significant influence on the gel growth kinetics—a full and strong theory on this subject has been developed by Charlesby.¹ Unfortunately, the general equation presented in monograph¹ consists of an infinite number of terms (mostly unknown). That is why a simple, as well as universal, expression is absent to date.

Another approach is proposed in the present work. The basic concept is the use of specific coordinates: logarithm of sol fraction versus logarithm of irradiation dose. The coordinates $\lg s$ versus $\lg D$ in fact are not new—they were used in earlier stages of the study of radiation chemistry of polymers,¹ but were not used widely. A possible reason for this is that the different slopes of the log-log plots were not explained at that time. However, it has recently been shown with computer simulation that logarithm of sol fraction indeed has linear dependence on logarithm of irradiation dose (D)⁸:

$$\lg s = b + m \cdot \lg D \quad (2)$$

with m being the slope coefficient having a negative value.

For initial MWDs of the Schulz-Zimm type the coefficient value has been found to depend on the polydispersity index.⁸ The present work shows the coefficient m value is also sensitive to the chain scission rate in the crosslinking system. Therefore, an experimental plot of $\lg s$ versus $\lg D$ together with an already known polydispersity index makes it possible to determine both crosslinking and scission efficiencies.

EXPERIMENTAL

To illustrate that the new method is workable, some experimental data were used from an article

on polyethylene irradiation.⁷ This work concerns the irradiation in the presence of acetylene gas, when the crosslinking process is accelerated to a great extent. The polymer sample used was linear low-density polyethylene with the following values of average molecular weights: $M_n = 22.05$, $M_w = 105.9$, and $M_z = 289.5$ kg/mol.⁷

The simulations were performed on a Pentium II desktop computer with the special software GelSim 5.2 (© A. V. Shyichuk, 1999). Its algorithm has been described in general elsewhere.⁹ The simulations were performed with initial MWD of the Schulz-Zimm type having the following averages: $M_n = 22.05$, $M_w = 106$, and $M_z = 199$ kg/mol. The data treatment was performed with Microsoft Excel 97.

RESULTS AND DISCUSSION

Figure 1 shows the original experimental data from the previous study.⁷ It can be seen that acetylene gas accelerates remarkably the gel formation rate. The same data transformed according to eq. (1) are presented in Figure 2. The plots are markedly curved, probably due to the difference between the initial distribution and the most probable distribution. On the other hand, the same data plotted as sol fraction versus dose with the logarithmic scales on the axes produce almost straight lines (Fig. 3). For both lines the coefficients m and b were determined with the least

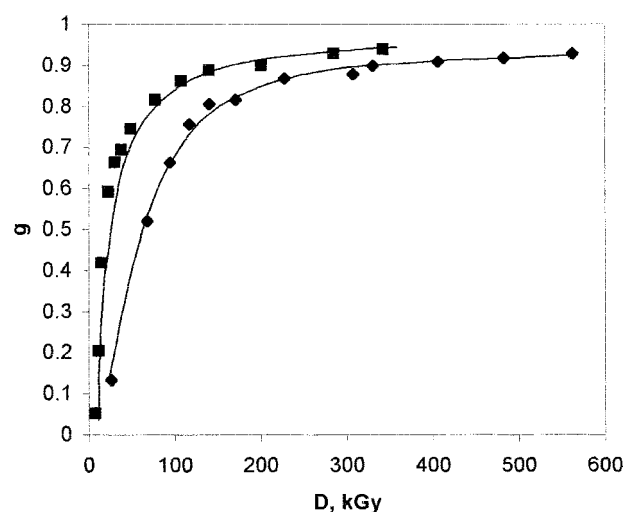


Figure 1 Dependence of gel fraction versus dose under irradiation of LLDPE.⁷ Acetylene pressure values were 0 (◆) and 1 atm (■).

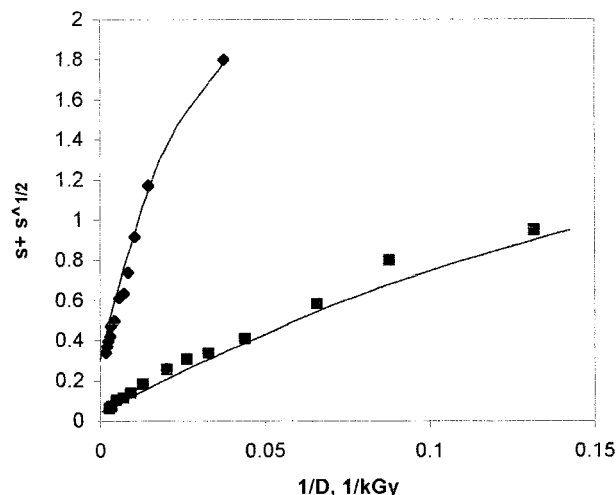


Figure 2 The Figure 1 data presented in the Charlesby-Pinner coordinates. Acetylene pressure values were 0 (◆) and 1 atm (■).

squares method, and are displayed in Table I. The coefficients enabled the dose of the starting gelation, D_g , to be calculated. In fact, the gel point was determined to be the point where the approximation line intercepts the horizontal line at $s = 1$, i.e., $\lg s = 0$. Considering the above, eq. (2) may be transformed into the following formula:

$$\lg D_g = -\frac{b}{m} \quad (3)$$

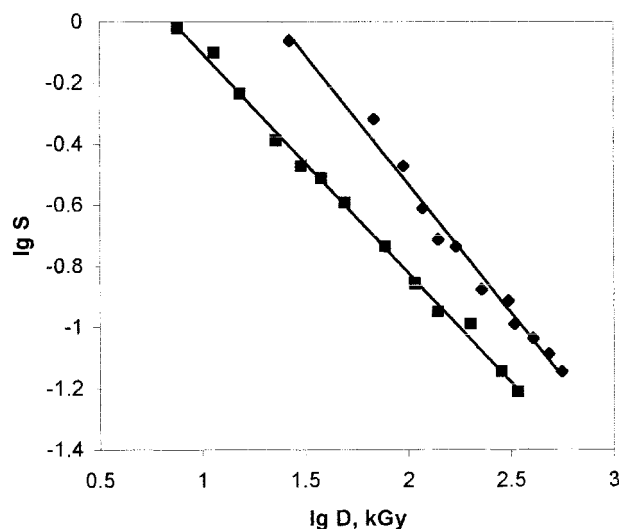


Figure 3 The Figure 1 data presented as sol fraction versus dose in the logarithmic coordinates. Acetylene pressure values were 0 (◆) and 1 atm (■).

Table I Kinetic Parameters of the Radiation Crosslinking Process at Different Concentrations of Acetylene Gas

Parameter	Acetylene Pressure (atm)	
	0	1
Coefficient m	-0.845	-0.718
Coefficient b	1.16	0.616
Sol-gel transition dose, (kGy [kJ/kg])	23.63	7.199
Ratio of scission to crosslinking rates	0.89	1.32
Crosslink concentration at gel-point (mol/kg)	0.0067	0.0079
Radiation yield of crosslinks (mol/kJ)	0.000284	0.001097
Radiation yield of scission (mol/kJ)	0.000252	0.00144

The values of gelation dose, calculated with eq. (3), are presented in Table I as well.

The obtained values of D_g lead, in principle, to corresponding values of radiation chemical yield of crosslinking reactions.¹ However, detailed consideration of the m values from Table I suggests that crosslinking of macromolecules is accompanied by competitive scission of macromolecules. In particular, for the initial MWD in question with polydispersity index $M_w/M_n = 4.8$, previous work predicts the value $m = -1.15$.⁸ Table I shows both the experimental values of m differ from the theoretical values. In other words, the gel fraction increases more slowly compared to the theoretical predictions, having in mind macromolecule crosslinking only. The probable cause of that deviation is macromolecule scission have place in parallel to crosslinking. In order to verify this assumption a few computer experiments were performed that simulated both crosslinking and scission occurring in parallel. The initial MWD was that of Schulz-Zimm type with the averages almost identical to the experimental ones (see Experimental). Results of the simulation are presented in Figure 4 as logarithm of sol fraction versus logarithm of crosslink concentration, N_c . It can be seen in Figure 4 that the logarithm of sol fraction versus $\lg N_c$ produces straight lines, with slopes dependent indeed on the ratio of scission to crosslinking rates, λ .

Considering that the crosslink concentration is proportional to irradiation dose

$$N_c = G_c \cdot D \quad (4)$$

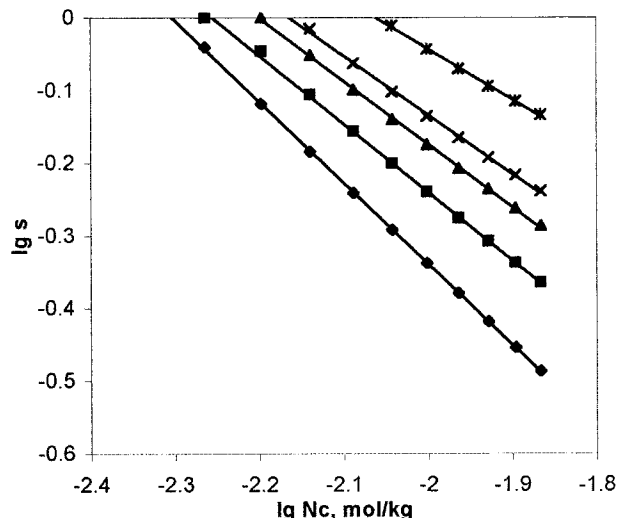


Figure 4 Log-log dependence of sol fraction on crosslink concentration according to the computer simulation at the following ratios of scission to crosslinking rate: 0.1 (◆); 0.5 (■); 0.8 (▲); 1 (×); 1.5 (*).

with G_c denoting radiation yield of crosslinks, we can rewrite eqs. (2) and (3) as the following:

$$\lg s = b_1 + m \cdot \lg N_c \tag{5}$$

$$\lg N_{c,g} = -\frac{b_1}{m} \tag{6}$$

with the same value of coefficient m as in eq. (2), and $N_{c,g}$ being crosslink concentration at gel point. Thus, the slope m is characteristic of a certain value of scission to crosslink ratio, λ .

The dependence of the slope m on the parameter λ has been plotted in Figure 5. The graph of m versus λ , taken together with experimental values of m (listed in Table I), allows for determination of real quantities of λ , i.e., the scission to crosslinking ratio in the considered process. This assessment is shown in Figure 5 with the experimental values of m and the corresponding values of λ . Furthermore, Figure 4 shows the crosslink concentration at incipient gelation, $N_{c,g}$ (as intercepts with horizontal at $\lg s = 0$). The higher the scission to crosslinking ratio, the higher the crosslink concentration needed for gel to start to form (see Fig. 6). Here, the predetermined above λ values result in corresponding values of crosslink concentration at incipient gelation, $N_{c,g}$ (see Table I). In turn, the last parameter, together with

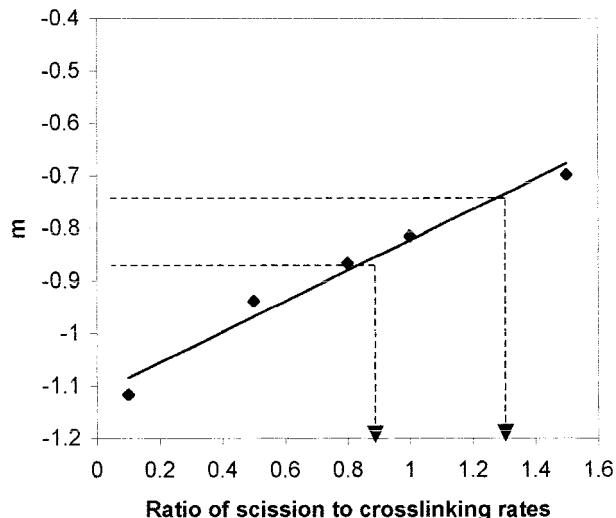


Figure 5 Slope coefficient m versus scission to crosslink ratio λ . The broken lines represent the experimental values of m and corresponding values of λ .

gelation dose (D_g), produces the radiation chemical yield of crosslinks, G_c :

$$G_c = N_{c,g}/D_g \tag{7}$$

The final step is the determination of radiation yield of scission, G_s . Its value is calculated as the product:

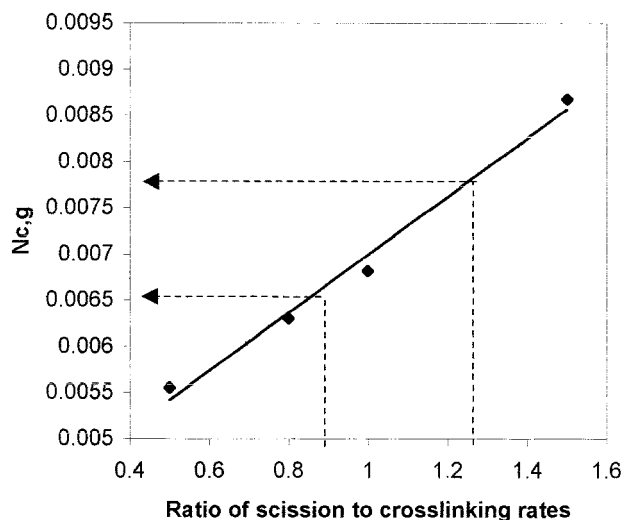


Figure 6 Crosslink concentration at incipient gelation versus scission to crosslink ratio. The broken lines represent the obtained values of λ and corresponding values of $N_{c,g}$.

$$G_s = \lambda \cdot G_c \quad (8)$$

All of the obtained values are listed in Table I.

CONCLUSIONS

Plotting sol fraction versus dose in the logarithmic coordinates is a convenient way to accurately determine the dose at incipient gelation. The scission to crosslink ratio was evaluated using Monte Carlo simulation with the log-log plot slope as an indicating parameter. As a result, both the crosslink and scission radiation yields were obtained.

REFERENCES

1. Charlesby, A. *Atomic Radiation and Polymers*; Pergamon Press: Oxford, 1960.
2. Inocuti, M. *J Chem Phys* 1963, 38, 2999.
3. Saito, O.; Kand, H. Y.; Dole, M. *J Chem Phys* 1967, 46, 3607.
4. Olejnickak, J.; Rosiak, J.; Charlesby, A. *Radiat Phys Chem* 1991, 38, 113.
5. Zhang, W.; Sun, J.; Qian, B. *Polym Commun* 1985, 59, 17.
6. Wanxi, Z.; Tianbai, H.; Jiachhen, S.; Baogong, Q. *Radiat Phys Chem* 1989, 33, 581.
7. Jones, R. A. *J Polym Sci* 1994, 32, 2049.
8. Shyichuk, A. V. *Eur Polym J* 1996, 9, 1167.
9. Shyichuk, A. V. *J Appl Polym Sci* 1996, 61, 1703.