ALEXANDER SHYICHUK, GALINA TOKARYK
PreCarpathian University, Bio-organic Chemistry Department
Shevchenko Str. 57, 76000 Ivano-Frankivsk, Ukraine
E-mail: shyichuk@pu.if.ua

# Competitive chain scission under photo-crosslinking of polyethylene

## RAPID COMMUNICATION

**Summary** — To determine the rate of macromolecular scission accompanying the photo-initiated crosslinking of polyethylene, a method was applied which consists in plotting sol fraction *vs.* time in the log-log coordinates. The slopes showed the backbone scission to accompany crosslinking. With the most effective photo-crosslinking initiator, 2-ethylanthraquinone, the scission rate was found to be 2.6 times the crosslinking rate.

**Key words**: macromolecule crosslinking, chain scission rate, sol-gel analysis.

Crosslinking of macromolecules is one way to improve their physical and mechanical properties. Crosslinking reactions may be evoked by UV or ionizing radiation and by special chemicals [1—5]. At the same time backbone scission takes frequently place and has a strong effect on the crosslinking efficiency. In order to optimize the crosslinking process, it is nesessary to know individually the extent of crosslinking and scission. Of the methods used to determine the crosslinking yield, the most popular is the complete extraction of soluble fraction (sol) in a boiling solvent. The data on sol fraction, *s*, may be treated with the Charlesby-Pinner equation by which the quantity ($s$+$s^{1/2}$) depends linearly on the reciprocal crosslink number or irradiation dose [1]. The Charlesby-Pinner equation holds only for the case when the initial MWD of a polymer is the most probable distribution. For that reason, a few modifications of the Charlesby-Pinner equation have been proposed [6, 7]. In this connection, another formula has been derived to calculate the content of sol fraction in a crosslinked polymer [8]:

$$\log s = b + m \cdot \log D \qquad (1)$$

*where: D is the radiation dose; b and m are constants depending on initial molecular weight distribution and crosslinking yield.*

With the radiation dose assumed to be linearly directly related to the irradiation time, the dose D can be replaced by time equation (1) with the same coefficient *m* value but a different *b*-value. The constant may be evaluated by means of a special computer software simulating the formation of an insoluble fraction (gel) under macromolecule crosslinking conditions [8, 9]. The present paper shows an example of application of the new computation tool to study photo-crosslinking efficiency.

### EXPERIMENTAL

The experimental data on gel content *vs.* irradiation time in the UV-initiated crosslinking of polyethylene [10] were taken as an example. Polyethylene films ($2 \cdot 10^{-4}$ m thick) were irradiated in vacuum at a residual pressure of 6.5 N · $m^{-2}$ by the full light of a DRT-1000 (1 kW) medium-pressure mercury lamp. A number of photo-initiators listed in Table 1 were used at concentrations of 0.01 mol/kg. Details of the photo-crosslinking experiments have been described elsewhere [10]. Computations were performed by using the scientific software GelSim5 [(c) Alexander Shyichuk, 1999]. The initial molecular weight distribution was of the Schulz-Zimm type with the following averages: $M_n$ = 42.8 kg/mol and $M_w$ = 290 kg/mol which corresponded to that of the experimental PE sample (LPLD-8020, Unitos).

### RESULTS AND DISCUSSION

Figure 1 demonstrates the original experimental data [10] plotted as log *s* *vs.* log *t* according to equation (1). The experimental relationships are seen to display sufficient linearity. The coefficients *m* and *b* were determined by the least-squares method and are listed in Table 1. With log *s* = 0 assumed to correspond to the time of incipient gelation, the gel-point, $t_g$, can be calculated as:

Table 1. **Kinetic parameters of the photo-crosslinking process with different initiators**

| Photo-initiator | $m$ | $b$ | $t_g$, min | λ | $N_{c,g}$, mol/kg | $V_c$ mol/kg ·min | $V_s$ mol/kg ·min |
|---|---|---|---|---|---|---|---|
| 2-ethylanthraquinone (◇) | -0.277 | -0.164 | 0.26 | 2.59 | 0.014 | 0.056 | 0.145 |
| 2,3-dichloro-1,4-naphthoquinone (□) | -0.245 | -0.103 | 0.38 | 2.76 | 0.017 | 0.045 | 0.125 |
| 1,4-naphthoquinone (Δ) | -0.279 | -0.080 | 0.52 | 2.58 | 0.014 | 0.028 | 0.072 |
| Tetrafluorobenzoquinone (●) | -0.345 | -0.036 | 0.79 | 2.22 | 0.010 | 0.013 | 0.029 |
| Tetrachlorobenzoquinone (+) | -0.231 | -0.030 | 0.74 | 2.83 | 0.018 | 0.025 | 0.070 |
| Benzoquinone (x) | -0.195 | -0.027 | 0.73 | 3.03 | 0.023 | 0.032 | 0.096 |
| Tetrabromobenzoquinone (o) | -0.142 | -0.001 | 1.02 | 3.31 | 0.045 | 0.045 | 0.148 |

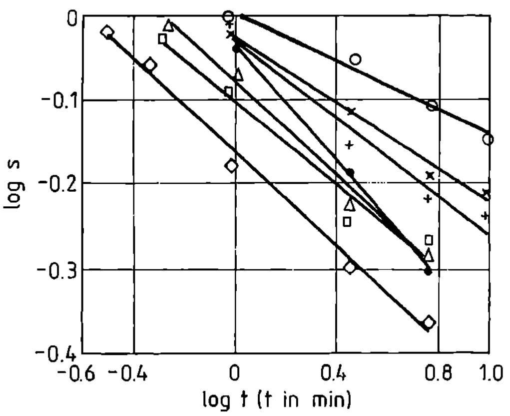

*Fig. 1. Sol fraction vs. UV-irradiation time with photo-initiators listed in Table 1*

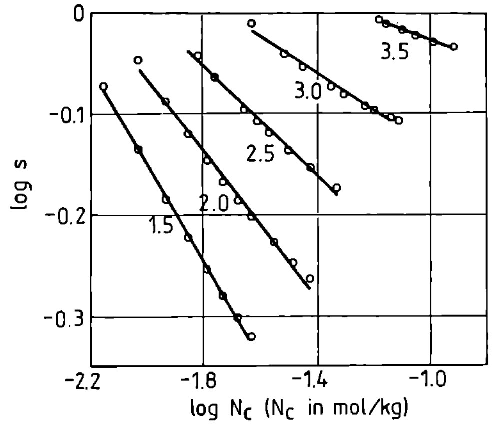

*Fig. 2. Sol fraction vs. crosslink concentration at the scission/crosslinking ratio indicated*

$$\log t_g = -\frac{b}{m} \qquad (2)$$

The sol-gel transition times were calculated by using eqn. (2) for all the experiments (Table 1). Comparison of these results with computer simulations showed that all the experimental slopes $m$ differed substantially from the value predicted by assuming the crosslinking was the only process. Computer simulation of polymer crosslinking with the initial *MWD* gave the slope $m$ equal to -0.765. On the other hand, the experimental slopes ranged from -0.142 to -0.345. This fact may be explained if we take into account the backbone scission reactions. A number of computer experiments was performed to simulate both crosslinking and scission occurring simultaneously at different rates. Results are plotted (Fig. 2) as the sol fraction *vs.* crosslink concentration $N_c$ in the log-log coordinates. The plots of log s *vs.* log $N_c$ show different slopes at different ratios of scission to crosslinking rate, λ. The slopes were plotted (Fig. 3) *vs.* scission/crosslinking ratio. From the data in Fig. 3, the parameter λ was calculated for all the experiments by the linear interpolation method (Table 1).

The concentration of crosslinks needed to start gelation, $N_{c,g}$, was also obtained by computer simulations. The concentration is seen to increase sharply as the parameter λ is increased (Fig. 3). With the pre-determined values of λ (Table 1), the crosslink concentrations at the gel-point were calculated for all the experiments by the linear interpolation method (Table 1). The crosslinking rate $V_c$, and the scission rate $V_s$, were determined as:

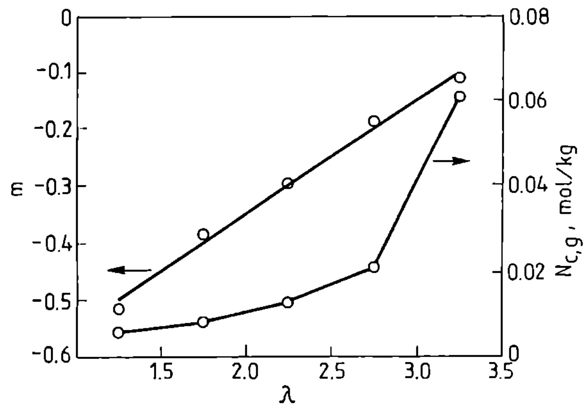

*Fig. 3. The slope m and crosslink concentration at the gel-point $N_{c,g}$ vs. scission/crosslink ratio λ*

$$V_c = \frac{N_{c,g}}{t_g} \qquad (3)$$

$$V_s = V_c \cdot \lambda \quad (4)$$

The photo-initiated crosslinking of polyethylene is accompanied by intensive backbone scission. Each quinone used provided a different rate of crosslinking and scission (Table 1). The highest crosslinking efficiency was due to 2-ethylanthraquinone, with the scission/crosslink ratio equal to 2.59. On the other hand, for the less effective photo-initiator tetrafluorobenzoquinone, the scission/crosslinking rates ratio was minimum. Obviously, the knowledge of crosslinking and scission rates together can help us select an optimum photo-initiator for given processing conditions.

## CONCLUSIONS

Plotting the sol fraction *vs.* irradiation time in the log-log coordinates is a convenient way to disclose backbone scission accompanying macromolecule crosslinking. The ratio of scission to crosslinking rate can be determined by computer simulations with the slope of the log sol *vs.* log time plot used as an indicator.

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