Polymer Bulletin 13, 401–406 (1985)

Polymer Bulletin

Polymerization Kinetics in Some One-Dimensional Systems

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Summary

Kinetic equations for the irreversible chemical reaction between adjacent units in one-dimensional systems are derived. Solutions, describing the influence of isolation and diffusion on the kinetics of reaction, are obtained. This solutions are compared with the results of corresponding Monte Carlo experiments.

Introduction

Present article concerns with the following peculiarities of the reaction in the condensed phase (1,2) :

1. some unreacted units, when surrounded by non-reactionable or reacted ones, take no part in reaction (isolation of units) ;
2. the rate of mixing up of the unreacted units is not fast enough for reaction to progress effectively (diffusionally controlled reaction).

The study of simple one-dimensional models enables us to look clear at separated and combined influence of diffusion and isolation on the kinetics of the reaction.

1. Reaction between fixed particles

We consider the following reaction model: A units are reacting with adjacent B units only, both transforming into C units; the reaction is irreversible and of the second order; initial distribution of unreacted units A and B and "holes" O is random; R is the initial ratio of components; G is a portion of units A, B and C in the infinite one-dimensional system.

"Isolation" corresponds to different situations when reactionable units A and B are surrounded by reacted diads CC, holes O or by the nearest neighbours of the same name. For instance in following part of the system

$$\ldots C\ A'\ C\ C\ O\ B'\ C\ C\ O\ A'\ O\ B\ A\ B\ O\ A'\ A\ B\ B'\ B'\ B\ldots$$

isolated units are marked. Using the method of multiplets (3) or more formalistic method based on the theory of stochastic processes (4) one can obtain the infinite set of exact kinetic equations, describing the reaction in the system under consideration:

$$\begin{aligned} A &= -2\cdot AB \\ AB &= -AB - ABA - BAB \qquad 1^\circ \\ ABA &= -2\cdot ABA - 2\cdot BABA \\ &\ldots\ldots \end{aligned}$$

(here and after the rate constant of the reaction assumed to be equal to 1).

Symbols A, AB, ABA, BAB and BABA denote the probabilities of finding corresponding unit, diad, triad etc in the system. In order to solve this equations one have to truncate the infinite set 1° with the use of some additional condition (5), for example approximation of superpositional type for joint probabilities:

$$ABA = AB\cdot BA/B \quad \text{and} \quad BAB = BA\cdot AB/A \qquad 2^\circ$$

Using this conditions 2° we have obtained an analytical solution of the form:

$$K = (x^2-s^2)^{-1/2}\cdot((1-s^2)^{1/2} + \frac{1}{G}\cdot\log(\frac{(x+(x^2-s^2)^{1/2})}{(1+(1-s^2)^{1/2})})) \qquad 3^\circ$$

$$x = f\cdot(1+s) - s\ ; \quad s = (R-1)/(R+1)$$

(here f is a fraction of unreacted A-units, s is a stoichiometric index (4)).

At this point, we have to note that conditions 2° are quite exact. Indeed, it is easy to see that all the equations 1° are simultaneously satisfied, provided all the joint probabilities of higher order simultaneously obey the conditions of the superpositional type:

$$ABA\ldots AB_{j+1} = ABA\ldots A_j\cdot BA\ldots AB_j/BA\ldots A_{j-1}$$

$$j = 2,3,4,\ldots$$

Flory looked into the kinetics of the reaction between adjacent units in an one-dimensional single-component system without holes (6). He calculated the fraction of units which remain unreacted untill the end of the reaction:

$$f_\infty = e^{-2} = 0.1353\ldots$$

Using the method of multiplets Cohen and Reiss had derived and solved the set of kinetic equations describing the reaction in this simplest system (7). They had obtained the exact analytical solution:

$$f(t) = \exp(-2\cdot(1-e^{-t})) \qquad 4^\circ$$

In order to ascertain wheather or not the kinetics of the reaction in the system considered differs sufficiently from the "ideal" second order kinetics we have plotted kinetic curves of effective reaction rate $K = AB/(A\cdot B)$ vs conversion of A-units (Fig.1).

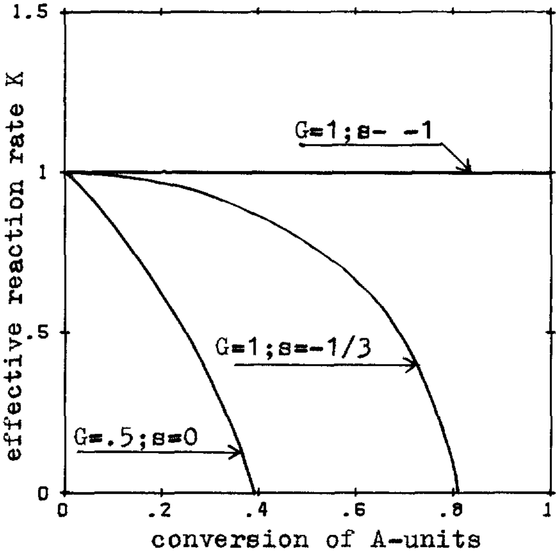

Figure 1. The dependence of effective second order reaction rate constant K on the conversion 1-f of A-units. G is the fraction of units, R is the ratio of components A and B, s is the stoichiometric index in the system of fixed units.

Striking variability of the kinetic curves reflects nontrivial influence of units isolation on the kinetics of irreversible chemical reaction. Depending on the values of G and R (or s) the shapes of the curves show on apparent changes of reaction mechanism. Indeed it is bimolecular one during all the reaction.

2. Reaction in one-dimensional system of jumping units.

No isolation

We consider the model of reaction between adjacent units in single-component one-dimensional system with randomly distributed holes. In addition we allow unreacted units to jump to adjacent unoccupied sites with the rate constant P. Once reacted the units leave the system and isolation does not appear in this case. Treating this process in quite analogous manner as it was described above we have obtained following infinite set of exact kinetic equations:

$$
\begin{aligned}
A &= -2\cdot AA \\
AA &= -AA - 2\cdot AAA + 2P\cdot(AOA - AAO) \\
AO &= -AAO + P\cdot(AOO - OAO + AAO - AOA) \\
OO &= 2P\cdot(OAO - AOO) \\
&\cdots\cdots
\end{aligned}
\qquad 5^{\circ}
$$

Using approximations of superpositional type for triads AAA, AOA, AAO, AOO and OAO we have solved this equations numerically. The results are shown in fig.2.

In fact the solutions in two opposite limits of very fast ($P \gg 1$) and very slow ($P \ll 1$) diffusion are exact. On one hand, when diffusion is negligible ($P \to 0$) the solution

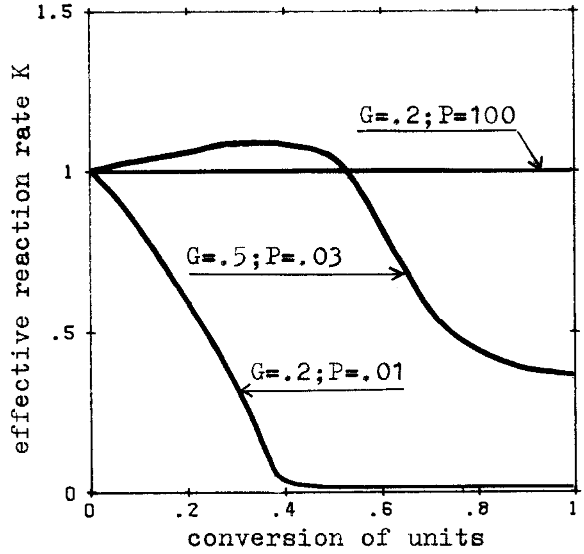

Figure 2. Calculated kinetic curves of reaction in the systems with different diffusion rates P.

of equations 5° coinsides with the exact analytical solution 4°. On the other hand, when the units are mixed up fast the distribution of units and holes in the system remains almost absolutely random, and the superpositional approximations of any order are almost exact. In this limit K=1.

It is interesting to compare the numerical solutions of the set 5° with the results of corresponding Monte Carlo experiments for intermediate range of P values. The Monte Carlo points and the numerical solutions coincide within the limits of the statistical errors, averaged over 10 realizations consisting of 100 units each. Thus, the kinetics of the reaction in the system considered is described quantitatively through all the reaction (both kinetically and diffusionally controlled ones).

Diffusion with isolation

We consider now the most complicated case: once reacted the units remain fixed in their sites for all time and constrain the unreacted units from diffusion. The set of kinetic equations in this case remains the same 5°. We used the approximations of superpositional type to solve these equations. One of the results is shown in fig.3 along with the results of corresponding Monte Carlo experiments, absolutely exact solution in the absence of diffusion and "almost exact" solution for diffusion without isolation. The solutions obtained in this section reflects qualitatively (not exactly) combined influence of diffusion and isolation on the reaction kinetics.

We are interested if the fraction of unreacted units f_∞ does depend on G and P when the reaction is completed? The results of MC experiments give us the possibility to make the following conclusion: f_∞ is independent of G and P, provided the initial distribution of units is random ($f_\infty=.135\pm.002$

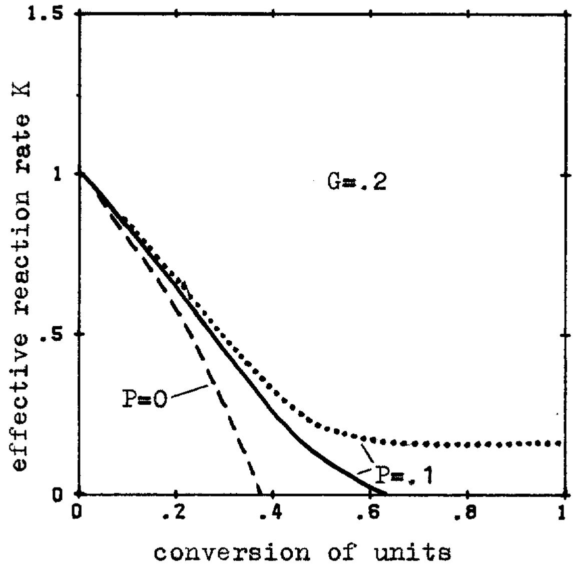

Figure 3. The relative effect of: (- - - -) isolation, (··········) diffusion and combined effect of diffusion and isolation (————) of units on the reaction kinetics.

and is consisted with the exact value $f_\infty = e^{-2} = 0.1353...$ obtained for the simplest Flory system G=1, P=0). However from tab.1 one can see that the numerical value of f_∞ depends at least on G. Our experience makes us sure that there may be the only reason of such discreapancy: the superpositional conditions are not justified on isolation increase. In this case diffusion is unable to restore the random units distribution broken by progressing reaction.

Table 1. Final fraction of unreacted (isolated) units f_∞

G	0.2	0.2	0.5	0.5
P	0.1	1.0	0.1	1.0
Monte Carlo	0.135	0.134	0.135	0.136
Kinetic equations	0.37	0.38	0.20	0.22

Conclusion

The performed study of simple one-dimensional models enables us to look clear at separated and combined influence of diffusion and isolation of units on irreversible chemical reaction kinetics. The method used may be developed in order to describe the parallel kinetics of chemical reaction and structural recovery in the dense polymer networks (8).

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Accepted February 11, 1985

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