

Equation of Consumption Rate of Free-Radical Vinyl Polymerization. II

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Synopsis

The vinyl polymerization reaction is a two-molecule reaction. However, it is more convenient to use a specially defined rate constant than to use the general constant, because a new radical is formed instantaneously in the same radical compound when one monomer combines with an existing radical in a living polymer or an initiator radical. This special rate constant is named the propagation constant and is proportional to the concentration of monomer when the polymer is formed from a unit mole concentration of the initiator radical. The specific propagation constant is related to the concentration of monomers which react in unit time and unit concentration of monomer and radical. Arnett's experiments are discussed in terms of the equation formulated. The value of $\Delta[M]/([M]_0 \cdot t)$ is found not to be a reaction rate but a value of $\ln [M]_0/[M]$ when $[M]_0 - [M]$ is very small. Autoacceleration of the polymerization is found with high concentrations of monomer which yield an increase in the velocity of propagation and also at low concentrations of initiator, which cause prolongation of the propagation stage. When the concentration of initiator is high, this phenomenon does not take place until enough initiator is consumed and the necessary low initiator level is reached. The time required is called the induction period. The larger the polymer molecule is, the higher the viscosity becomes.

INTRODUCTION

In a previous paper,¹ an equation was formulated for the rate of consumption of free radicals in vinyl polymerization which showed that the number of high polymers molecules of a certain kinetic chain length produced would be the same as the number of moles of effective free radicals and that the consumption rate and polymerization rate were different from each other. The rate of consumption of monomer has a second-order dimensional quality, i.e., the propagation rate has an effect on the degree of polymerization and the increasing rate of the number of polymers. The equation previously formulated involves two important elements: one is that some free radicals evolved from the initiator become polymers on reacting with monomers and others become diradicals and that, therefore, there is an efficiency factor for the radicals; the other is the problem of kinetic chain length. The chain length, that is, the limiting degree of polymerization, was put in the equation as follows:

$$-d[M]/dt = -k_p[M][R\cdot]k_M[M][R\cdot]d[R\cdot]/k_t[R\cdot]^2(k_M[M][R\cdot] + k_R[R\cdot]^2)dt$$

In the present paper the reaction constant has been redefined as the propagation constant, for the reaction of monomer with one molecule of radical in unit time. Accordingly, k_p is proportional to the concentration of monomer. The results of Arnett² and others upon which present polymerization theory is based can be well explained by the proposed equation.

THEORY

Rate Constant of Propagation and Chain Length

It is very convenient to use a newly defined rate constant in polymerization. In a bimolecular reaction, molecules of both the reacting components disappear in equivalent amounts. Vinyl polymerization is also a two-molecular reaction, but it is different from the general reaction in that as soon as a free radical disappears in a chain radical, formation of a new free radical occurs in the same molecule. Therefore, the problem is how fast the additive polymerization of monomers takes place upon one free radical, or how many monomer units will be added to one free radical in unit time. It is thus necessary to consider the rate constant of propagation k_p , which is defined as the number of molecules of monomer acting on one free radical per unit time under standard conditions when the monomer is present in unit concentration. This propagation rate is believed to be proportional to the monomer concentration and there should be no reason that the propagation rate should always be constant even when the concentration of monomer changed. Therefore, if the concentration of monomer is $[M]$, the propagation rate is $k_p[M]$. When the concentration of effective free radical is $[R\cdot]$, each radical molecule of which will react in the same way, the total number of reacted monomer units is given by $k_p[M][R\cdot]$. The rate of disappearance chain radicals is in proportion to the square of the concentration of chain radical, the rate constant of termination being k_t , and so its rate is $k_t[M\cdot]^2$. The moles of chain radical are equivalent to the effective radical, $[R\cdot]_{\text{eff}}$. Hence, $k_t[M\cdot]^2 = k_t[R\cdot]_{\text{eff}}^2$. If the total number of monomer polymerized per unit time is divided by the number of molecules of the effective radical that disappeared, the kinetic chain length will be calculated as $\nu = k_p[M][R\cdot]/k_t[R\cdot]_{\text{eff}}^2$.

DISCUSSION

Rate of Propagation

In the previous paper, k_p was used to denote the polymerization constant but according to its new definition as propagation constant, it should have been written K_p . The polymerization reaction occurs, first, between radical and monomer, and then between monomer and monomer, until at last the free radical in a molecule disappears. Therefore, the velocity of addition of monomers on per effective radical per unit time is

$$v_p = k_p[M]$$

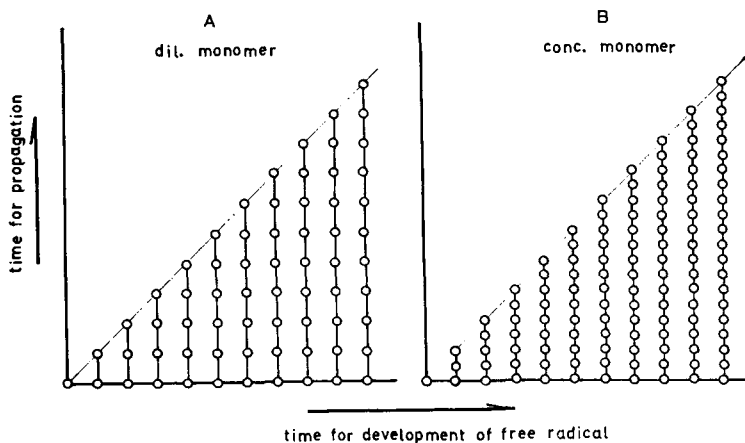
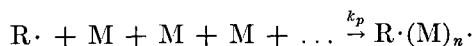


Figure 1.

for the reaction



Here k_p is the velocity constant for the addition of a certain number of monomers greater than one under standard conditions. Figure 1 shows the relation between the concentration of monomer and propagation rate.

There does not seem to be an absolute rate of propagation or an absolute life of radical. These change according to the conditions. If we look at Figure 1 in the previous paper and Figure 1 in this report, we can make some assumptions about the exact mechanism of propagation.

Initial Reaction

As the polymerization proceeds, the extent of the reaction changes with the changes in concentration of the reactants, i.e., monomer and initiator. When the balance of the material is calculated in the initial state, it is easy to know the reaction state, because the quantity of raw materials does not change much. The results of Arnett² will now be discussed on the basis of the present theory.

The integrated formula (25) in the previous paper, where a is k_M/k_R and b is k_p/k_t , becomes

$$[2(1 - b)/b] \ln ([M]_0/[M]) = k_d t + \ln [(2[I]/a[M] + 1 - b)/(2[I]_0/a[M]_0 + 1 - b)] \quad (1)$$

When $[M]_0 - [M]$ and $[I]_0 - [I]$ are small,

$$\ln ([M]_0/[M]) = ([M]_0 - [M])/[M]_0 = \Delta[M]/[M]_0 \quad (2a)$$

$$\ln ([I]_0/[I]) = ([I]_0 - [I])/[I]_0 = k_d[I]_0 t/[I]_0 \quad (2b)$$

$$\ln [(2[I]/a[M] + 1 - b)/(2[I]_0/a[M]_0 + 1 - b)] = \ln 1 = 0 \quad (2c)$$

and

$$[(1 - b)/b] \ln([M]_0/[M])^2 = [(1 - b)/b][([M]_0 - [M])/[M]_0]^2 \quad (3a)$$

$$\ln [I]_0/[I] = k_d t \quad (3b)$$

$$\ln ([I]_0/[I])/t = k_d$$

$$\ln ([I]_0/[I])/2 = k_d t/2 \quad (3c)$$

$$\ln ([I]_0/[I])^{1/2} = ([I]_0^{1/2} - [I]^{1/2})/[I]^{1/2} \quad (3d)$$

The change of monomer or initiator or the combination of monomer and initiator is expressed in various types of equations depending on the degree of change. Use has been made at some of these equations in analyzing the results of Arnett's experiments.² Table IV of Arnett gives results of the experiments with AIBN at 50°C.; as the temperature is comparatively low for the thermal decomposition, the amount of radical developed was very small. In the runs reported in Table VI of Arnett's paper, though the temperature was high, the amount of radical developed was also small, quantity (10⁻⁴ mole/l.) In these cases, it is formulated from eqs. (3a)–(3d) as follows. The left-hand term of eq. (1) becomes

$$2(1 - a)/a \ln ([M]_0/[M]) = [2(1 - a)/a]([M]_0 - [M])/[M] = [2(1 - a)/a]\Delta[M]/[M]$$

or

$$(1 - a)/a \ln ([M]_0/[M])^2 = [(1 - a)/a][([M]_0 - [M])/[M]]^2 = [(1 - a)/a](\Delta[M]/[M])^2$$

The right-hand term of eq. (1) is

$$k_d t = \ln ([I]_0/[I]) = ([I]_0 - [I])/[I]$$

Equation (1) then becomes

$$[(1 - a)/a]\Delta[M]_0/[M] = \ln ([I]_0/[I])^{1/2} = k_d t/2$$

$$[(1 - a)/a]\Delta[M]/t[M] = \ln ([I]_0^{1/2}/[I]^{1/2})/t = ([I]_0^{1/2} - [I]^{1/2})/t = k_d/2 \quad (4)$$

It is not proper to consider $\Delta[M]/t$ to be the velocity of the polymerization and that it is proportional to the square of the concentration of initiator. When the development of the radical is great, as in the case of Arnett's² experiments at 77°C., the calculation should be made by the relation of $\ln ([M]_0/[M])$ and $\ln ([I]_0/[I])$ of eq. (1). This calculation yields a different value in each experiment, as shown Table V of Arnett's experiments. Hence, the velocity of the polymerization cannot be considered directly proportional to square root of the concentration of initiator.

The Case of Extremely Small Quantity of Initiator

In the previous paper¹ it was explained that when initiator was used in a small quantity and monomer in large quantity, the reaction could be formulated as following the relation, $\ln ([M]_0/[M]) = (k_p/k_t)k_d t$. But, when the concentration of initiator becomes much lower, and the change is expressed in $([I]_0 - [I])/[I]_0$ instead of $\ln ([I]_0/[I]) = k_d t$, the change will be formulated probably as follows:

$$([M]_0 - [M])/[M]_0 = (k_p/k_t)([I]_0 - [I])/[I]_0 \quad (5)$$

The Case of Extremely Large Quantity of Monomer

When the reaction takes place at extremely high concentration of monomer, as in the case of bulk polymerization, we observe the violent reaction termed the autoacceleration conversion. In the previous paper it was noted that the concentration of monomer $[M]$ was directly concerned. The rate of propagation is proportional to the concentration of monomer as $k_p[M]$. If the initial concentration of monomer is infinite, the product of $k_p[M]$ will also be infinite, and the value of $\ln ([M]_0/[M])$ will become infinite, too, in the equation, $\ln ([M]_0/[M]) = (k_p/k_t)k_d t$. The occurrence of autoacceleration conversion was noted some time after the reaction began. The retarded reaction in the initial state is probably caused by the large quantity of initiator or rather by the comparatively large quantity of free radical developed, and chain length of polymer formed is the shorter. We know that the viscosity is proportional to the degree of polymerization. The decomposition of initiator takes place according to an exponential function. Therefore, the decrease in initiator concentration is large at first and then becomes small; therefore after some time the concentration of initiator becomes comparatively low, and the amount of free radical formed also becomes smaller. Hence, after some time, the chances for a termination reaction to occur become lower than at the beginning of the reaction. In short, the autoacceleration conversion is attributable to the fast rate and increase in duration or the propagation caused by the extremely high concentration of monomer and some lowered concentration of initiator. The phenomenon would not then be due to the viscosity of the reaction medium; rather, the viscous state would result from the fast propagation, namely, autoacceleration conversion.

CONCLUSION

The rate constant of vinyl propagation, k_p , is shown by the degree of polymerization of polymer in unit time, i.e., the number of monomers reacting with one radical at unit time and unit concentration of monomer. This definition is very convenient for understanding the theory of vinyl polymerization. Into this supposition, a new concept is introduced, namely, that the propagation rate is proportional to the concentration of the monomer. Therefore the higher the monomer concentration, the faster

the reaction becomes. The value of $([M]_0 - [M])/([M]t)$ in Arnett's experiments is not the velocity of the reaction, but it is a result of approximate calculation of the small change in the concentration of monomer or initiator, due to the low temperature of reaction or to the low concentration of the materials.

References

1. H. Sasaki, (Part I).
2. L. M. Arnett, *J. Am. Chem. Soc.*, **74**, 2027 (1952).

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