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Kinetics of Free Radical Copolymerization. IV. Rate of Initiation in the Copolymerization System Ethyl Acrylate-Styrene-Benzene

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ABSTRACT

Dependence of the rate constant of initiation on the overall concentration and composition of monomer has been investigated in the free radical copolymerization of ethyl acrylate and styrene in bulk and in benzene solution at 50°C. The rate constant of initiation has been determined by the inhibition method using triphenyl-verdazil as the stable free-radical inhibitor. An equation has been derived to calculate the rate constant of initiation in a copolymerization system, where both monomers undergo a pseudounimolecular side reaction with the inhibitor. The rate constant of initiation in the copolymerization mixture is a linear composition of rate constants determined separately in the pure constituents of the system.

INTRODUCTION

The initiation rate of copolymerization by chemical initiation is described by

$$W_1 = 2k_1fx \quad (1)$$

where k_1 is the decomposition rate constant of the initiator, f is the factor of initiator efficiency, and x is the concentration of the initiator.

The decomposition rate constant of azo-bis-isobutironitrile (AIBN), which is one of the most common free radical initiators, is known to depend on the nature of the solvent [1-3]. The solvent effect on the factor of initiator efficiency f , the other constant in the rate equation of initiation, was also observed and described [4]. Therefore it is expedient to determine the initiation rate experimentally, and inhibition by a stable free radical is considered to be the most reliable experimental method [5].

Our studies on the inhibition kinetics in the ethyl acrylate-styrene-benzene copolymerization system are presented in this paper.

EXPERIMENTAL

Monomers (Fluka, purum grade) and benzene (reagent grade) were purified by standard methods [6-8]. Triphenyl-verdazil (TPV), a stable free-radical inhibitor, was prepared as described in Ref. 9 and purified by repeated crystallization from an acetone-methanol mixture.

The inhibition method applied was described in Ref. 7.

KINETIC TREATMENT

When polymerization is inhibited by a stable free radical, the rate constant of initiation can be calculated from the length of the inhibition period:

$$t_i = \frac{1}{2k_1f} \frac{z_0}{\bar{x}} \quad (2)$$

where t_i is the length of the inhibition period, z_0 is the initial concentration of the inhibitor, and \bar{x} is the average concentration of the initiator during inhibition.

During inhibition of the polymerization of certain reactive monomers, such as styrene [10], ethyl acrylate [6], or acrylonitrile [11], the stable free radical was found to undergo a side reaction with the monomer besides serving as a radical trap. This inhibitor-consuming side reaction induced a decrease of inhibition time and a slight deviation from linearity in the $t_i = f(z_0/\bar{x})$ function. Provided that only this side reaction takes place between the monomer and the stable free radical during inhibition, it can be taken into account and the rate constant of initiation can be calculated on the basis of the following expression [7, 10]:

$$t_i = \frac{1}{2k_{1f}} - \frac{1}{\alpha} \ln \left(1 + \alpha \frac{z_0}{x_0} \right) \quad (3)$$

$$\alpha = \frac{k' m_0}{k_{1f}} - \frac{1}{2f} \quad (4)$$

where k' is the rate constant of the side reaction and m_0 is the initial concentration of the monomer.

In the copolymerization system under investigation, both monomers were found to undergo a side reaction with the inhibitor in their homopolymerizations [6, 10]. Therefore, two side reactions had to be considered during the inhibition of copolymerization: an inhibition-consuming side reaction between triphenyl-verdazil and styrene and another between triphenyl-verdazil and ethyl acrylate. Accordingly, these reactions can be taken into account by means of a procedure similar to that reported on the inhibition kinetic study of homopolymerization [7, 10].

Chain propagation during inhibition is negligible under such conditions. Thus the following elementary reactions take place in the system in the presence of a stable free radical inhibitor.

(a) Decomposition of initiator:



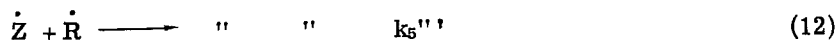
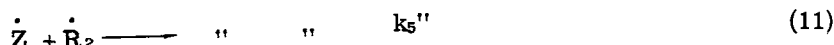
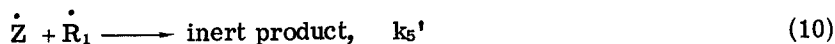
(b) Initiation:



(c) Side reactions with inhibitor:



(d) Inhibition:



where X is the symbol for initiator, \dot{R} stands for the primary radical formed by decomposition of the initiator, \dot{R}_1 and \dot{R}_2 are propagating radicals, M_1 and M_2 are symbols for monomers, and \dot{z} is the stable free-radical inhibitor.

Based on the above kinetic scheme, the differential equations describing the system can be constructed (concentrations are designated by the corresponding minuscule):

$$dr/dt = 2k_1fx - k_1'rm_1 - k_1''rm_2 - k_5''r_z \quad (13)$$

$$dr_1/dt = k_1'rm_1 + k''zm_1 - k_5'zr_1 \quad (14)$$

$$dr_2/dt = k_1''rm_2 + k''zm_2 - k_5''zr_2 \quad (15)$$

$$-dz/dt = k''zm_1 + k''zm_2 + k_5'zr_1 + k_5''zr_2 + k_5''zr \quad (16)$$

On the assumption of quasistationary conditions, radical concentrations are constant:

$$dr/dt = dr_1/dt = dr_2/dt = 0 \quad (17)$$

Considering Eq. (17) the sum of Eqs. (13)-(16) gives the following simple differential equation describing the consumption of the stable free radical:

$$-dz/dt = 2k_1fx + 2(k'm_1 + k''m_2)z \quad (18)$$

Since the decomposition of the initiator is a strictly unimolecular process in copolymerization as well, the concentration of initiator at a certain time t is given by the usual exponential expression:

$$x = x_0e^{-k_1t} \quad (19)$$

Substituting this expression for x in Eq. (18), we have

$$-dz/dt = 2k_1fx_0e^{-k_1t} + 2(k'm_1 + k''m_2)z \quad (20)$$

(In case $m_2 = 0$, the expression derived for the inhibition kinetics of homopolymerization prevails.) Equation (20) is actually a first-order linear inhomogeneous differential equation:

$$-dz/dt = Ae^{-k_1t} + Bz \quad (21)$$

where $A = 2k_1fx_0 = W_1^0$, the initial decomposition rate of the initiator, and

$$B = 2(k'm_1 + k''m_2) \quad (22)$$

The solution of Eq. (20) (under conditions $m_1 = \text{const}$, $m_2 = \text{const}$, boundary conditions $t = 0$, $z = z_0$) is

$$z = (z_0 + \frac{A}{B - k_1})e^{-Bt} - \frac{A}{B - k_1} e^{-k_1t} \quad (23)$$

At the end of the inhibition period, $t = t_i$ and $z = 0$. Substituting these values for t and z into Eq. (23) and rearranging, we obtain the following expression for the length of the inhibition period:

$$t_i = \frac{1}{2k_1f} - \frac{1}{\alpha} \ln \left(1 + \alpha \frac{z_0}{x_0} \right) \quad (24)$$

where

$$\alpha = \frac{B - k_1}{A} x_0 = \frac{2(k'm_1 - k''m_2) - k_1}{2k_1f} \quad (25)$$

These equations are again identical with the equations derived for homopolymerization, except for the expression for α which contains the rate constants of both side reactions and the concentration of both monomers.

It has been proven by numerical methods that the rate constants can be determined by the empirical linear approximate equation [10]:

$$\left(\frac{z_0}{x_0 t_i} \right)^{3/2} = (2k_1f)^{3/2} \left\{ 1 + 0.740 \alpha \frac{z_0}{x_0} \right\} \quad (26)$$

instead of using the exact but in z_0/x_0 nonlinear Eq. (24). In case $\alpha z_0/x_0 \leq 10$, the error of this calculation is $\leq 1\%$. Consequently, if experimental data are plotted according to Eq. (26), from the slope and intercept of the straight line both constants of Eq. (24), α and $2k_1f$, can be readily obtained. It should be noted that the rate constants k' and k'' can be directly determined by studying the thermal reaction

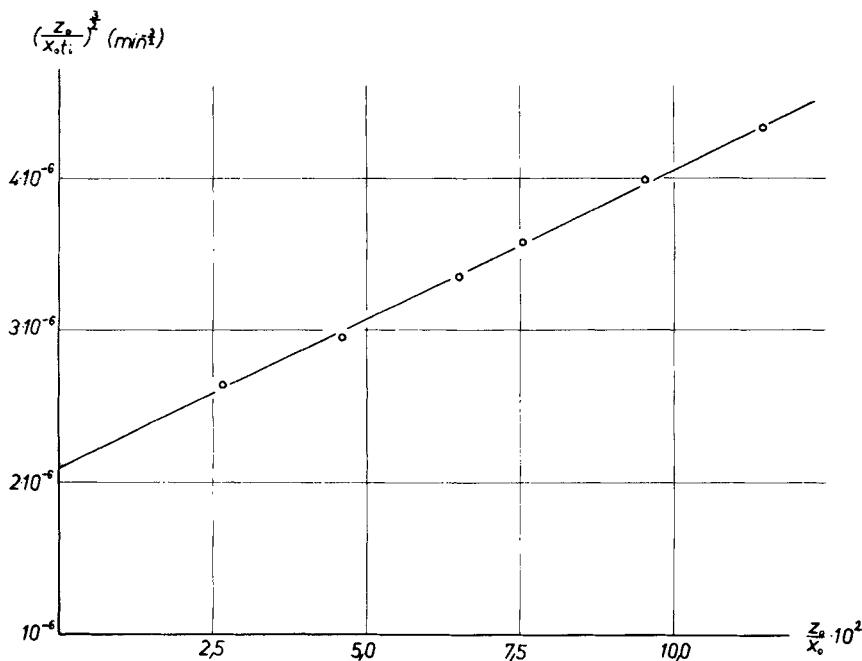


FIG. 1. Determination of initiation rate constant according to Eq. (26) in EA/St/AIBN copolymerization system, $\chi_{EA} = 0.2155$.

TABLE 1. Inhibition Kinetic Data of EA/St/AIBN Copolymerization System at 50°C, $\chi_{EA} = 0.2155$

$x_0 \times 10^2$ (mol/dm ³)	$z_0 \times 10^3$ (mol/dm ³)	t_i (min)	$\left(\frac{z_0}{x_0 t_i}\right)^{3/2}$	$2k_1 f$ (min ⁻¹)
5.840	1.563	140	2.643	
5.707	2.645	225	2.956	
5.756	3.750	291	3.350	$1.612 \times 10^{-4}{}^a$
6.395	4.838	324	3.568	
6.165	5.898	380	3.995	
5.971	6.846	432	4.326	

^aCorrected value (by thermal initiation of styrene).

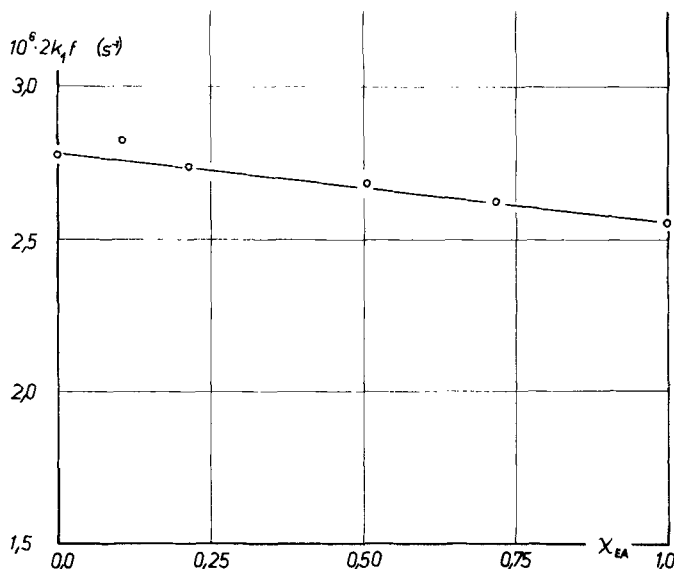


FIG. 2. Dependence of initiation rate constant on the molar fraction of EA ($\chi_{EA} = \frac{m_{EA}}{m_{EA} + m_{St}}$) in EA/St/AIBN/Bz copolymerization system, $m_{EA} + m_{St} = 4.2 \text{ mol/dm}^3$.

(without initiator) of M_1 and/or M_2 monomer and \dot{Z} stable free radical [7].

The experimental results of inhibition kinetic investigation of the ethyl acrylate-styrene-benzene system were evaluated on the basis of Eq. (26). The method is demonstrated in Fig. 1, and the corresponding experimental data are summarized in Table 1.

The rate constant of initiation with a given composition of the reaction mixture was calculated from the intercept of the straight line. This value was also adjusted by taking into account the thermal initiation of styrene as described in Ref. 12.

RESULTS AND DISCUSSION

Although several papers have been published on the ethyl acrylate-styrene copolymerization system [13-15], neither the rate nor the kinetics of initiation has been discussed. Therefore, our findings could not be compared with or supported by earlier results.

According to our observations, the linear composition of the rate constants determined separately in the pure components shows close

TABLE 2. Rate Constant of Initiation in EA/St/AIBN Copolymerization at 50°C

χ_{EA}	Number of experiments	$2k_{if} \times 10^4$ (min^{-1})	Refs.
0.0000	-	1.734	[5]
0.0976	5	1.694	Present investigation
0.2155	6	1.612	" "
0.3488	4	1.563	" "
0.5057	5	1.592	" "
0.7197	5	1.564	" "
1.0000	6	1.531	[6]

agreement between calculated and experimentally determined values of the initiation rate constant in ethyl acrylate-styrene-benzene copolymerization systems of different composition. The dependence of $2k_{if}$ on monomer composition is considered to be linear within experimental error (Fig. 2 and Tables 2 and 3). Therefore the rate constant of initiation can be calculated on the basis of

$$2k_{if} = (1.58 - 0.5\chi_{EA} + 0.15\chi_{St}) 10^{-4} \text{ min}^{-1} \quad (27)$$

where χ_{EA} and χ_{St} are the molar fractions of the monomer in solution, e.g.:

$$\chi_{EA} = \frac{m_{EA}}{m_{EA} + m_{St} + s} \quad (28)$$

where s is the concentration of solvent.

The factor of initiator efficiency f can be calculated from the decomposition rate constant of AIBN and the initiation rate constant. The decomposition rate constant of AIBN is $1.41 \times 10^{-4} \text{ min}^{-1}$ in styrene [2] and $1.21 \times 10^{-4} \text{ min}^{-1}$ in ethyl acrylate [6]. The factor of initiator efficiency is 0.63 in ethyl acrylate and 0.62 in styrene, which is practically identical, hence the solvent effect on the rate constant of initiation may be attributed to solvent effect on the decomposition kinetics of AIBN.

Our studies indicate that it is worthwhile to extend the kinetic investigation of copolymerization to initiation kinetics as well, since

TABLE 3. Rate Constant of Initiation in EA/St/AIBN/Bz Copolymerization System at 50°C

$m_{EA} + m_{St}$ (mol/dm ³)	χ_{EA}	Number of experiments	$2k_{if} \times 10^4$ (min ⁻¹)	Refs.
6.64	0.0000	-	1.709	[5]
6.64	0.1045	6	1.768	Present investigation
6.64	0.2116	6	1.596	" "
6.64	0.5057	5	1.598	" "
6.64	0.7197	5	1.568	" "
6.64	1.0000	6	1.531	[6]
4.20	0.0000	-	1.668	[5]
4.20	1.045	5	1.694	Present investigation
4.20	0.2155	5	1.643	" "
4.20	0.5057	5	1.609	" "
4.20	0.7197	5	1.575	" "
4.20	1.0000	6	1.531	[6]

the separation of kinetic effects on initiation from those on other kinetic parameters provides more accurate knowledge of the copolymerization system.

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