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SHORT COMMUNICATION

A WAY TO GEL-POINT DETERMINATION

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Abstract—In order to linearize the representation of gel-formation kinetics, logarithmic coordinates for sol fraction and irradiation dose are proposed. Slopes have been obtained for initial molecular weight distributions (Schulz type) with polydispersities in the range 1.5–6. The high linearity of the approximation, together with the pre-known slope, can reduce the experimental inaccuracy of gel-point determination. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Crosslinking of macromolecules is frequently used to modify polymer properties. Crosslinks are produced by means of ionizing radiation or chemical reactions. A simple method of determining crosslinking yield is through gel fraction measurement. The representation of gel formation kinetics is usually linearized by the coordinates $(s + \sqrt{s})$ vs reciprocal dose according to the widely known Charlesby–Pinner equation [1]:

$$s + \sqrt{s} = 2/\delta \tag{1}$$

Here, s is sol fraction in the crosslinked polymer and crosslinking coefficient δ is equal to the average number of monomer units crosslinked per initial weight-average macromolecule. The intercept of the plot with the axis at $s + \sqrt{s} = 2$ gives the dose of incipient gel formation. The gelation dose corresponds to the condition: $\delta = 1$ [2].

Equation (1) is valid only when the initial molecular weight distribution (MWD) is the most probable distribution. However, the Charlesby–Pinner equation is frequently used for different distributions, to which it is not applicable. In those cases, the experimental plots in the Charlesby–Pinner coordinates are convex upwards or downwards depending on whether the initial MWD is broader or narrower than the most probable distribution. Therefore, it has been proposed to modify the original Charlesby–Pinner equation [3]. The modified version involves virtual dose, the value of which is chosen by a computer to reach the closest approximation to a straight line.

One more way of linearizing the representation of gel formation from experimental kinetics is proposed in the present paper. It consists of the use of logarithmic scales for sol fraction and radiation dose. These logarithmic coordinates were used a few decades ago for plotting solubility of crosslinked polymers [2], but later the well known Charlesby–Pinner coordinates became common. The objective of this paper is to draw attention to logarithmic coordinates, which are simple to use and give obvious results.

EXPERIMENTAL PROCEDURES

Gel formation kinetics have been obtained from Monte Carlo computer simulation. This model has already been used to study the process of simultaneous crosslinking and scission of macromolecules [4]. Six MWDs of the Schulz type [5] have been used as the initial ones. The computer experiments have been performed on a PC AT/286 with Turbo Pascal 6.0 language.

RESULTS AND DISCUSSION

The computer experiments have yielded accurate dependencies of sol fraction versus number of crosslinks for the MWDs studied. All these dependencies appeared to be well represented by logarithmic scales (see Fig. 1). Here, only the plots of

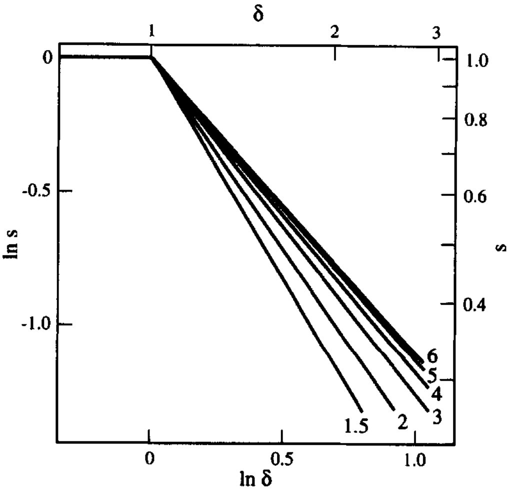

Fig. 1. Logarithmic representation of gel-formation kinetics. Numbers near curves mark initial polydispersity M_w/M_n.

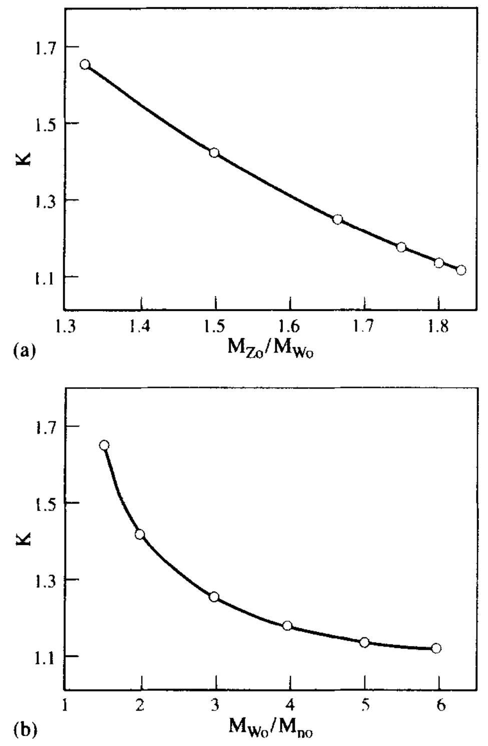

Fig. 2. Dependences of slope K vs z-average polydispersity (a) and weight-average polydispersity (b).

MWDs with initial polydispersities of 1.5 and 2 are slightly convoluted. So the following equation may be written:

$$\ln s = -K \times \ln \delta. \qquad (2)$$

The above mentioned relation is true beyond the gel-point, since before this the sol fraction is equal to unity. The crosslinking coefficient is directly proportional to the radiation dose, r:

$$\delta = 1.04 \times 10^{-6} \times G \times r \times M_w, \qquad (3)$$

where G is the number of crosslinked monomer units per 100 eV absorbed [2]. A combination of equations (2) and (3) leads to:

$$\ln s = -K \times \ln(1.04 \times 10^{-6} \times G \times M_w) - K \times \ln r \quad (4)$$

with the first term being a constant. So, the log–log plot of sol fraction vs dose will also be linear with the same slope K. The plot of intercept with axis at $\ln s = 0$ gives the gel-point dose, from which the radiation yield may be easily calculated with equation (3). Slopes of the logarithmic representations have been calculated and their values are shown in Fig. 2(a) and 2(b). If the polydispersity of the initial MWD is pre-known, then the slope may be determined from the presented plots. This enables us to plot the approximate straight line to experimental points more accurately. If the initial polydispersity is unknown, then the slope of the approximate line makes it possible to estimate the breadth of the MWD. For very broad MWDs, the estimation is not accurate since the slope value depends slightly on polydispersity (see Fig. 2).

CONCLUSION

The proposed logarithmic coordinates can approximate experimental data of sol–gel analysis with a straight line. A high linear approximation gives a high accuracy of gel-point determination. If the polydispersity of a polymer studied is predetermined, then an approximate slope will be known and the treatment of experimental data will be more accurate.

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