

# Digital Model of Macromolecule Crosslinking

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## SYNOPSIS

A digital model of the MWD changes under polymer crosslinking is described in detail. The model yields full MWD, its average molecular weights and other average parameters, and the gel point and gel fraction vs. the crosslinks number. The model is verified to be in essential agreement with the crosslinking theory predictions. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

The general theory of macromolecule crosslinking was developed long ago.<sup>1-3</sup> At the initial stage, the crosslinking of polymer chains results in star-branched macromolecules with increasing sizes. At a specific crosslinking degree, a networklike structure starts to form. This extremely large macromolecule is named a gel. The crosslink number needed for the gel incipency is inversely proportional to the weight-average molecular weight of the polymer.<sup>1,2</sup> The gel may be swollen by means of complete extraction of the soluble polymer part called the sol. The gel fraction depends on the crosslink density. In the case of the Flory initial molecular weight distribution (MWD), the dependence is expressed by the well-known Charlesby-Pinner equation<sup>3</sup>:

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

Here,  $s$  is the sol fraction and the crosslinking coefficient  $\delta$  is equal to the average number of monomer units crosslinked per initial weight-average macromolecule. In the case of another MWD, the dependence differs from the Charlesby-Pinner relation. Gel fractions vs. crosslink density have been computed with numerical methods for some of the Schulz MWDs.<sup>4</sup> At the same time, many researchers handle real MWDs which have been presented in the form of tables and which frequently differ from the aforementioned distributions. In those cases, the gel fractions vs. the crosslinking density are un-

known and, respectively, the sol-gel analysis is unapplicable. In the present article, a method for the computation of the gel fraction is described. It consists of Monte Carlo simulation of the MWD changes under the crosslinking process. That method is applicable to any MWD. A similar model has been already used,<sup>5</sup> and the high molecular tail of the MWD was predicted with an approximation. In contrast with Ref. 5, the present model keeps the whole MWD in the computer memory. Such a model requires a very much larger array, but it is more adequate and makes it possible to detect the sol-gel transition. The choice of the random macromolecule needs more time in the case of the large array of MWD. In spite of this fact, the developed quick algorithm speeds up the computations.

## SIMULATION ALGORITHM

The current integral MWD is kept in the computer memory as an array of the numbers  $i(p)$ , where  $p$  is the polymerization degree of a single polymeric species and  $i$  is the cumulative mass fraction of all species with a polymerization degree (DP) from 1 to  $p$  included. In research practice, the differential form of MWD (mass fraction of a single polymeric specie vs. its DP) is usually used. It is more obvious as compared to the integral form, but the latter one is used immediately under the program execution (see below). The general algorithm of the Monte Carlo simulation of crosslinking is shown in Figure 1. The first segment inputs the initial MWD from the keyboard and transforms one into the integral form. Further, the choice of a macromolecule is per-

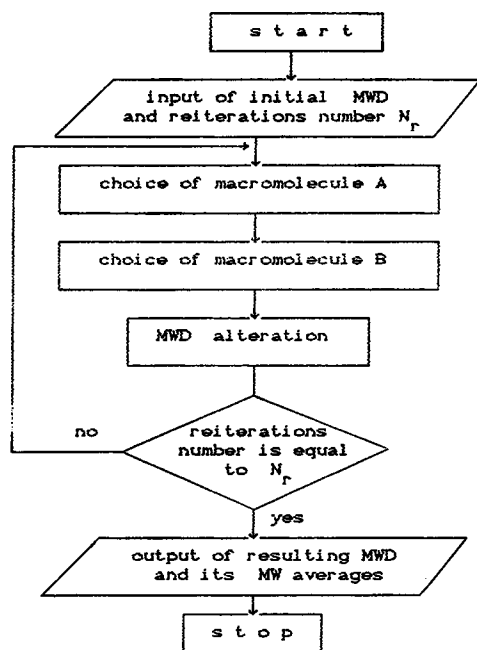


Figure 1 General algorithm of the model of macromolecule crosslinking.

formed at random. The choice subroutine uses a random number, which is generated by the standard procedure RANDOM (see Fig. 2). The generated standard random numbers have even probability in the range 0 to 1. At the same time, under the statistic crosslinking in question, the probability of the choice of a macromolecule with a specific DP is proportional to the weight fraction of the molecules with such a DP. Therefore, the initial even distribution of the random numbers is transformed by the program to the shape of the current MWD. The transformation is performed by the method of inverse function. For a standard random number  $R$ , the corresponding value of the DP  $p$  is found which satisfies the condition

$$\text{max value of } p \text{ such that } i(p) \leq R$$

where  $i(p)$  is the normalized integral MWD. Instead of simple consecutive screening, the dichotomy is used to find the required value of  $p$  (Fig. 2). Every next range of the finding is twice that of the foregoing one and, therefore, the subroutine of the macromolecule choice is very quick.

The current MWD is altered after the crosslinking because two molecules have disappeared and one new one has appeared. The special subroutine executes the alteration immediately on the integral MWD (Fig. 3). That way results in a thrift of computer time. If the crosslinked macromolecule has

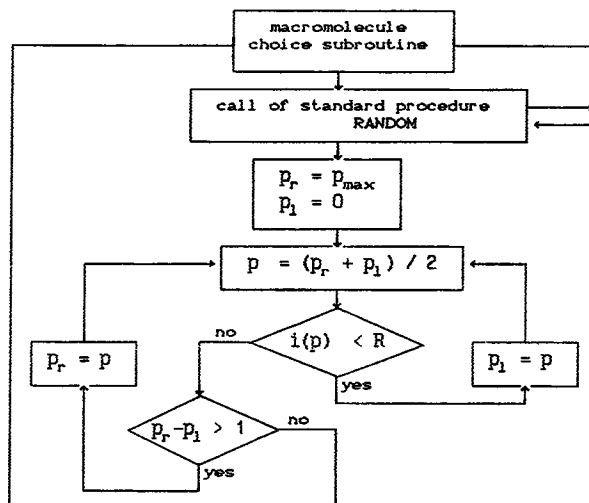


Figure 2 Algorithm of the random macromolecule choice procedure.

the DP at more than the  $P_{\max}$  value, then that molecule is added to gel. The gel fraction is the mass fraction of all macromolecules with DPs more than the  $P_{\max}$  value. To verify the model validity, the

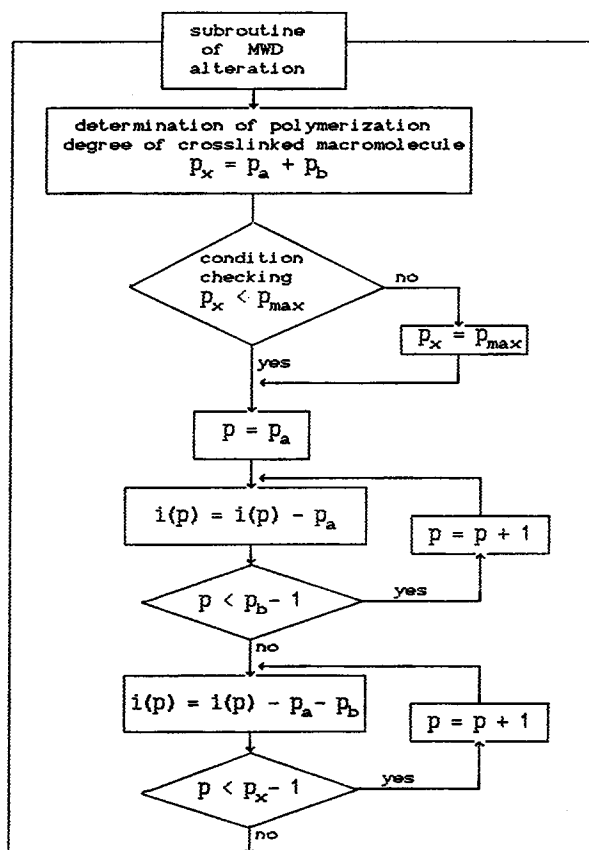
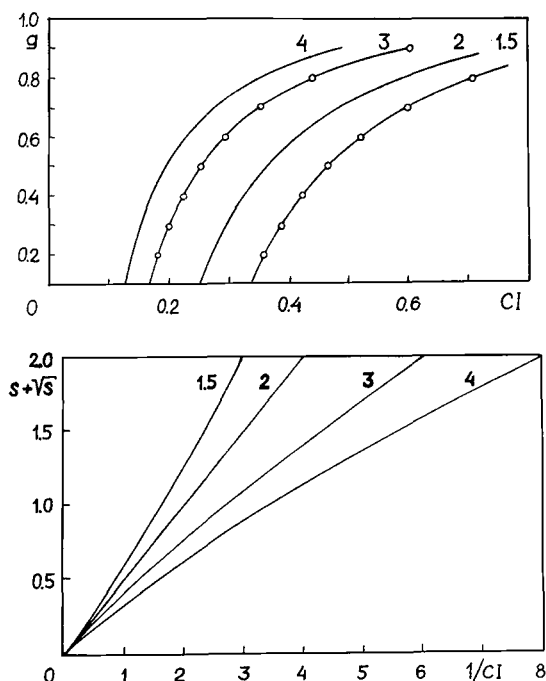


Figure 3 Algorithm of the MWD alteration procedure.



**Figure 4** (a) Gel fraction vs. crosslinking index for initial Schulz MWDs. (b) Treated data in the Charlesby-Pinner coordinates. Nos. near lines mark the polydispersity index of initial MWDs.

mentioned limiting value must be fairly large—about 10 times as large as the DP maximum from the initial MWD.

The general crosslink number  $N_x$  is equal to the reiteration number  $N_r$  (Fig. 1). To reach the required crosslinking degree of the simulated polymer,  $N_x$  must be proportional to the initial number of the macromolecules,  $N_0$ :

$$N_x = CI \times N_0$$

where the crosslinking index CI is equal to the average crosslink number per initial number-average macromolecule. To reduce the computation time, it is reasonable to decrease the initial macromolecule number and, respectively, also the numbers  $N_x$  and  $N_r$ . However, the decrease of the macromolecule number under a certain level leads to the appearance of molecular weight average fluctuations. This level depends much on the MWD shape and it is a quantity in the range of  $10^3$  to  $10^8$  macromolecules.

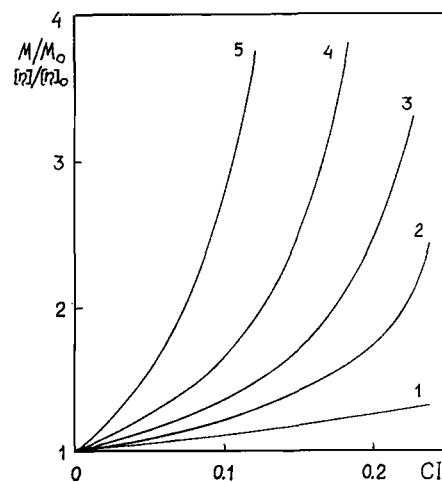
The resulting MWD is transformed to the usual differential form and is output on the print as the table of numbers: the weight fraction vs. molecular weight. The scale of molecular weight may be made according the calibration of a gel-chromatograph which is at the disposal of a researcher.

## MODEL VERIFICATION

It is known that Monte Carlo models are very sensitive toward features of the program realization.<sup>6</sup> Therefore, the model validity was verified using a comparison of the simulation results with the predictions of the general theory of macromolecule crosslinking. Under the computer experiments, gel is formed indeed after the specific number of the crosslinks. The gel points [Fig. 4(a)] correspond very well to the condition  $\delta = 1$ .<sup>1</sup> The kinetics of the gel formation is in essential agreement with that calculated in Ref. 3 with numerical methods [see Fig. 4(a)]. For the initial most probable distribution, the plot in the Charlesby-Pinner coordinates ( $s + \sqrt{s}$ ) vs.  $1/\delta$  results in a straight line [Fig. 4(b)]. In the cases of other distributions, the plots are curved markedly [Fig. 4(b)].

## CONCLUSION

The algorithm of the digital model of macromolecule crosslinking is described in detail. The model has been verified as reliable. The model yields the gel fraction vs. crosslinking density for any polymer, if the initial MWD of the polymer is known. Besides the gel-formation kinetics, the model yields the changes of the molecular weight averages (Fig. 5). That makes it possible to determine the crosslinking index before the gel point. In addition, the model yields the changes of intrinsic viscosity (Fig. 5) which is simply the measurable parameter. All the



**Figure 5** Relative changes of (1) number-average, (4) weight-average, and (5) z-average molecular weights and (2, 3) intrinsic viscosity. Mark-Houwink exponent (2)  $a = 0.5$  and (3)  $a = 0.7$ . The Flory initial distribution.

mentioned parameters are more sensitive to the crosslinking than to the number-average molecular weight (Fig. 5). Thus, the developed digital model will be of help to researchers who handle the crosslinking of polymers.

**Note:** The computations of the gel formation kinetics for a real polymer sample may be performed on request, if the initial MWD of the polymer is available.

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