

Comparison of the Structure of Step-Growth Networks Obtained by Monte Carlo Simulation and Branching Theory

ERICH HÄDICKE, HERBERT STUTZ

Polymer Research Laboratory, BASF Aktiengesellschaft, 67056 Ludwigshafen, Germany

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ABSTRACT: To facilitate the characterization of polymer networks, a comparison was made between branching theory and Monte Carlo simulations using an amine-cured epoxy as an example for step-growth polymer networks. The primary objective was the validation of the simulation results with the existing statistical theories by a cross-check, to ensure that simulations can also be used for the characterization of real, highly complicated multicomponent systems, which are intractable by theories. Commercially available software was used for simulation; the theoretical calculations were performed using the approach of Macosko and Miller. In general, the results of both methods are consistent; the simulation revealed some uncertainties only in the vicinity of the gel point. Since the statistical theories have been validated experimentally, it may be concluded that the simulation can also successfully be used for the treatment of real, highly complicated multicomponent systems, which for practical purposes are intractable by statistical theories. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 929–935, 2002

Key words: network evolution and structure; Monte Carlo simulation; amine-cured epoxy

INTRODUCTION

Real polymer networks always contain a certain amount of defects arising from incomplete curing, side reactions, interfering degradation, and so forth. As outlined schematically in Figure 1, these network defects lead not only to unconnected molecules remaining as soluble material but also to pendant chains connected with only one end to the network. In addition, unreacted functional groups of the curing agent reduce the connectivity of the network.

Polymer networks can be characterized by statistical theories, such as, for example, Gordons's

cascade process,¹ the recursive method of Macosko and Miller,² and others. A different approach uses simulations based on Monte Carlo (MC) methods. Both have their own advantages and drawbacks. The statistical theories allow precise and reliable predictions of the growing network but are difficult to adjust to real systems, which include complex mixtures of monomers with different molecular weights and functionalities, reactivities of functional groups, side reactions, and so on. This is much easier done by Monte Carlo simulations.

Because the statistical theories have been validated experimentally by several groups using different systems (see Stutz et al.³ and references therein), they can be used together with available experimental data to check the reliability of Monte Carlo simulations. This was performed

Correspondence to: E. Hädicke (erich.haedicke@basf-ag.de).

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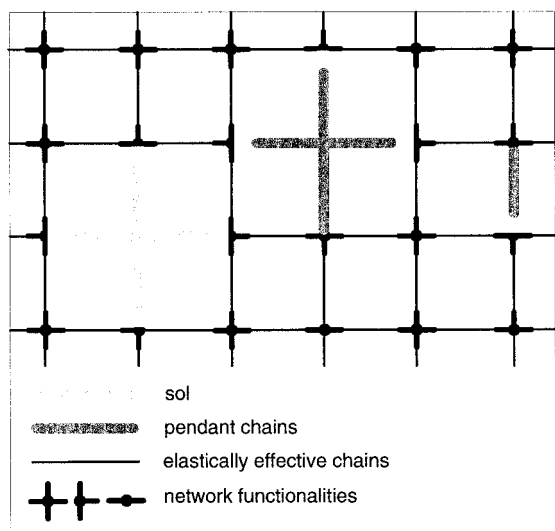


Figure 1 Schematic representation of flaws in real networks.

here using a commercially available Monte Carlo software for an amine-cured epoxy as a representative example of step-growth networks.

NETWORK CHARACTERIZATION

The statistical calculations were performed using the recursive method of Macosko and Miller,² the MC simulations by the commercially available software DryAdd.⁴ This software, developed by Claybourn and Reading,⁵ runs on a personal computer.

Both methods allow calculation of all network parameters, such as number- and weight-average molecular weights prior to gelation, the gel point, and postgel properties such as amount and molecular weights of the sol, amount of pendant,

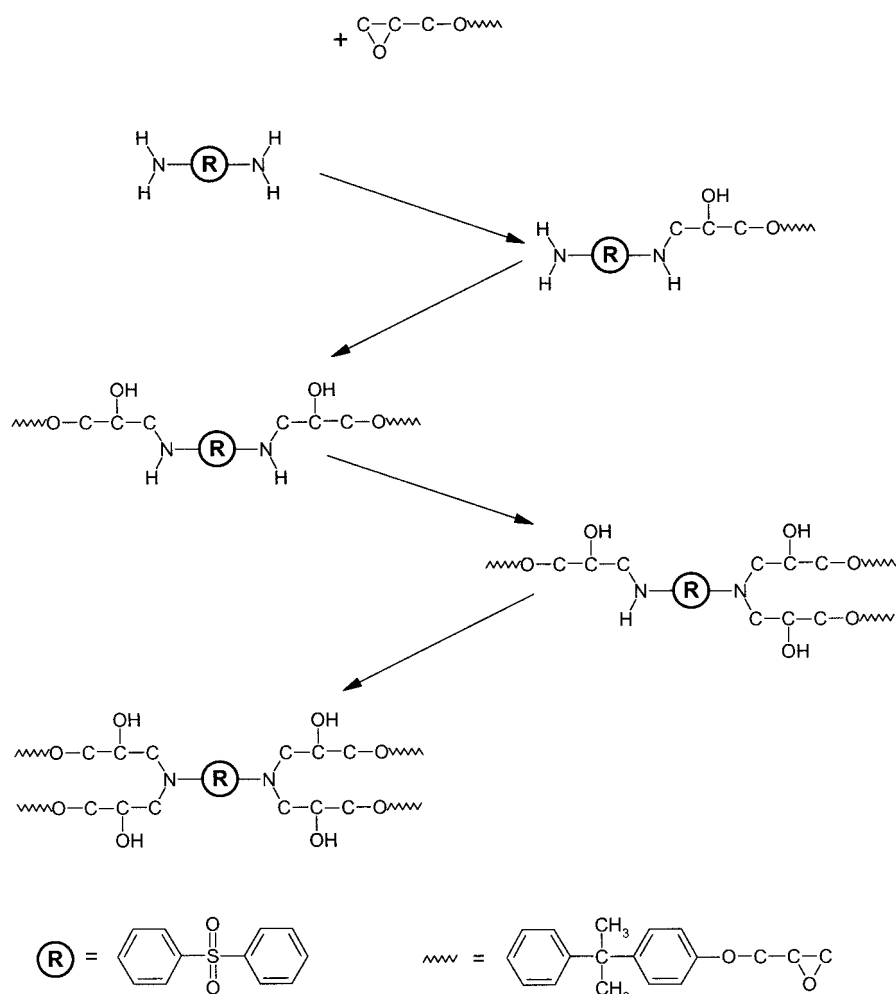


Figure 2 Reaction sequence of curing epoxies by amines by step-growth addition.

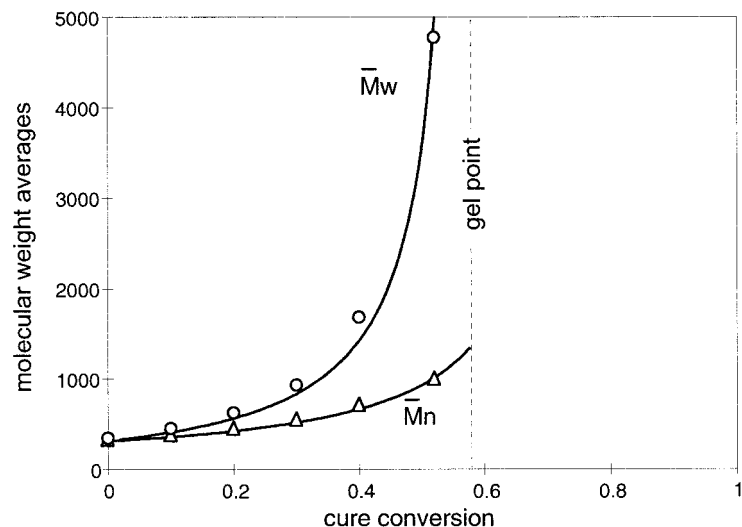


Figure 3 Evolution of the molecular weight averages in the pregel region. Comparison between branching theory (lines) and simulation (dots).

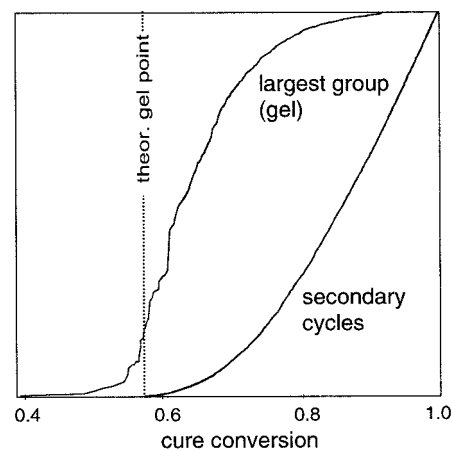
elastically effective chains, crosslink density and molecular weight averages between crosslinks, and the functionality distribution of the crosslinks in the network at any instant of the reaction.

RESULTS AND DISCUSSION

The calculations were made for an amine-cured epoxy as a representative example of an A_4B_2 network (curing of a difunctional epoxy B_2 , e.g., diglycidyl-bisphenol A) by a tetrafunctional amine A_4 such as diaminodiphenylsulfone. This system was chosen because it is characterized best and appropriate experimental data are available for comparison.³

The curing mechanism is outlined in Figure 2. Curing proceeds by stepwise addition of an epoxy group to an amine without side reactions. Given that all amine protons have approximately the same reactivity, they are alkylated subsequently, such that a certain distribution of amine functionalities exists until the reaction is complete.

The evolution of the molecular weight averages prior to gelation is shown in Figure 3. Here the MC results are represented as dots, those from the branching theory as continuous lines. Because chain extension and branching proceed simultaneously, the weight average increases faster than the number average. The agreement between branching theory and MC simulation re-



Secondary Cycles

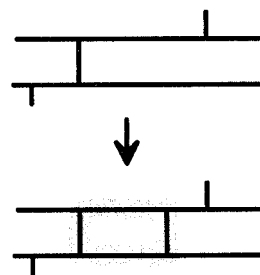


Figure 4 Estimation of the gel point from simulation data.

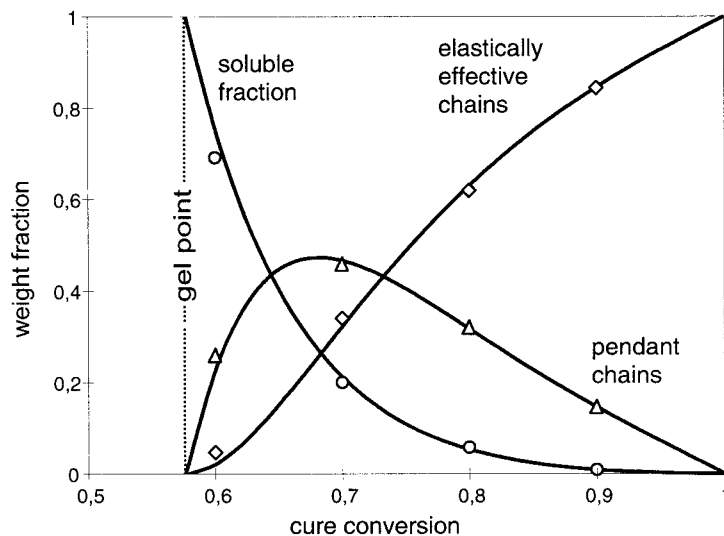


Figure 5 Development of a growing network postgelation. Comparison between branching theory (lines) and simulation data (dots).

sults is good; small deviations observed occasionally may be attributed to statistical variations of the limited number of molecules under consideration in the vicinity of the gel point. Deviations caused by statistical variations can be eliminated by averaging repeated runs.

One of the most important criteria of network formation is the gel point. It is the conversion at incipient formation of a gel. The gel point is dependent on stoichiometry, functionality, and reactivity differences of the functional groups, but not on the molecular weight of the constituents.

To identify the gel point, the MC software recommends the largest group (i.e., gel) or the incipient formation of secondary cycles as criteria. *Secondary cycles* are defined here as cycles formed within the same molecule, the onset and sudden increase of which are an indication for gelation.

This is shown in Figure 4, where the amounts of largest group and secondary cycles are plotted versus cure conversion. The theoretical gel point from branching theory ($p_{\text{gel}} = 0.577$) is indicated here as a dotted line.

It is evident from Figure 4, that the secondary cycles are better suited to characterize the gel point, given that their onset coincides with the theoretical gel point from branching theory. In contrast, the largest group already begins to increase considerably below the theoretical gel point. Its inflection point seems to correlate better

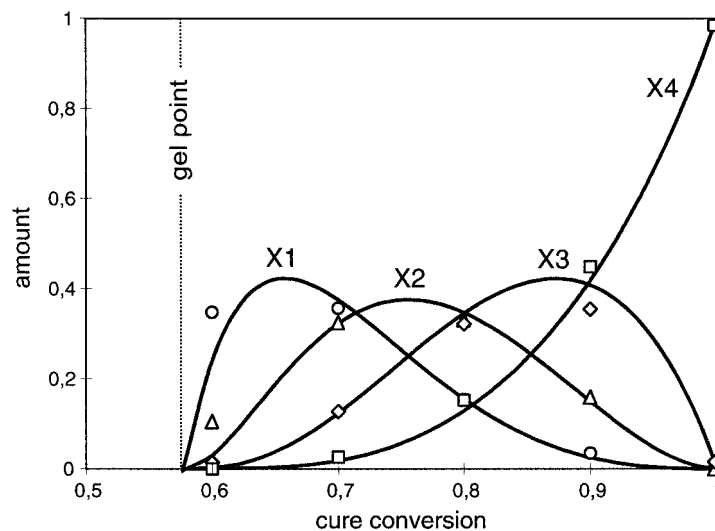
with the theoretical gel point, although it is difficult to identify it with suitable accuracy.

The next points to be discussed are the fractions of solubles and both pendant and elastically effective chains. Directly at the gel point, the system consists of one single chain with infinite molecular weight (which reaches from one end of the reactor to the other); all other chains are still unconnected and therefore soluble. On passing the gel point, these soluble chains are successively captured and bound in a first step with one single bond to the network, until they react further and become part of the elastically effective network. In that way the soluble chains first become pendant chains in the network and are finally transformed into elastically effective network chains.

This evolution is shown in Figure 5, in which the simulation results are again represented as dots and those from branching theory as lines.

Here the agreement is comparable with the previous results of the determination of the molecular weights in the pregel region. The general trends are correct and slight deviations are observed only in the vicinity of the gel point. The deviations diminish with increasing degree of cure. It seems that this might not be a general problem of the simulation, but more a result of the limited number of molecules, especially in the vicinity of the gel point.

Similar trends were also observed with the network functionality distributions in Figure 6.



Network Defects by Incomplete Reaction

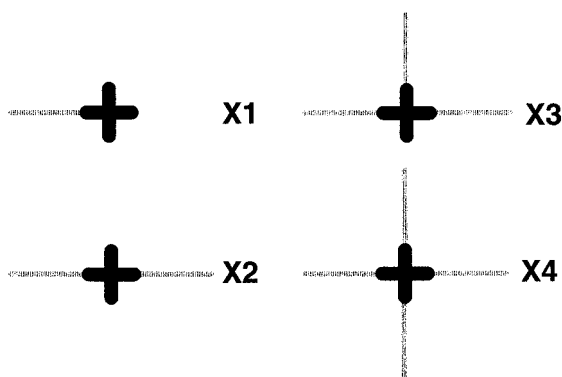


Figure 6 Functionality distribution of the curing agent in a growing A_4B_2 network. Comparison between branching theory (lines) and simulation data (dots).

Here, again, significant deviations are observed primarily in the vicinity of the gel point, which again diminish with increasing degree of cure.

Different functionalities of the network junctions are attributed to the subsequent alkylation of all four amino protons of the curing agent. Thus, by the addition of an epoxy group a molecule of the curing agent is transformed first into a chain end (functionality X1), by the second addition to a linear chain unit (functionality X2), and finally to tri- and tetra-functional crosslinks (functionalities X3 and X4).

The crosslink density (represented here as $X_3 + X_4$) and average molecular weights between crosslinks are shown in Figures 7 and 8.

Here, again, the simulation data deviate from the theoretical ones only in the vicinity of the gel point to some extent, whereas at higher cure conversions the agreement once again is good. The increase in the crosslink density levels off in the very final cure stages, because here the remaining trifunctional crosslinks are converted to tetra-functional ones, which are counted as a sum without weighing them for functionality. Because the molecular weight between crosslinks is inversely proportional to the molecular weight between crosslinks, the found deviation near the gel point is more pronounced in Figure 8 because of the very low crosslink densities in the vicinity of the gel point.

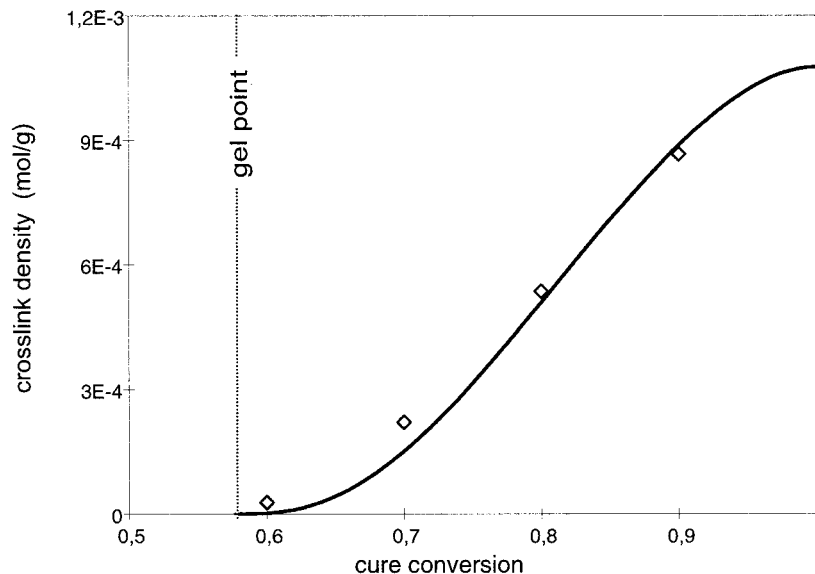


Figure 7 Comparison of the crosslink density obtained from branching theory and simulation of a DGBA/DDS network.

CONCLUSIONS

To check the reliability of an MC simulation for the characterization of polymer networks, a comparison was made with branching theory using an amine-

cured epoxy as a representative example of step-growth networks. The amine-cured epoxy was chosen because experimental data are available for this network and the validity of the theoretical predictions was confirmed in the literature.

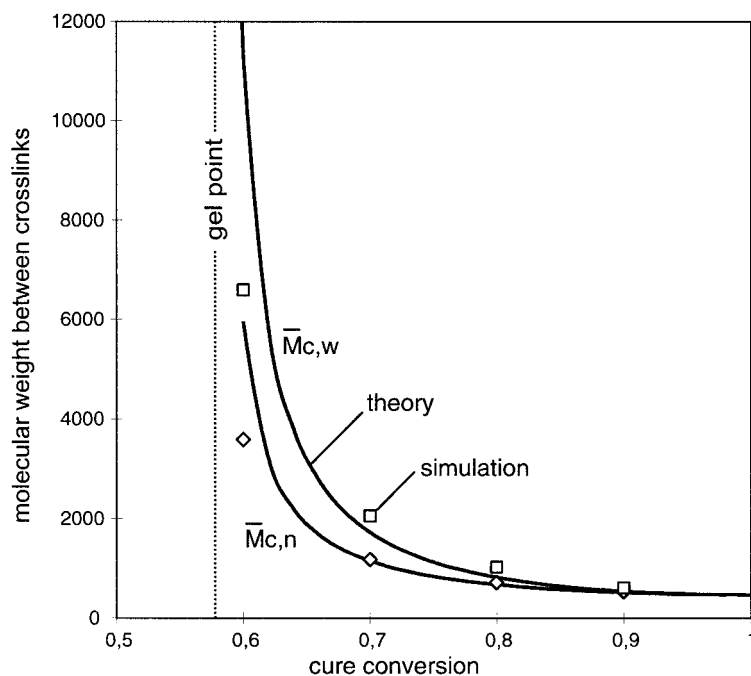


Figure 8 Molecular weight averages between crosslinks of a step-growth DGBA/DDS network. Comparison between branching theory and simulation.

The agreement is good in both the pregel and the postgel region. Some deviations are observed only in the close vicinity of the gel point. This seems not to be a major problem of the simulation, but more a result of the limited number of species in that region.

Some uncertainty arises only from the determination of the gel point. Here the onset of secondary cycles (i.e., reactions within the same molecule) seems to be suited best as the criterion; nevertheless, the gel point can be determined only with some uncertainty.

So, some special features of networks, such as cyclization, side reactions, reactivity differences, or loss of reactive groups, which are primarily estimated from gel point shifts, can hardly be determined from gelation data predicted by simulations.

Overall, it may be concluded that the results of simulations are correct and consistent with the

statistical theories. We may, therefore, expect that it may also be applied successfully to the highly complex multicomponent systems used in practice, which are intractable by statistical theories.

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