Kinetics of Vinyl Chloride Polymerization with Mixture of Initiators

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Abstract   Kinetic models for the rate constants of vinyl chloride polymerization in the presence of initiator mixtures were proposed. They may be used to design the initiator recipes for the vinyl chloride polymerization with uniform rate at different temperatures at which various grades of poly(vinyl chloride) will be prepared.
Keywords   poly(vinyl chloride), polymerization kinetics, initiator

1 INTRODUCTION

The productive capacity of a reactor for vinyl chloride (VC) polymerization can be increased by intensifying the heat transfer of the reactor and/or by selecting an adequate initiator mixture system. VC polymerization is a highly exothermic process and characterized by the auto-acceleration effect causing uneven heat evolution during the process. It has been reported[1] that the heat will be evolved more uniformly if an initiator with half-life $(t_{1/2}) \approx 2\,\mathrm{h}$ is used. However, any single initiator cannot meet this requirement at different temperatures at which various grades of poly(vinyl chloride) (PVC) will be prepared since $t_{1/2}$ of an initiator is dependent on temperature. This problem may be solved by using a mixture of two or more initiators, one of them with $t_{1/2} < 2\,\mathrm{h}$, and others with $t_{1/2} > 2\,\mathrm{h}$.

This paper presents the model of decomposition of initiator mixture systems and the kinetics of VC polymerization in the presence of initiator mixtures. The final objective is to design the proper recipes of initiator mixture for the VC polymerization with uniform heat generation rate but without heat peak at different polymerization temperatures to increase the productive capacity of a definite reactor to a maximum degree.

2 EXPERIMENTAL

2.1 Analysis of peroxides

The relation between peroxide concentration [I] and time t during its homolysis may be expressed as

$$\ln \frac{[\mathrm{I}]}{[\mathrm{I}]_0} = -k_{\mathrm{d}}\,t \qquad (1)$$

The rate constant k_{d} may be calculated from the slope of the plot of $\ln[\mathrm{I}]/[\mathrm{I}]_0$ vs. t. The half-life $(t_{1/2} = 0.693/k_{\mathrm{d}})$ is usually used commercially in-

stead of k_{d}. The dependence of k_{d} on temperature T obeys Arrhenius-type relationship.

$$k_{\mathrm{d}} = A\mathrm{e}^{-E_{\mathrm{d}}/RT} \qquad (2)$$

The Frequency factor A and activation energy E_{d} of peroxide homolysis may be calculated from the intercept and slope of the plot of $\ln k_{\mathrm{d}}$ vs. $(1/T)$.

The key problem is to determine the concentration of peroxide during its homolysis. The initiators of peroxides(AKZO-NOBEL Peroxides Co., Tianjin) were analyzed via the conventional iodometry. The solvent and catalyst are two important factors affecting the accuracy of analysis. Isopropanol is an excellent solvent for various peroxides and was preferably selected in the analysis. Cupric and ferric ions were used as catalysts in the analysis of peresters and diacyl peroxides respectively, but no catalyst was used while analyzing peroxydicarbonates for their higher activities.

2.2 Polymerization of vinyl chloride

The suspension polymerization of vinyl chloride was carried out in a 5 L autoclave with a real-time monitoring device. A small amount of inert gas as tracer was injected into the autoclave before polymerization. The concentration of the tracer in the gas phase was continuouly monitored during the polymerization by a gas chromatograph and converted into conversion by a computer with specially designed software. Thus, the conversion-time data were easily obtained continuously.

3 RESULTS AND DISCUSSION

3.1 Kinetic model of the rate of decomposition of initiator mixtures

It may be considered that no reaction will take place between the same kinds of initiators, such as

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peroxides. Thus, the decomposition rate of a mixture of two or more initiators may be expected to be the summation of the individual rates of these initiators. The overall rate constant of decomposition of an initiator mixture may be correlated from the rate constants of the individual initiators

$$k_d = \sum_{i=1}^{n} k_{d\,i} \frac{[I]_i}{[I]} = \sum_{i=1}^{n} k_{d\,i} F_i \qquad (3)$$

where k_d and $k_{d\,i}$, $[I]$ and $[I]_i$ are the rate constants of decomposition and concentrations of overall and individual initiators respectively, and F_i is the mole fraction of initiator i in the initiator mixtures.

The values of k_d of 6 peroxides were determined at 4 temperatures. Fig. 1 shows $\ln k_d$-$(1/T)$ plots from which the frequency factors and activation energies may be calculated. The values of k_d at 50 and 60°C, and the temperatures for $t_{1/2} = 1\,h$ and $10\,h$ were calculated further from Eq. (2) and listed in Table 1.

The values of k_d of Tx151/Tx23 mixture predicted from Eq. (3) are in good agreement with the experimental data at 52, 55, 58 and 61°C, as shown in Fig. 2.
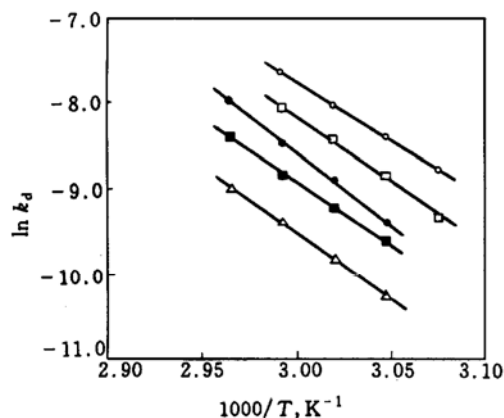

Figure 1 $\ln k_d$-$(1/T)$ plot of initiators
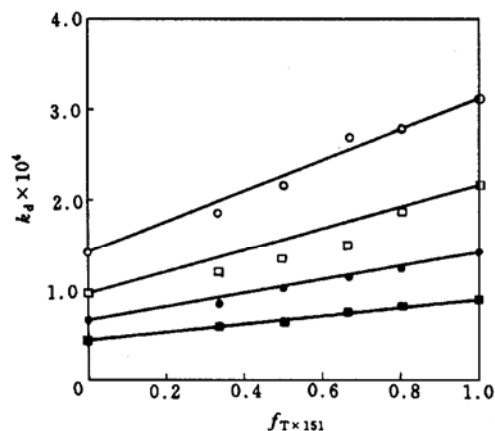O Tx99; □ Tx151; ● TxEHP; ■ Tx23; △ Tx257

Figure 2   Rate constants of decomposition vs mole fraction for Tx151/Tx23 initiator mixture
O 52°C; □ 55°C; ● 58°C; ■ 61°C; —— model value

More comparison is given in Table 2. The good agreement shows that the additive model for the rate constants of decomposition of initiator mixtures [Eq. (3)] is valid and reliable so that it may be used in the kinetic model of vinyl chloride polymerization in the presence of mixture of initiators.

3.2 Modified kinetic model of VC polymerization

PVC-VC is a partially soluble pair. VC polymerization will take place in monomer phase (phase 1) and polymer-rich phase (phase 2) from the beginning to a critical conversion (X_f) at which the monomer phase disappears. Xie[2] proposed a kinetic model of VC polymerization with a single initiator.

The overall initiation rate of a mixture of initiators may be considered to be the summation of the initiation rates of individual initiators if no reaction takes place between them. The overall initiation rate of an initiator mixture in phase j $(j = 1$ or $2)$ may be expressed as

$$R_{Ij} = \sum_{i=1}^{n} (R_{Ii})_j = 2 \sum_{i=1}^{n} f_i k_{di} [I]_{ij} \qquad (4)$$

The model of vinyl chloride polymerization is now modified by using the overall initiation rate of initiator mixture instead of that of a single initiator and expressed as Eqs. (5) and (6).
When $X < X_f$

$$\frac{dX}{dt} = \frac{1}{N_0 M_m} \left\{ k_{p1} [(J_1^2 + 4k_{t1} J_2)^{1/2} - J_1] \frac{M_1}{2k_{t1}} + \right.$$
$$\frac{k_{p2}}{k_{t2}^{1/2}} \left[2 \sum_{i=1}^{n} (f_i k_{d\,i} [I]_{i2})(1 - k'_{de}) + 2K \sum_{i=1}^{n} f_i k_{d\,i} [I]_{i1} \frac{V_1}{V_2} + \right.$$
$$\left. \frac{J_1 V_1}{2k_{t1} V_2} (J_1^2 + 4k_{t1} J_2) - J_1 \right]^{1/2} M_2 \left. \right\} \qquad (5)$$

where $J_1 = K k_{fm1} [M]_1$ and $J_2 = \sum_{i=1}^{n} (f_i k_{d\,i} [I]_{i1})(1 - K) + k_{de}(f_i k_{d\,i} [I]_{i2}) V_2 / V_1$
When $X > X_f$

$$\frac{dX}{dt} = \frac{k_{p2}}{N_0 M_m} \left\{ 2 \sum_{i=1}^{n} (f_i k_{d\,i} [I]_{i2}/k_{i2}) \right\}^{1/2} M_2 \qquad (6)$$

Most of the model parameters, such as kinetic parameters, volume of two phases, concentration-conversion relation, etc., are known[2], but the initiator efficiency of a single initiator is correlated by least square regression from the conversion-time data of the vinyl chloride polymerization as shown in Fig. 3 and listed in Table 3.

Table 1 Kinetic parameters of initiator decomposition

Initiator	M_I	Frequency factor A, s^{-1}	Activation energy E_d, kJ·mol^{-1}	Rate constant k_d, s^{-1}		T, °C	
				50°C	60°C	$T_{1/2} = 1\,h$	$t_{1/2} = 10\,h$
Tx99	306.4	4.53×10^{14}	115.03	1.156×10^{-4}	4.167×10^{-4}	53.9	37.0
Tx151	300.5	2.12×10^{16}	126.82	6.721×10^{-5}	2.764×10^{-4}	57.4	41.7
TxEHP	346.5	9.00×10^{18}	144.76	3.594×10^{-5}	1.805×10^{-4}	60.4	46.3
Tx23	244.4	3.00×10^{15}	123.52	3.239×10^{-5}	1.287×10^{-4}	63.0	46.4
Tx257	216.5	1.80×10^{16}	130.11	1.672×10^{-5}	7.154×10^{-5}	67.2	50.9
Tx36	314.5	2.84×10^{15}	128.34	5.110×10^{-6}	2.145×10^{-5}	76.6	59.2

Tx99= cumyl neo-decanoate peroxide; Tx151= 2,4,4-trimethylamyl neo-decanoate peroxide;
TxEHP= bis(2-ethylhexyl)peroxydicarbonate; Tx23=*tert*-butyl neo-decanoate peroxide;
Tx257=*tert*-butyl neo-heptanoate peroxide; Tx36=bis(3,5,5-trimethylhexanoyl)peroxide

Table 2 Rate constants of decomposition of initiator mixture

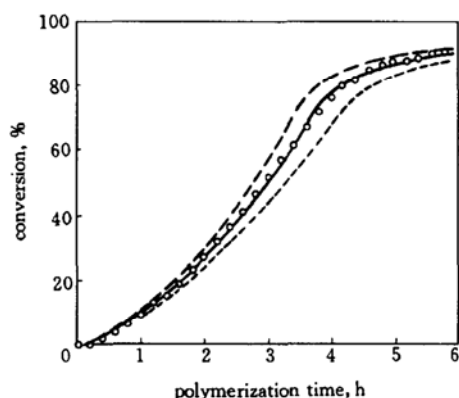| Initiator mixture (ratio)	T, °C	k_d, s^{-1}	
		Exp. data	Model values
Tx99/Tx23 (2/1)	58	2.19×10^{-4}	2.46×10^{-4}
Tx151/TxEHP (2/1)	55	1.35×10^{-4}	1.22×10^{-4}
Tx99/TxEHP (2/1)	58	2.60×10^{-4}	2.57×10^{-4}
TxEHP/Tx257 (2/1)	58	1.05×10^{-4}	1.06×10^{-4}
TxEHP/Tx23/Tx36(0.5764/0.2412/0.1844)	57	9.26×10^{-5}	8.8×10^{-5}
Tx99/TxEHP/Tx23/Tx36(0.3936/0.3936/0.1206/0.0922)	51	7.83×10^{-5}	7.35×10^{-5}

Figure 3 Conversion-time curve of vinyl chloride
polymerization with Tx23 as initiator at 57°C
O exp data; f: ······ 0.70; —— 0.85; - - - - - 1.0

Table 3 Initiator efficiency

Temperature, °C	TxEHP	Tx99	Tx151	Tx23	Tx36
51	0.95	0.70	0.85		
57	0.85			0.85	0.55
62	0.70			0.65	0.50

Finally, the model may be used to design the recipes of a mixture of 2 or more initiators for preparing various grades of PVC at different temperatures in a shorter time (4.5—5 h) with nearly constant rate (heat load distribution index $\leqslant$ 1.1) so as to increase considerably the productive capacity of the reactor. Figs. 4 and 5 are typical conversion-time curves of vinyl chloride polymerization in the presence of initiator mixtures at different temperatures. Fig. 6 shows that the uniform heat generation rate can be obtained during the vinyl chloride polymerization from the recipe design of mixture of initiators. The good

agreement of model values with experimental data shows that the kinetic models of initiator decomposition rate constant and of VC polymerization in the presence of initiator mixtures are valid and reliable.
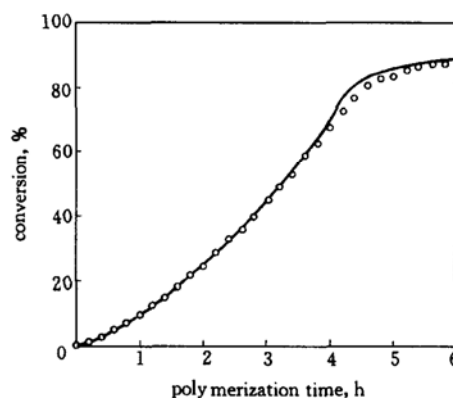

Figure 4 Conversion-time curve of vinyl chloride
polymerization with TxEHP/Tx99 as
initiators at 51°C
O exp data; ——model value

4 CONCLUSIONS

(1) A model for the rate constant of decomposition of initiator mixtures was proposed from the additive property and verified by experiments.

(2) A kinetic model of vinyl chloride polymerization in the presence of initiator mixture was derived by using the overall initiation rate of initiator mixture.

(3) A proper recipe of initiator mixture may be designed to realize a polymerization process of vinyl chloride with uniform heat generation rate at different temperatures for preparing various grades of poly(vinyl chloride).
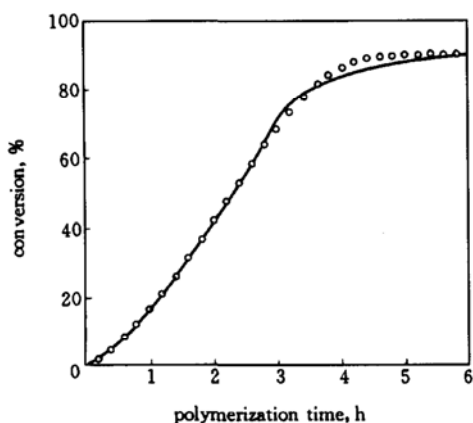
Figure 5 Conversion-time curve of vinyl chloride polymerization with TxEHP/Tx23/Tx36 at 62°C
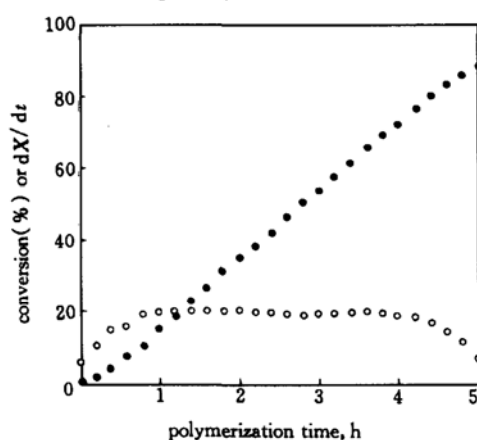
O exp data; ——model value

Figure 6 Conversion-time curve of vinyl chloride polymerization with TxEHP/Tx23/Tx36 at 57°C

O dX/dt; ● conversion

NOMENCLATURE

A	frequency factor
E_d	activation energy of initiator homolysis, $kJ \cdot mol^{-1}$
F	mole fraction of initiator
f	initiator efficiency
$[I]$	concentration of initiator, $mol \cdot L^{-1}$
K	solubility of vinyl chloride in water
k_d	rate constant, s^{-1}
k_{de}	radical desorption rate constant, s^{-1}
k'_{de}	chlorine radical desorption rate constant, s^{-1}
k_{fm}	chain transfer to monomer rate constant, $L \cdot mol^{-1} \cdot s^{-1}$
k_p	propagation rate constant, $L \cdot mol^{-1} \cdot s^{-1}$
k_t	termination rate constant, $L \cdot mol^{-1} \cdot s^{-1}$
M	mass of monomer, g
$[M]$	concentration of monomer, $mol \cdot L^{-1}$
M	molecular weight
N_0	initial number of moles of VCM, mol
R	universal gas constant, $J \cdot mol^{-1} \cdot K^{-1}$
R_I	initiation rate, $L \cdot mol^{-1} \cdot s^{-1}$
t	reaction time, s
$t_{1/2}$	half-life, h
T	temperature, °C or K
V	reaction volume, L
X	conversion, %
X_f	critical conversion, %

Subscripts

0	initial state
1	monomer phase
2	polymer phase
I	inititor
i, j	component i or j
m	monomer

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