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A comparison of methods to determination of macromolecule crosslinking yield from gel fraction data

RAPID COMMUNICATION

Summary — Three methods of linearization of sol-gel analysis data are considered. The commonly used Charlesby-Pinner (Ch-P) method often yields non-linear plots. The same data may easily be linearized by using the virtual dose concept proposed by Charlesby and Rosiak (Ch-R). Very good linear representation of the data is also obtained by plotting the sol content versus irradiation dose in the double natural logarithmic scale (LLS). All the three methods result in rather similar values of gel dose and scission-to-crosslinking ratio. At the same time, both Ch-R and LLS methods seem to be more accurate due to the higher values of the coefficients of linear correlation.
Key words: crosslinking by irradiation, sol-gel analysis, crosslinking computer simulation, data treatment.

Mechanical and thermal properties of thermoplastic polymers may be improved by means of macromolecules' crosslinking. The crosslinking between macromolecules is introduced usually *via* high-energy irradiation [1—5] or *via* compounding with peroxides [6—8]. Under both the processing ways macroradicals are generated and further recombined resulting in crosslinking of macromolecules. For example, crosslinked polyolefins are typical materials for cable insulation. The radiation crosslinking rate may be accelerated using crosslinking promoters, such as acetylene [9] or triallyl isocyanurate [10]. Very active crosslinking coagents are silanes as well [11].

In order to optimize the polymer modification technology, a radiation or chemical yield of macromolecules' crosslinking should be evaluated quantitatively. The most simple and reliable way to evaluate crosslinking extent is the measurement of insoluble fraction (gel) content. The usual computation tool for crosslinking yield determination is the famous Charlesby-Pinner (Ch-P) equation [12]:

$$s + s^{1/2} = p_o/q_o + 2/(q_o \cdot u_{w,o} \cdot D) \qquad (1)$$

where: *s — content of soluble fraction (sol), p_o — average number of main chain scissions per monomer unit and per unit dose, q_o — proportion of monomer unit crosslinked per unit dose, $u_{w,o}$ — initial weight-average degree of polymerization, D — irradiation dose or crosslinking agent concentration (in the case of chemical crosslinking).*

Sometimes the sol-gel data evaluation in the coordinates $(s + s^{1/2})$ *versus* (1/D) may be rather complicated,

e.g., in the cases where the initial molecular weight distribution (*MWD*) differs from the most probable distribution implicitly considered in Ch-P equation [13]. Since many industrial polymers show very broad *MWD*, a few modified equations have been developed. The most reliable version, so called Charlesby-Rosiak (Ch-R) equation operates with a virtual dose [13]:

$$s + \sqrt{s} = \frac{p_o}{q_o} + \left(2 - \frac{p_o}{q_o}\right)\left(\frac{D_v + D_g}{D_v + D}\right) \qquad (2)$$

where: D_g — *gel-point dose*, D_v — *virtual dose.*

The virtual dose value may be computed with special software [14].

Another convenient method for determination of crosslinking yield is plotting sol content *versus* irradiation dose in natural logarithmic scales (LLS method) supported with computer simulations on gel formation for a given initial *MWD*. This method may be applied for initial *MWD* of the Schulz-Zimm type in the cases where competitive chain scission occurs in parallel to macromolecular crosslinking [15, 16]. The slopes of plots of sol content *versus* irradiation dose in the logarithmic scale are dependent on the macromolecules' scission rate. For that reason the comparison of experimental plot slope with that simulated enables calculation of both crosslinking and scission yields [15, 16].

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In the present paper LLS method is compared with both Ch-P and Ch-R equations. Acetylene enhanced radiation crosslinking of polyethylene [9] has been taken as an example for application of the three methods.

SIMULATION METHODS

Experimental data concerning gel formation kinetics were taken from the paper by Jones on irradiation of high-modulus polyethylene fibres [9]. The macromolecular crosslinking simulations were performed with the software GelSim6 using the advanced simulation algorithm [17]. The simulations have been performed with initial *MWD* of Schulz-Zimm type having averages equal to the experimental ones: $M_n = 12$ kg mol^{-1} and $M_w = 130$ kg mol^{-1}. The computation procedure is described in details in a previous paper [16]. Ch-R plottings were performed using GelSol95 software [14], which optimizes the virtual dose value in order to obtain the best linearity of the transformed data. For all linear approximations the least squares method was applied.

RESULTS

The experimental data of Jones [9] are presented in Fig. 1. The same data are plotted in Ch-P coordinates in Fig. 2. One can see that Charlesby-Pinner transformation results in a non-linear dependence. In other words, the gel dose and scission-to-crosslinking ratio cannot be accurately determined by using Charlesby-Pinner transformation. On the other hand, the Charlesby-Rosiak transformation results in far better linearity (compare Fig. 2 and 3). At the same time, LLS method provides excellent linear transformation of the experimental data (see Fig. 4).

The accuracy of the methods in question was estimated by means of the coefficients of linear correlation (*R*). The results of accuracy evaluation are presented in
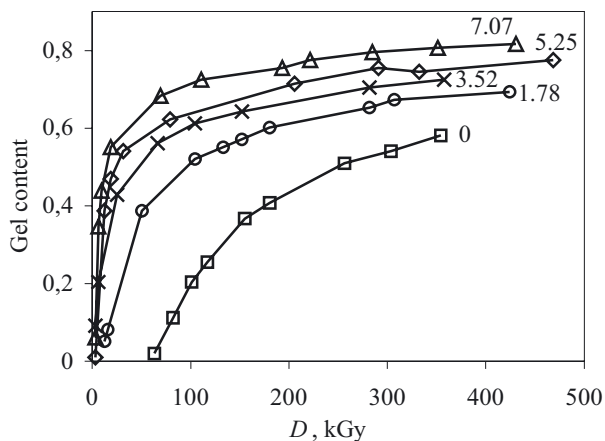

Fig. 1. Dependence of gel fraction on irradiation dose in polyethylene irradiation [9]; acetylene concentrations have been indicated by the numbers nearby the curves
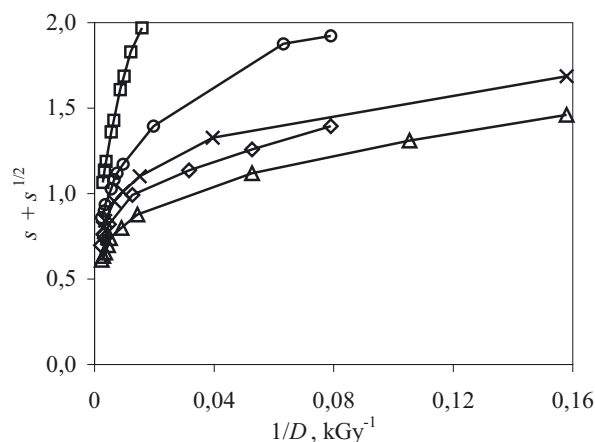

Fig. 2. Gel fraction data from Fig. 1 presented in Charlesby-Pinner coordinates; denotations as in Fig. 1
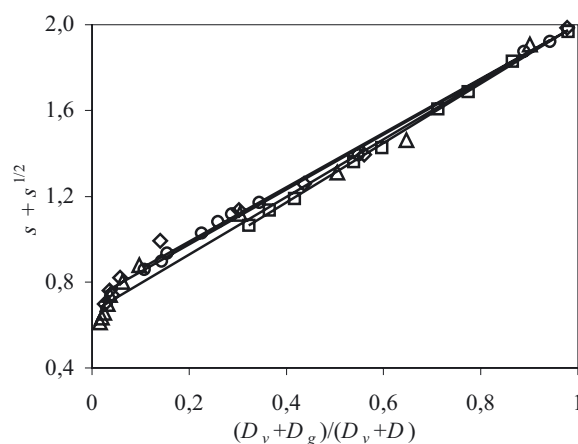

Fig. 3. Gel fraction data from Fig. 1 presented in Charlesby-Rosiak coordinates; the plots were made using GelSol95 software [14]; denotations as in Fig. 1
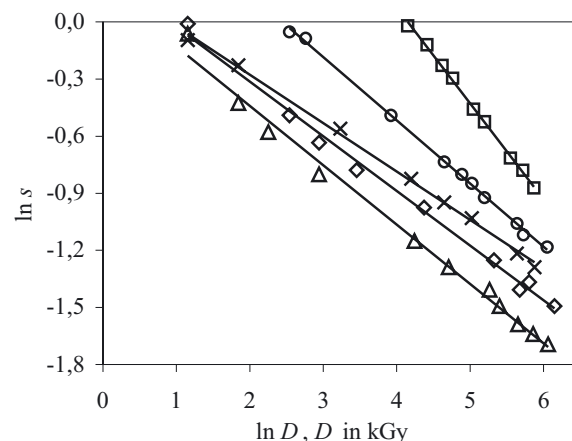

Fig. 4. Gel fraction data from Fig. 1 presented using LLS method; denotations as in Fig. 1

Fig. 5 by using R^2 rather than R to avoid negative values from LLS method. One can see that both the improved methods (Ch-R and LLS) have markedly increased correlation coefficients indicating far better fitting to the experimental data. In some cases the correlation coefficients reach the value of 1 corresponding with the best linearity (see Fig. 5). It is obvious that both Ch-R and LLS
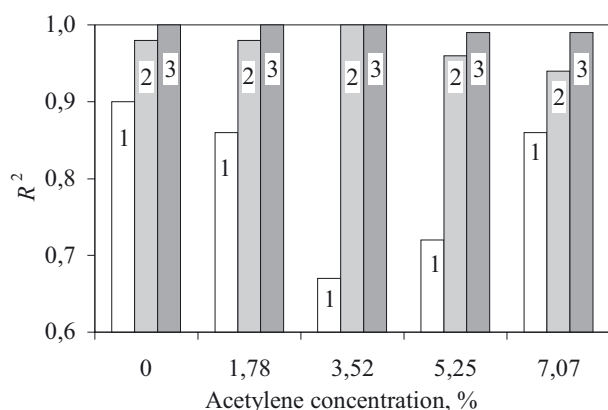
Fig. 5. Values of the squares of correlation coefficients (R^2), dependent on acetylene concentration, for the fittings obtained using different methods of data linearization: 1 — Ch-P, 2 — Ch-R, 3 — LLS
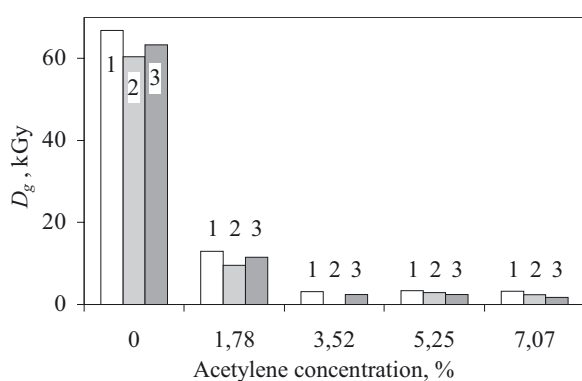

Fig. 6. Gel dose values (D_g), dependent on acetylene concentration, obtained by different methods of data linearization; the bar denotations are the same as in Fig. 5
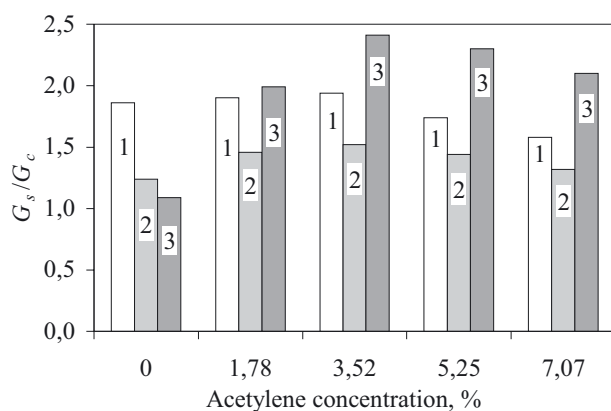

Fig. 7. Scission-to-crosslinking ratios (G_s/G_c), dependent on acetylene concentration, obtained by different methods of data linearization; the bar denotations are the same as in Fig. 5

methods provide better accuracy of the crosslinking rate determination than Ch-P method which resulted in R^2 coefficients ranged from 0.67 to 0.9. One can also see that LLS method have somewhat increased correlation coefficients comparing to Ch-R method (Fig. 5).

Figures 6 and 7 demonstrate the gel dose values and scission-to-crosslinking ratios, respectively, obtained by means of all the methods in question. All the three me-

thods are consistent indicating decreased gel dose values with increasing acetylene concentration (see Fig. 6). The only one gel dose value obtained with Ch-R method at acetylene concentration 3.52 % seems not reliable — it equals zero. The data presented clearly indicate that the most efficient crosslinking is observed under high concentrations of acetylene gas. The possible mechanism of the accelerating effect may be found in paper [16]. At the same time, the more accurate Ch-R and LLS data clearly indicate macromolecules' scission is relatively significant in the presence of acetylene gas (see Fig. 7). The data suggest that irradiation in the absence of acetylene gas provides less scission of macromolecules under the processing and for that reason better mechanical properties of the resulting crosslinked polymer samples can be expected.

CONCLUSION

Both Ch-R and LLS methods provide improved accuracy of macromolecules' crosslinking rate determination. The accurate data on scission and crosslinking yields may be helpful to optimize the polymer modification technology.

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