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# Intramolecular Cyclization in Tetrafunctional Monomer Free Radical Polymerization

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Tetrafunctional monomer free radical polymerization was simulated by Monte-Carlo algorithm. Two mechanisms of cyclization were taken into account: interaction of two free radicals (chain termination) and that of a free radical with the double bond ("intramolecular propagation" of the chain). The considerable cyclization of polymers at the very beginning of the reaction was revealed. Intramolecular chain propagation provides the main factor contributed. The number of cycles by the termination mechanism makes up no more than 20% of total amount. The cycle size distribution dependencies on polymerization rate constants for two cyclization mechanisms were shown to be essentially different. The pregel stage of free radical polymerization of diallyl isophthalate and diallyl sebacate was investigated experimentally. The number of cycles was evaluated from the material balance of the double bonds. The significant cyclization of polymers was found out: a single cycle requires on average 6–8 monomer units. The results prove the intramolecular cyclization should be taken into account in interpreting experimental data and in creating a theory of branched free radical polymerization.

**KEY WORDS** Free radical polymerization, tetrafunctional monomer, intramolecular cyclization, Monte-Carlo simulation

Intramolecular cyclization is a complicated problem of the theory of formation of branched and network polymers. The classic gelation theory<sup>1</sup> is constructed without taking such reactions into consideration. However experimental results show that already in the early stages intensive cyclization takes place in such systems.<sup>2,3</sup> As a consequence the gel point cannot be accurately predicted by the classic theory. Present work is devoted to the theoretical and experimental study of intramolecular cyclization in tetrafunctional monomer free radical polymerization.

## **MONTE-CARLO SIMULATION**

### **Model and Simulation Procedure**

Tetrafunctional monomer free radical polymerization was simulated on a body-centered cubic lattice. Free monomer was not fixed on the lattice and may diffuse freely. Becoming attached to the propagating polymer chain each monomer was placed on the lattice. The chain conformation was constructed with the intersection of neighboring bonds being forbidden and probabilities of trans and gauche rotating isomers equal.



icals  $C_R$  and double bonds  $C_D$  in the chain at each of the steps and establishing their coordinates. Intramolecular reactions were considered to be possible between the reacting groups situated on neighboring sites of the lattice (such a pair of groups we call "contact"). The number of contacts of free radical-free radical  $C_{RR}$  and free radical-double bond  $C_{RD}$  were determined. The rates of elementary reactions were calculated from

$$V_P = k_P \cdot C_M \cdot C_R \quad (1)$$

$$V_I = k_I \cdot C_I \cdot C_D \quad (2)$$

$$V_T = k_T \cdot C_{RR} \quad (3)$$

$$V_{IP} = k_P \cdot C_{RD} \quad (4)$$

Here  $V_P$ ,  $V_I$ ,  $V_T$  and  $V_{IP}$  are the rates of reactions of the chain propagation, initiation of pendant double bonds, intramolecular termination and intramolecular propagation, respectively,  $k_P$  and  $k_T$  are the rate constants of the propagation and termination, respectively,  $C_M$  is the concentration of the monomer.

Two random processes were incorporated into the model of polymerization: both the subsequent state of the system and the waiting time of transition were selected at random. At each step it was necessary to determine which of the above reactions (1)–(4) will be realized. The stage number  $j$  ( $j = 1-4$ ) was calculated from the condition

$$\sum_{i=1}^{j-1} \alpha_i \leq \xi_1 < \sum_{i=1}^j \alpha_i,$$

where  $\alpha_i = V_i/V$  is the probability of the  $i$ -th elementary step ( $i = 1-4$ ) and  $V = V_P + V_I + V_T + V_{IP}$ . If several variants were feasible for the  $j$ -th reaction one of them was selected at random. The waiting time of a given stage was calculated as

$$\tau_m = -\ln \xi_2/V,$$

where  $\xi_1$  and  $\xi_2$  are the random numbers uniformly distributed over the interval (0,1) and  $m$  is the stage number. The total time of polymerization  $t = \sum \tau_m$ . Ratios of rate constants typical for free radical polymerization were employed.<sup>7</sup> The termination constant was taken as  $10^6 \cdot k_p$ . The variation of polymerization conditions was modeled by changing the rate constant  $k_I$ .

Thus in our model the reaction route at every step was determined with the actual probabilities of all elementary stages being taken into consideration. Unlike this in the well known kinetic gelation model<sup>4-6</sup> all the probabilities were assumed equal. To our opinion consideration of different probabilities of free radical-free radical and free radical-double bond interactions can change quantitative regularities of gelation in free radical systems.

## RESULTS AND DISCUSSION

Of particular interest is the estimation of the relative importance of intramolecular cyclization in systems investigated. The probability of cyclization defined by the formula  $w_c = (V_T + V_{IP})/V$  can be introduced as a suitable parameter here. The time dependence of  $w_c$  is shown in Figure 2. The probability of cyclization increases monotonically with time and with increasing rate of initiation. At small  $k_i$  the contribution of intramolecular propagation prevails; however, with increasing number of free radicals in the macromolecule intramolecular termination becomes possible and consequently the overall probability of cyclization rises. It is also apparent from Figure 2 that the probability of cyclization is by no means negligible in the systems investigated. Hence the intramolecular cyclization should necessarily be taken into consideration in creating a theory of branched free radical polymerization.

The concentration of pendant double bonds in macromolecule (the degree of residual unsaturation)  $x$  was calculated. This characteristic is plotted in Figure 3 as a function of degree of polymerization  $N$ . The maximum  $x$  value equals to 0.5 and is achieved if only one double bond in each monomer molecule has reacted and there is no cyclization; a linear macromolecule with pendant double bonds is then formed. Both branching and cyclization reduce the value of  $x$ .

Figure 3 shows that  $x$  is always markedly smaller than 0.5, regardless of the rate of initiation. This supports the presence of branchings and cycles. Even at  $k_i/k_p = 0.001$ , when the propagating chain has only one free radical and no branching is occurring,  $x = 0.4$ . In this case the cyclization proceeds via the mechanism of intramolecular propagation. Thus intramolecular cyclization can not be neglected in tetrafunctional monomer free radical polymerization even at the minimal rate of initiation and the polymerization is not linear.

The number and the sizes of cycles were calculated in computer experiment.

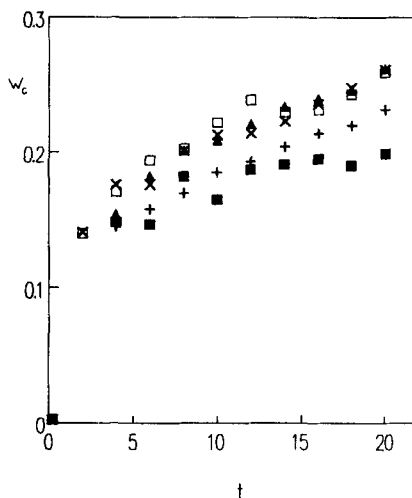


FIGURE 2 Dependencies of the cyclization probability on time.  $k_i/k_p = 0.001$  (■); 0.01 (+); 0.03 (▲); 0.05 (×); 0.1 (□).

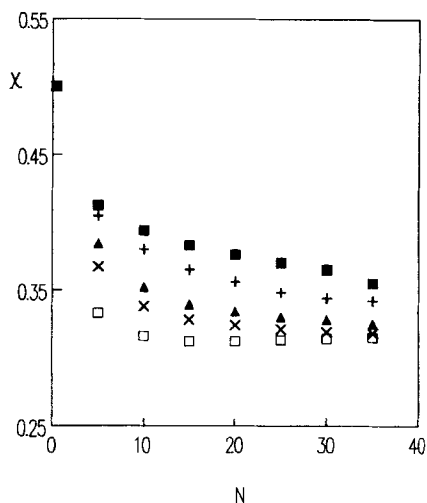


FIGURE 3 Dependencies of the chain residual unsaturation degree on polymerization degree.  $k_t/k_p = 0.001$  (■); 0.01 (+); 0.03 (▲); 0.05 (×); 0.1 (□).

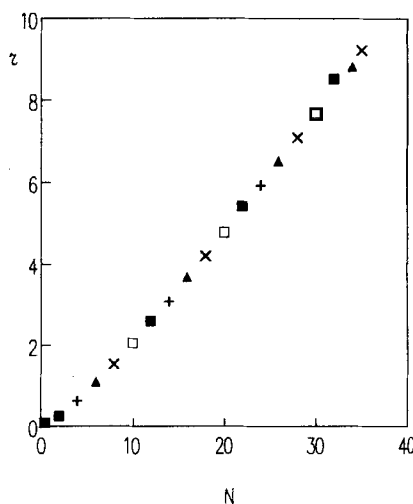


FIGURE 4 Dependencies of the average number of cycles in the chain on polymerization degree.  $k_t/k_p = 0.001$  (■); 0.01 (+); 0.03 (▲); 0.05 (×); 0.1 (□).

The number of cycles was determined by the number of stages of cyclization, i.e. solely independent cycles were taken into consideration. When the sizes of cycles were calculated the availability of earlier formed cycles was neglected. The branched chain was considered as a tree and the sizes were determined as the shortest distance between two points on the tree.

The plots of the number and the sizes of cycles vs. the degree of polymerization are shown in Figures 4 and 5. One can see that at the very beginning of the reaction the number of cycles is rather great. The dependencies of  $r$  vs.  $N$  are practically

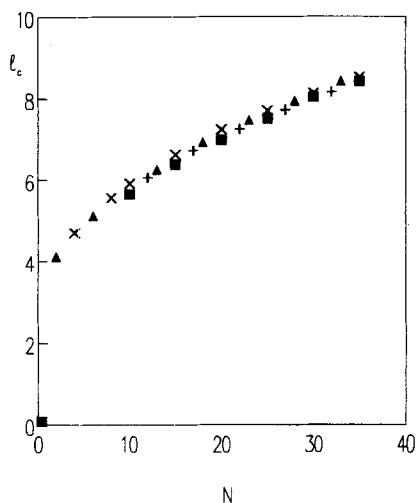


FIGURE 5 Dependences of the average sizes of cycles in the chain on polymerization degree.  $k_t/k_p = 0.01$  (■);  $0.03$  (+);  $0.05$  (▲);  $0.1$  (×).

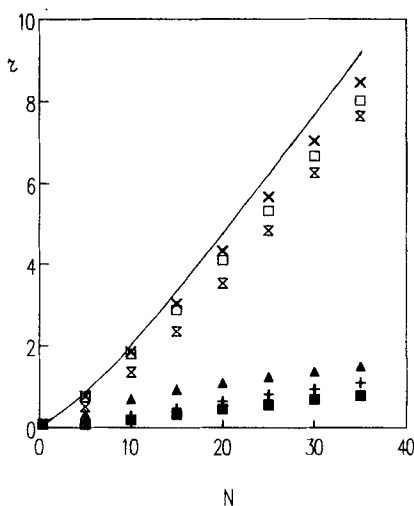


FIGURE 6 Dependences of the average number of cycles on polymerization degree. Cyclization via mechanisms of intramolecular chain propagation (×, □, ⊠), intramolecular chain termination (▲, +, ■) and via the two mechanisms together (solid curve).  $k_t/k_p = 0.05$  (×, ■);  $0.1$  (□, +);  $1.0$  (⊠, ▲).

linear. Both characteristics are practically independent on the initiation rate. This result is not completely understood, since the branching parameters are essentially depend on  $k_t/k_p$ .

To explain the results observed the relation of two cyclization mechanisms was considered. Figure 6 shows the number of cycles for each of the separate mechanisms taken into account as well as the result for the summed case. It is seen, that in all  $k_t$  the reaction of intramolecular chain propagation provides the main con-

tribution. The number of cycles via the termination mechanism increases with increasing  $k_t$ , but in all cases it makes up no more than 20% of total amount.

Consider the intramolecular propagation reaction in detail. Histograms of size distribution of these cycles are presented in Figure 7. For the intramolecular chain propagation the distribution practically doesn't depend on polymerization kinetics. In all cases the highest probability is the one of four-bond cycles (monomer cycli-

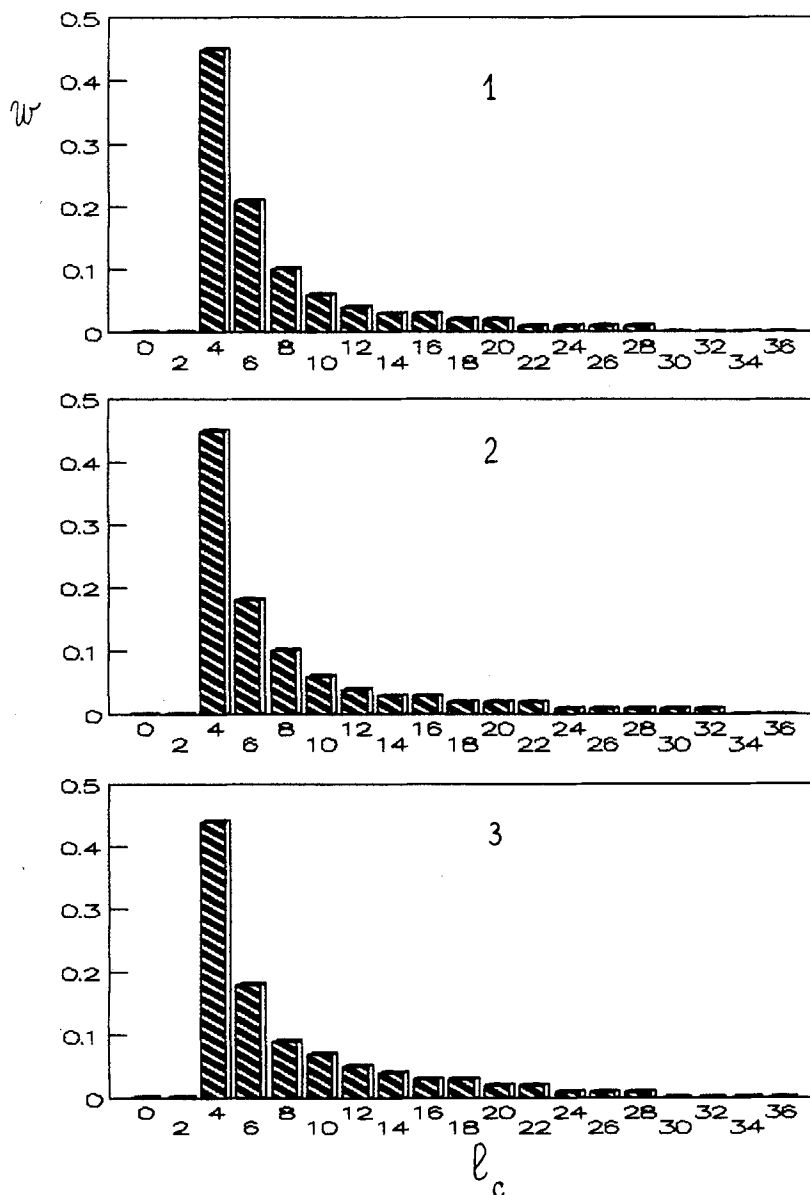


FIGURE 7 Histograms of distribution by the sizes of cycles via mechanism of intramolecular chain propagation. Here and in Figure 8  $k_t/k_p = 5.0$  (1); 0.1 (2); 0.05 (3).



zation on itself). As the concentration of double bonds on the macrochain is rather high (see above), this factor is the main one to determine the reaction. As a result, independence of the sizes of cycles on polymerization rate constants is observed.

For the intramolecular termination reaction the dependence of the distribution by the sizes of cycles on polymerization rate constants were shown to be essentially different (Figure 8). In this case the distribution significantly changes with  $k_t/k_p$ .

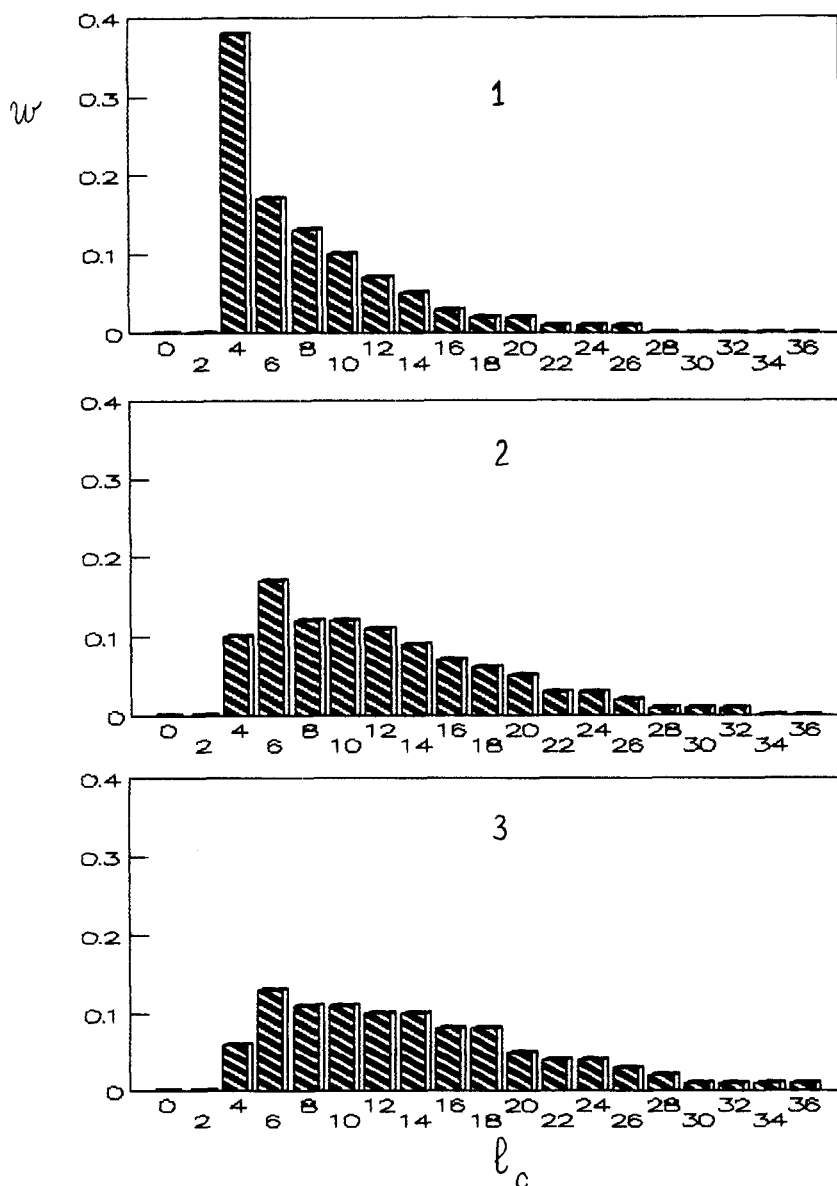


FIGURE 8 Histograms of distribution by the sizes of cycles via mechanism of intramolecular chain termination.

At high initiation rates the formation of four-bond cycles is the most probable. With decreasing  $K_t$  their probability drops and at  $k_t/k_p = 0.05$  it proves to be less than for the cycles containing 6–18 bonds. As with decreasing  $k_t$  the concentration of free radicals in the macromolecule drops, an average distance between them along the chain increases. Hence a portion of large cycles also increases.

Thus, at the pregel stage of tetrafunctional monomer free radical polymerization intramolecular cyclization of two types is possible. The main contribution is provided by intramolecular propagation of the chain. This reaction is governed by the concentration factor and in no way can not be excluded. Additional cyclization by chain termination mechanisms also occurs. This reaction may be regulated by the special selection of the polymerization rate constants.

## EXPERIMENTAL

Experimental investigation of intramolecular cyclization in network polymer formation is rather problematic. A highly effective method for quantitative investigation of this reaction in free radical systems is chemical degradation of branched polymers by groups situated near the branching point.<sup>8</sup>

We consider the pregel stage of free radical polymerization of diallyl esters (DAE) of aromatic and aliphatic dicarboxylic acids—diallyl isophthalate (DAIPH) and diallyl sebacate (DAS). Due to degradational chain transfer the gelation in these systems occurs at 22–24% conversion. The topological characteristics were investigated at 11.5% and 18.6% conversion for DAIPH and DAS respectively.

The branched polymers were obtained by bulk free radical polymerization in the presence of benzoyl peroxide. The polymerizate was dissolved in acetone and then precipitated by petroleum ether or hexane. Polymers were fractionated by fractional precipitation from 3.5% solutions in benzene. 11 fractions of PDAIPH with  $P_n = 7-407$  and 4 fractions of PDAS with  $P_n = 28-191$  were isolated. The saponification of branched polymers were carried out. The obtained polyallyl alcohol was poured over with acetic anhydride and polyallyl acetate was precipitated. The evaluation of topological parameters were based on analysis of MM of both the original branched polymers and their linear chains, i.e. the reacetylated products of alkali hydrolysis. The MM were determined by ebullioscopic and GPC methods. The degree of residual unsaturation of polymers was determined by ozonization and IR spectroscopy.

Table I shows the topological characteristics of fractions of PDAIPH and PDAS. The analysis showed that the polymers investigated are rich in double bonds. The degree of residual unsaturation  $x = 0.32-0.38$  for PDAIPH and  $x = 0.40-0.43$  for PDAS. For both polymers this characteristic is substantially less than 0.5, which indicates to the formation of branchings and cycles.  $x$  scarcely change in number with the MM of the polymer change in an agreement with the Monte-Carlo results (see Figure 3).

The number of branches in a macromolecule  $n$  was determined from the simple ratio of the degrees of polymerization of the macromolecule itself and their linear branches  $n = P_n/P_{n,b}$ . The linear dependence of the number of branching points

TABLE I  
Topological characteristics of branched diallyl esters polymers

Polymer	Fraction <i>N</i>	<i>X</i>	<i>P<sub>n</sub></i>	<i>P<sub>n,b</sub></i>	<i>n</i>	<i>m</i>	<i>m/P<sub>n</sub></i>	<i>r</i>	<i>r/P<sub>n</sub></i>
PDAIPH	1	0.38	406.5	13.5	30.1	29.1	0.07	68.4	0.17
	2	0.36	218.0	14.0	15.6	14.6	0.07	46.4	0.22
	3	0.33	138.5	13.8	10.0	9.0	0.07	38.1	0.28
	4	0.35	99.5	14.0	7.1	6.1	0.06	23.7	0.24
	5	0.35	67.0	12.0	5.6	4.6	0.07	15.5	0.23
	6	0.37	48.3	12.0	4.1	3.1	0.06	9.5	0.20
	7	0.32	34.6	12.0	2.9	1.9	0.06	10.6	0.31
	8	0.31	27.6	13.4	2.0	1.0	0.04	9.5	0.34
	9	0.42	19.5	14.0	1.4	0.4	0.02	2.7	0.14
	10	0.39	13.0	13.4	—	—	—	2.9	0.22
	11	0.43	7.3	—	—	—	—	—	—
PDAS	1	0.40	191.0	15.5	12.3	11.3	0.06	26.9	0.14
	2	0.42	106.4	12.1	8.8	7.8	0.07	9.2	0.09
	3	0.43	74.5	12.1	6.2	5.2	0.07	6.7	0.09
	4	0.41	28.4	12.1	2.3	1.3	0.05	3.8	0.13

$m = n - 1$  on polymerization degree was revealed (in agreement with the computer simulation).  $m = 0.073 \cdot P_n - 0.8$  for PDAIPH and  $m = 0.061 \cdot P_n + 0.01$  for PDAS. The degree of branching of the two polymers  $m/P_n$  practically coincide. At different concentration of double bonds this must result in difference of their cyclization.

The number of cycles  $r$  was evaluated from the material balance of double bonds in the macromolecule, i.e.  $r = P_n \cdot (1 - 2x) - m$ . This equation provides a means of allowing for the contribution of only the intramolecular propagation cyclization mechanism, since recombination of the radicals is not accompanied by breaking of the double bonds. The values obtained are thus low estimates. As the portion of cycles by recombination mechanism is no more than 20% of the total  $r$  (see above the results of computer simulation) this proves the correctness of experimental  $r$  values.

The significant cyclization of polymers was revealed: a single cycle requires 6–8 monomer units in the average. It is interesting to point out that the degree of cyclization of PDAE is substantially higher than their degree of branching: a single branch requires 12–14 monomer units in the average. The linear dependence of  $r$  on polymerization degree was revealed (as in computer simulation):  $r = 0.23 \cdot P_n + 0.58$  for PDAIPH and  $r = 0.15 \cdot P_n - 1.9$  for PDAS. The degree of cyclization  $r/P_n$  is considerably higher for PDAIPH than for PDAS. This conclusion is in conformity with polymer's unsaturation and branching.

Thus the theoretical and experimental results reveal a significant intramolecular cyclization in the pregel stage of tetrafunctional monomer free radical polymerization. This is a characteristic feature of polymerization mechanism of network formation. This conclusion is extremely important for understanding the mechanism and describing the kinetics of gelation and should be taken into account in interpreting experimental data and in creating a theory of branched free radical polymerization.

**References**

1. P. J. Flory, *Principles of Polymer Chemistry*, Ithaca, NY, 1953.
2. K. Dušek, H. Galina and J. Mikes, *Polym. Bull.*, **3**, 19 (1980).
3. K. Dušek and J. Spevaček, *Polymer*, **21**, 750 (1980).
4. H. J. Herrmann, D. P. Landau and D. Stauffer, *Phys. Rev. Lett.*, **49**, 412 (1982).
5. H. J. Herrmann, D. Stauffer and D. P. Landau, *J. Phys. A*, **16**, 1221 (1983).
6. R. Bansil, H. J. Herrmann and D. Stauffer, *Macromolecules*, **17**, 998 (1984).
7. G. Odian, *Principles of Polymerization*, McGraw-Hill, New York, 1981.
8. W. Simpson and T. Holt, *J. Polymer Sci.*, **18**, 335 (1955).