# **Computer Simulation of Network Formation in Polymers**

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Received 12 January 1998; accepted 27 January 1998

ABSTRACT: The theory of dynamic systems was used for a simulation of the transition between branched and network macromolecular structures. The system of difference equations was proposed as a corresponding model. The dependence of the limit fraction of crosslinked units on the values of equation coefficients was investigated; linear and oscillatory types of this dependence were determined. The elaborated model was used to analyze experimental data for irradiated polyethylene. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2569–2574, 1998

Key words: branched macromolecules; network; transition; simulation; polyethylene

# **INTRODUCTION**

The modulus of macromolecular systems with different contents of branched and cyclic (network) components was investigated on the basis of the topological approach.<sup>1</sup> According to this approach, the transition from linear macromolecules to the continuous network structure takes place through the following topological forms: linear macromolecules  $\rightarrow$  branched macromolecules  $\rightarrow$ branched macromolecules with individual cycles (network fragments)  $\rightarrow$  three-dimensional network. This scheme is true, in part, for the radiation-induced network formation in polymers.<sup>2</sup>

The phenomenological model<sup>1</sup> of macromolecular systems does not permit, in a general case, estimation of the dose dependence of the topological components content. Therefore, research of the foregoing transition on the basis of the theory of dynamic systems<sup>3–5</sup> is of interest.

### BACKGROUND

The theory of dynamic systems has been used for a simulation of many physical and chemical systems.<sup>3,6,7</sup> The transition between different topological forms as a result of irradiation is a typical dynamic process,<sup>6</sup> described by differential or difference equations. It is necessary to make a mathematical model of this process. The model must take into account the following steps of network formation:

- Formation of branched macromolecules on the basis of linear macromolecules;
- Primary cycles formation on the basis of branched macromolecules;
- Secondary cycles formation on the basis of primary cycles and already-formed second-ary cycles;
- Formation of branched macromolecules as the result of a partial scission of the network, that is, a partial regeneration of the branched macromolecules.

We shall designate the fraction of the crosslinked units conforming to the branched structure as x and the one conforming to the cyclic (network) structure as y. x and y are fractions of the total amount of monomeric units in a specimen.

It is possible to obtain the following system of difference equations:

$$x_{i+1} = k_1 x_i (1 - x_i - y_i) - k_2 x_i^2 (1 - x_i) + k_3 y_i \quad (1)$$

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Journal of Applied Polymer Science, Vol. 70, 2569-2574 (1998)

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Coefficients I				Parameters		
$k_1$	$k_2$	$k_3$	$k_4$	$x_i$	$y_i$	Notes
≤1	0	0	0	0	0	
> 1	0	0	0	>0	0	Oscillations of $x_i$ at $k_1 > 2.5$
> 1	0	0	>0	>0	0	Oscillations of $x_i$ at $k_1 > 2.5$
>1	0	>0	>0	>0	0	Oscillations of $x_i$ at $k_1 > 2.5$
> 1	>0	0	0	>0	>0	Oscillations of $x_i$ and $y_i$ at $k_1 > 2.3$
> 1	>0	0	>0	>0	>0	Oscillations of $x_i$ and $y_i$ at $k_1 > 2$ and $k_4 > 5$
>1	>0	>0	>0	>0	>0	

 Table I
 General Characteristics of the Crosslinking Parameters

 Depending on the Model Coefficients

$$y_{i+1} = k_2 x_i^2 (1 - x_i) - k_3 y_i + k_4 y_i^2 (1 - y_i) \quad (2)$$

In the right part of eq. (1), the first term characterizes the formation of the branched structure on the basis of the linear macromolecules, the second term characterizes the consumption of the branched macromolecules for the formation of the primary cyclic structure, and this dependence is quadratic as the network structure is formed by interaction between the branched macromolecules, formed independently. In eq. (1), the third term characterizes an increase of the branched macromolecule content as a result of scission of the network structure.

In right part of eq. (2), the first and second terms are, naturally, analogous to the second and third terms of eq. (1) with opposite signs. In eq. (2), the third term characterizes the network formation as the result of the interaction of the cycle chains formed independently, that is, a secondary process of network formation. The limiting factors  $(1 - x_i - y_i), (1 - x_i), \text{ and } (1 - y_i) \text{ take into}$ account the finiteness of the macromolecular system. In the foregoing equations, *i* is the number of iterations; the physical meaning of the iterations is dependent on the particularities of concrete systems. For example, in the case of the irradiation of polymers, the number of iterations is associated with the absorbed dose of radiation. The coefficients  $k_1, k_2, k_3$ , and  $k_4$  characterize the intensity of the corresponding processes.

#### **RESULTS AND DISCUSSION**

The problem of this research was to develop a numeric solution of eqs. (1) and (2), a graphic presentation of the results, and an analysis of

these results. The program "Mathcad" was used for the solution and presentation.

The data for the irradiated low-density polyethylene<sup>2</sup> (LDPE) were used as the basis for the solution of the equations. However, the results can be also recalculated for other polymers. The initial fraction of the branched units  $x_0$  is 0.001. This value corresponds to the gel point (gel dose for radiation crosslinking). It was anticipated that there are only the initial traces of the cyclic structure in the gel point, namely,  $y_0 = 0.000001$ .

The values of the coefficients  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$  were varied in turn. The general characteristics of the obtained results are shown in Table I. On the basis of these results, the following conclusions were made:

The branched macromolecules and the network are formed under defined conditions. The formation of the branched macromolecules takes place at the coefficient  $k_1 > 1$  and the formation of the network takes place only at  $k_2 > 0$ , namely, at  $k_2$  $> 0, k_4 = 0$ , and at  $k_2 > 0, k_4 > 0$ . Thus, the formation of the primary cycles is essential for the following growth of the network.

The results are shown in Figures 1–4 in some detail. The fractions of the branched structure  $x_i$ , the cyclic structure  $y_i$ , and also  $y_i/(x_i + y_i)$ , that is, the network fraction per one crosslinked unit, have analogous S-resembling iteration dependence, namely, three sections of relative curves:

- The first section with a slow increase of x<sub>i</sub>, y<sub>i</sub>, and y<sub>i</sub>/(x<sub>i</sub> + y<sub>i</sub>);
- The second section with a quick increase of  $x_i$ ,  $y_i$ , and  $y_i/(x_i + y_i)$ ;
- The third section leads rapidly to a limit of  $x_i$ ,  $y_i$ , and  $y_i/(x_i + y_i)$ , namely, a plateau takes place.



**Figure 1** Iteration dependencies of the parameters  $(\cdots) x_i$ ,  $(-) y_i$ , and  $(- \cdot -) y_i/(x_i + y_i)$  at (a)  $k_1 = 2$ ,  $k_2 = 2$ ,  $k_3 = 0$ ,  $k_4 = 2$ , (b)  $k_1 = 2$ ,  $k_2 = 2$ ,  $k_3 = 0$ ,  $k_4 = 4.9$ , (c)  $k_1 = 2$ ,  $k_2 = 2$ ,  $k_3 = 1.2$ ,  $k_4 = 2$ , and (d)  $k_1 = 2$ ,  $k_2 = 2$ ,  $k_3 = 0$ ,  $k_4 = 6$ .

However, the third section has a peculiarity, namely, the oscillations of  $x_i$ ,  $y_i$ , and  $y_i/(x_i + y_i)$  take place under certain values of the coefficients. Some examples of the iteration dependencies of the parameters  $x_i$ ,  $y_i$ , and  $y_i/(x_i + y_i)$  are shown in Figure 1, namely:

- Simple (typical) linear dependence [Fig. 1(a)];
- Complex linear dependence [Fig. 1(b)];
- Regular oscillations [Fig. 1(c)];
- Chaotic oscillations [Fig. 1(d)].

The limiting magnitude of  $y_i$  corresponding to a plateau is an important value. The elastic properties of crosslinked polymers are dependent on this limit magnitude. We shall designate this limit magnitude as  $y_{\text{lim}}$ . Similarly, we shall use  $x_{\text{lim}}$  equivalent to  $(x_i)_{\text{lim}}$  and  $n_{\text{lim}}$  equal to  $[y_i/(x_i + y_i)]_{\text{lim}}$ . In Figure 2–4, the dependencies of  $y_{\text{lim}}$ ,

 $x_{\text{lim},}$  and  $n_{\text{lim}}$  as functions of the coefficients  $k_1, k_2, k_3$ , and  $k_4$  are shown.

An increase of the coefficient  $k_1$ , that is, an intensification of the branched macromolecule formation, results in an increase of  $y_{\lim}$ ,  $x_{\lim}$ , and  $n_{\rm lim}$  [Fig. 2(a)]. An increase of the coefficient  $k_1$  at the constant coefficients  $k_2$ ,  $k_3$ , and  $k_4$  corresponds to a predominance of the formation of the branched macromolecules, for example, as a result of interaction of the reactive macromolecular groups. The parameter  $y_{lim}$  is little dependent on the coefficient  $k_2$  at constant coefficients  $k_1$ ,  $k_3$ , and  $k_4$ , apparently as a result of a decrease of the branched macromolecule content [Fig. 2(b)]. Thus, an intensification of the primary cycles formation is insufficient to increase the total cycles content, although at the same time, the primary cycles formation is necessary for network formation. The coefficient  $k_3$  can increase because of the network chain scission, for example, on oxidation.



**Figure 2** Dependencies of the parameters (1)  $y_{\text{lim}}$ , (2)  $x_{\text{lim}}$ , and (3)  $n_{\text{lim}}$  on the coefficients (a)  $k_1$  and (b)  $k_2$  at (a)  $k_2 = 2$ ,  $k_3 = 2$ ,  $k_4 = 2$  and (b)  $k_1 = 2$ ,  $k_3 = 0$ ,  $k_4 = 2$ .

In this case, the parameter  $y_{\text{lim}}$  decreases and, simultaneously,  $x_{\text{lim}}$  increases and  $n_{\text{lim}}$  decreases [Fig. 3(a)].

The primary network chains, formed on the basis of the branched macromolecules, can interact with each other. As a result of this interaction, the secondary network chains are formed. In turn, the formed secondary network chains also can interact with each other. An intensity of this process is characterized by the coefficient  $k_4$ . An example of the iteration dependence for this process is shown in Figure 1(b). This dependence can have a stepwise form as the result of a change in the structural mechanism of cycles formation. An intensification of the secondary cycles formation, that is, an increase of the coefficient  $k_4$ , leads to an increase of the parameters  $y_{\text{lim}}$  and  $n_{\text{lim}}$  and a decrease of  $x_{\text{lim}}$  [Fig. 3(b)]. The increase of  $y_{\text{lim}}$  as a function of the coefficient  $k_4$  is more than the increase of  $y_{\text{lim}}$  in the case of the dependence of  $y_{\text{lim}}$  on  $k_1$ ; however, the former takes place only at large values of  $k_4$  [Fig. 3(b)].

Also, simultaneous identical increases of the coefficients  $k_1, k_2$ , and  $k_4$  are possible. The parameters  $y_{\text{lim}}, x_{\text{lim}}$  and  $n_{\text{lim}}$  increase as a result of an increase of the coefficients  $k_1, k_2$ , and  $k_4$  [Fig. 4(a)]. Therefore, different values of the coefficient  $k_3$  were used at  $k_3/k_4$  equal to 0.2. This ratio is equivalent to the parameter  $\Delta$ .<sup>2</sup> The values of  $\Delta$  equal to 0.1–0.3 take place for the polymers studied.<sup>2</sup> In this case,  $y_{\text{lim}}$  increases approximately in the same manner as in the case of the dependence



**Figure 3** Dependencies of the parameters (1)  $y_{\text{lim}}$ , (2)  $x_{\text{lim}}$ , and (3)  $n_{\text{lim}}$  on the coefficients (a)  $k_3$  and (b)  $k_4$  at (a)  $k_1 = 2$ ,  $k_2 = 2$ ,  $k_4 = 2$  and (b)  $k_1 = 2$ ,  $k_2 = 2$ ,  $k_3 = 0$ .



**Figure 4** (a) Dependencies of the parameters (1)  $y_{\text{lim}}$ , (2)  $x_{\text{lim}}$ , and (3)  $n_{\text{lim}}$  on the coefficients  $k_1$ ,  $k_2$ , and  $k_4$  at  $k_1 = k_2 = k_4$ ,  $k_3/k_4 = 0.2$ . (b) Phase portrait of the model at  $k_1 = 3$ ,  $k_2 = 2$ ,  $k_3 = 0$ ,  $k_4 = 2$ .

of  $y_{\text{lim}}$  on the coefficient  $k_1$  [Fig. 2(a)]. Thus, an effect of the branched macromolecules on the network formation is also essential in this case. Also, this was confirmed by the phase portrait on the basis of an elaborate model. An example of a phase portrait is shown in Figure 4(b). The dependence of  $y_i$  on  $x_i$  increases nonlinearly. Therewith, the spiral-resembling part of this curve is associated with a transition to the oscillation regime.

Now, we shall analyze some experimental results on the basis of the iteration dependencies of the  $y_i$  obtained by computer simulation. Herewith, identical initial values of the experimental and model results were coincident and experimental dose values were converted into a number of iterations. The experimental results for LDPE<sup>8</sup> and for the system LDPE-6% triallylisocyanurate (TAIC)<sup>9</sup> were used. In Figure 5, the experimental data are shown as squares; the curves correspond to the mathematical model expressed as eqs. (1) and (2) at definite values of the coefficients  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$ . Figure 5(a,b) corresponds to LDPE and the system LDPE-TAIC, respectively. Values of the doses were recalculated into a number of iterations as a result of a multiplication of doses (MGy) by 0.14 in the case of LDPE and by 130 in the case of the LDPE-TAIC system.

(a)



**Figure 5** ( $\Box$ ) Experimental data and (solid line) model dependencies for (a) LDPE and (b) LDPE-6% TAIC at (a)  $k_1 = 2, k_2 = 2.2, k_3 = 0.2, k_4 = 2$  and (b)  $k_1 = 1.35, k_2 = 3, k_3 = 0, k_4 = 8$ .

The experimental results conform adequately to the model curves with coefficients  $k_1 = 2$ ,  $k_2 = 2.2$ ,  $k_3 = 0.2$ , and  $k_4 = 2$  for LDPE [Fig. 5(a)] and with coefficients  $k_1 = 1.35$ ,  $k_2 = 3$ ,  $k_3 = 0.0$ , and  $k_4 = 8$  for the LDPE–TAIC system [Fig. 5(b)].

In the case of LDPE<sup>8</sup>,  $k_1 = k_4 \approx k_2$ , that is, the efficiencies of the formation of the branched structure and network are alike. In the case of the LDPE–TAIC system,  $k_1 < k_2 < k_4$ ; this corresponds to a more efficient network formation with participation of SF products<sup>9</sup> as a result of the chain-formation process. Thus, there are common characteristics in both polymeric systems, namely, network formation takes place through the stage of the branched macromolecules. However, the chemical structure of the branched products is different, namely, this structure is homogeneous in the case of LDPE and heterogeneous in the case of the LDPE–TAIC system.

# CONCLUSIONS

In the present research, a simplified model was used for the analysis of the transitions between topological forms of macromolecules. The diffusion or migration of the reacting macromolecular forms was not considered. In fact, investigations<sup>9-11</sup> showed that the diffusion effect was absent in the case of the irradiated polymers at temperatures higher than the glass transition temperature  $T_g$ . It is true, in part, for LDPE also. However, it does not occur in the case of the polymers with high degrees of crystallinity, for example, high-density polyethylene. It is possible to make a more detailed model by inclusion of additional terms into eqs. (1) and (2), for example, corresponding to complex topological forms, steric and diffusion limitations, or the consumption of additives.

Nevertheless, by use of this simplified model, it is possible to make important conclusions based on the present research:

• The limit fraction of the crosslinked units is sufficiently less than 1 in the case of the polymer without crosslinking additives, as the coefficient  $k_4$  is small, for example,  $k_4 = 2$ . This limit fraction corresponds to 1 crosslinked unit per 7–10 monomeric units. This is a cause of a partial conservation of crystallites in polymers even at high doses.<sup>8</sup> In a crosslinked polymer (without additives), the branched and network structures coexist

usually even at high doses (equivalent large numbers of iterations).

- In the presence of crosslinking additives, the limit fraction of the crosslinked units is near 1, as the coefficient  $k_4$  is large. Therefore, the branched structure can convert to the network structure completely and the polymeric crystallites also can disappear completely.
- There is a definite range of dose values or equivalent iteration numbers corresponding to a maximum rate of crosslinking in dependence on the dose or the number of iterations. In some cases, experimental detection of this range can be encumbered as a result of the transition of a crosslinked polymer into a glasslike state.
- At definite values of the coefficients  $k_1, k_2, k_3$ , and  $k_4$ , oscillations of the parameters  $y_{\text{lim}}$ ,  $x_{\text{lim}}$  and  $n_{\text{lim}}$  take place in the plateau region (Fig. 1). Even on the the basis of a few examples, it is possible to come to the conclusion that the appearance of oscillations may be related to the value of the coefficients or their ratio. However, detailed additional research on this problem is necessary. These data are important, particularly for a solution of the problem of the radiation stability of polymers and the preservation of the mechanical characteristics of polymeric materials used under irradiation.

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