

ON COPOLYMERIZATION KINETICS OF N-VINYL PYRROLIDONE METHYL METHACRYLATE AT HIGH CONVERSION

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ABSTRACT

In this work, Fourier transform infrared spectroscopy was used to study the copolymerization kinetics of N-vinyl pyrrolidone-methyl methacrylate (VP-MMA) at high conversion. Through computer simulation, copolymerization rate equation based on the free volume theory, diffusion theory and modified MH model was established. The activation energy of copolymerization was also estimated.

Hydrogel is the polymer network which can be swollen by water. It is a kind of functional polymer material and has been widely used in biomedical field since 1960^[1]. The copolymer of VP-MMA is the hydrogel that has been widely used especially as material for soft cornea contact lens. As to VP-MMA copolymerization system, the authors are not aware of any other publications on the quantitative study of the copolymerization kinetics at high conversion except a preliminary survey on copolymerization kinetics at low conversion by Braun et al.^[2]. In this work, Fourier transform infrared spectroscopy was used to study the copolymerization kinetics of N-vinyl pyrrolidone-methyl methacrylate at high conversion. Based on the free volume theory, the relationship between copolymerization rate constants k_p , k_t and the free volume, molecular weight of the system was found out. Then, the copolymerization rate equation at high conversion was established. The activation energy of the copolymerization was also estimated by this equation after a series of reasonable assumption and simplification. The results can be used as the theoretical basis for its practical uses.

EXPERIMENTAL

1. Materials

Material	Resourcer	Purification method	B.P.	Refractive index
VP	BASF	vacuum distillation	53°C/1mmHg	$n_D^{25} = 1.5114$
MMA	Beijing Chemical Plant	vacuum distillation after removal of the inhibitor	46°C/97mmHg	$n_D^{25} = 1.4121$
ABIN	Beijing Chemical Plant	recrystallized twice		

2. Equipment

FTIR: 5 DX FTIR made by Nicolet Cooperation Resolution 4cm^{-1}

3. Experiment of copolymerization kinetics

Copolymerization was carried inside a KBr cell, which was made of pieces of KBr crystal and sealed with 10 μ thick teflon film. This film was also used to control the thickness of the cell. First the cell was situated in a thermostat which was adjusted at the required temperature. The heating medium is air. Then the copolymerization feed prepared was injected into the reaction cell by means of an injector when the temperature of the cell was stable. In situ FTIR was used to track the whole copolymerization process with programmed scanning. The quantitative treatment of the stored spectra was carried out by the computer.

The spectra of VP, MMA and their mixture (VP/MMA = 43/57) were shown in Fig.1 to 3. The quantitative band of VP was assigned to 1409—1358cm⁻¹, the quantitative band of MMA was assigned to 1181—1151 cm⁻¹ and the peak at 2888 cm⁻¹ was used as the calibration standard peak.

The conversion of certain monomer can be calculated as follows:

$$P(t) = (A_0 - A_t) / (A_0 - A_\infty) \times 100\%$$

where A_0 , A_t and A_∞ are the peak area of the quantitative band of that monomer at $t=0$, t and ∞ (conversion = 100%) respectively.

According to the following equation, the total conversion of monomers can be calculated.

$$P_T = f_{vp} P_{vp} + (1 - f_{vp}) P_{MMA}$$

where f_{vp} is the mole fraction of VP in the feed.

The molecular weights of the copolymers at different conversions were determined by membrane osmometry and viscometry respectively.

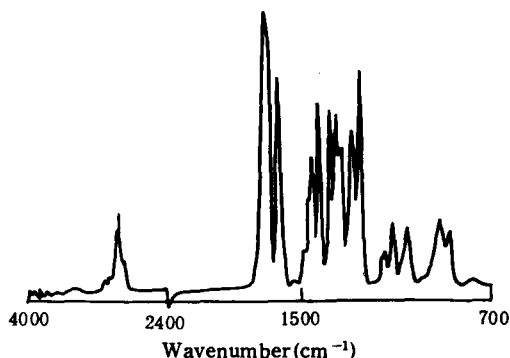


Fig.1 IR spectra of VP-MMA

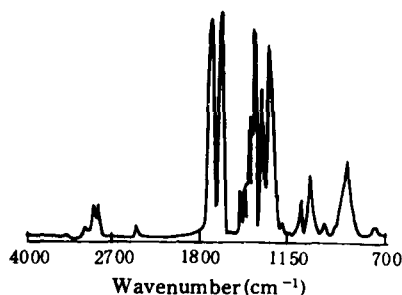


Fig.2 IR spectra of VP

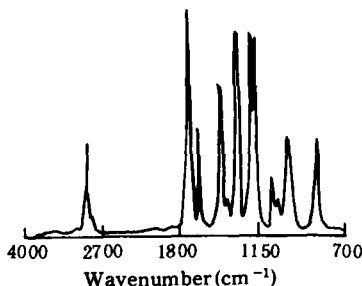


Fig.3 IR spectra of MMA

RESULTS AND DISCUSSION

1. The simulation of copolymerization rate equation at high conversion

For homopolymerization at high conversion, MH model based on the free volume theory was presented by Marten and Hamielec^[3] in 1979 to calculate the polymerization rate and molecular weight at high conversion. This model was suitable to MMA polymerization. In 1981, Hamielec^[4] adopted this model to the copolymerization of St-AN with some modification. In this work, based on the free volume theory, the present authors try to modify this model and apply it to calculate the copolymerization rate of VP-MMA system at high conversion.

(1) The establishment of the model

The following equation can be used to calculate the copolymerization rate at high conversion:

$$\frac{-d([M_1] + [M_2])}{dt} = \frac{k_t^{\frac{1}{2}} r_1 [M_1]^2 + 2[M_1][M_2] + r_2 [M_2]^2}{k_t^{\frac{1}{2}} r_1 [M_1] / k_{11} + r_2 [M_2] / k_{22}} \quad (1)$$

where k_t and k_p are not constants but changeable while the conversion is varied. The key to the question is to find out the quantitative relationship between k_t , k_p and the free volume and molecular weight. According to Marten's free volume theory, the rate constant of termination does not change with the free volume as long as the termination is chemically controlled. In this stage k_t is a constant. However, when the free volume of the system becomes equal to or less than a critical value, termination becomes diffusion instead of chemically controlled. The rate constant of termination in this stage follows equation (2).

$$k_t = (\psi_1 / \bar{M}_w^n) \exp(-A / V_F) \quad (2)$$

where ψ_1 and A are constants, $\bar{M}_w$ and V_F represent weight average molecular weight and the free volume of the system respectively. If V_{Fcr1} represents the critical free volume of the system, the rate constant of termination at this critical point can be calculated by equation (3).

$$k_{tcr} = k_{t0} = (\psi_1 / \bar{M}_{wcr}^n) \exp(-A / V_{Fcr1}) \quad (3)$$

combining (2) and (3), we have

$$k_t = k_{t0} (\bar{M}_{wcr} / \bar{M}_w)^n \exp(-A(1/V_F - 1/V_{Fcr1})) \quad (4)$$

where $\bar{M}_{wcr}$ and V_{Fcr1} are the critical weight average molecular weight and free volume respectively, n and A are constants which determine the rate of change of k_t with molecular weight and free volume. For VP-MMA system, it is believed that diffusion controlled termination is present right from the beginning of the reaction, therefore k_t can be calculated with equation (4) in the whole copolymerization process. The critical free volume for the termination reaction is taken to be the free volume of the system at zero conversion.

With a similar analysis, the following equation can be obtained under diffusion controlled propagation:

$$k_p = k_{p0} \exp(-B(1/V_F - 1/V_{Fcr2})) \quad (5)$$

where k_{p0} represents the propagation rate constant in chemical controlled propagation. V_{Fcr2} represents the critical free volume at the point when propagation changes from chemical to diffusion controlled. So in the whole polymerization process, we have

$$\text{MAA: } k_{11} = \begin{cases} (k_{11})_0 & V_F > V_{Fcr11} \\ (k_{11})_0 \exp(-B(1/V_F - 1/V_{Fcr11})) & V_F \leq V_{Fcr11} \end{cases} \quad (6)$$

$$\text{VP} \quad k_{22} = \begin{cases} (k_{22})_0 & V_F > V_{Fcr22} \\ (k_{22})_0 \exp(-C(1/V_F - 1/V_{Fcr22})) & V_F \leq V_{Fcr22} \end{cases} \quad (7)$$

The free volume of the system can be calculated as follows:

$$V_F = (0.025 + \alpha_p(T - T_{gp}))\varphi_p + (0.025 + \alpha_{M1}(T - T_{gM1}))\varphi_{M1} \\ + (0.025 + \alpha_{M2}(T - T_{gM2}))\varphi_{M2} \quad (8)$$

where α is the difference in thermal expansion coefficient above and below T_g (subscripts p , M_1 , M_2 , stand for polymer, monomer 1 and monomer 2). φ is the volume fraction.

(2) The result of simulation

There are a large number of parameters in the model, some of the parameters such as $(k_{11})_0$, $(k_{22})_0$, r , T_g and α can be reasonably taken as known from the literatures or can be estimated from the data. The parameters, including k_{t0} , n , A , B , C , V_{Fcr11} and V_{Fcr22} must be calculated with computer. The conversion-time curves and the residual monomer composition-time curves can simultaneously be obtained through tracking the whole copolymerization process with FTIR. After the equation of conversion-time curve was found out by the computer, by differentiation this equation the polymerization rate-time curve can be obtained. If the variation of the copolymer molecular weights with conversion is also known, the above unknown parameters can be estimated by Marqat method. The criterion is as follows:

$$\text{Min} \left(\sum_{i=1}^n (R_p - R_c)^2 \right) \quad (9)$$

where R_p is the copolymerization rate measured, R_c is the copolymerization rate calculated with equation (1).

These literature values of the parameters are given in Table 1, and the parameters from the experimental data are given in Table 2. Table 3 is the results of computer simulation. The curves simulated with the computer and the experimental points gained from FTIR are shown in Figure 4 and 5. The model gives fairly good agreement with the measured conversion and polymerization rate data. The expressions of the rate constants at 70°C are as follows:

$$k_t = 4.08 \times 10^6 (\bar{M}_{wcr} / \bar{M}_w) \exp(-1.109(1/V_F - 7.353)) \quad (10)$$

$$k_{11} = \begin{cases} 600 & V_F > 0.108 \\ 600 \exp(-0.497(1/V_F - 9.260)) & V_F \leq 0.108 \end{cases} \quad (11)$$

$$k_{22} = \begin{cases} 5625 & V_F > 0.078 \\ 5625 \exp(-0.889(1/V_F - 12.821)) & V_F \leq 0.078 \end{cases}$$

In order to determine k_t at any other temperature T , the following equation ought to be used:

$$k_{t0} = (k_{t0})_{70^\circ\text{C}} \exp(-E/R(1/T - 1/343)) \quad (12)$$

where E must be estimated in this case.

If the expression of k_t and k_p is available, according to the copolymerization theory, not only the copolymerization rate but also the variation of the molecular weights and the distribution of the sequence length of the copolymer with conversion can be predicted.

2. The calculation of the total activation energy of the copolymerization

Generally speaking, if only copolymerization rate is available, the total activation energy of the

Table 1 Literature values of the parameters used in the model

Parameter	r_1	r_2	$(k_{11})_0$	$(k_{22})_0$	$T_{\theta M_1}$	$T_{\theta M_2}$	$T_{\theta P}$	αM_1	αM_2	αp
Value	4.06	0.00772	$1.62 \times 10^7 \exp\left(-\frac{3500}{T}\right)$	$1.88 \times 10^8 \exp\left(-\frac{3573}{T}\right)$	229°K	288°K	343°K	1.35×10^{-3}	1×10^{-3}	3.39×10^{-3}
Literature cited	(5)	(5)	(6)	(6)	measured		measured	estimated values		

Table 2 Values measured (VP:MMA = 43:57 (mol)) polymerized at 70°C

$R \times 10^3$	1.29	1.38	2.03	2.71	3.23	3.50	3.50	3.12	2.51	1.75	0.968	0.726	0.565	0.484	0.323
ϕ_M	0.565	0.535	0.509	0.436	0.383	0.307	0.307	0.067	0.030	0	0	0	0	0	0
ϕ_V	0.435	0.428	0.418	0.401	0.393	0.381	0.375	0.360	0.296	0.267	0.252	0.226	0.215	0.199	0.183
ϕ_P	0	0.038	0.073	0.163	0.224	0.302	0.473	0.573	0.674	0.734	0.748	0.775	0.786	0.802	0.817
$[M_1]$	5.31	4.99	4.74	4.00	3.48	2.75	1.34	0.57	0.25	0	0	0	0	0	0
$[M_2]$	4.08	3.98	3.87	3.68	3.57	3.51	3.28	3.10	2.51	2.26	2.13	1.90	1.80	1.67	1.53
$\bar{M}_w$	1	1	1.03	1.12	1.52	2.14	2.71	2.76	2.76	2.76	2.76	2.76	2.76	2.76	2.76
$\frac{\bar{M}_w}{\bar{M}_{wcr}}$	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70

Annotation: the unit of R is mol/dm³·s, the unit of $[M]$ is mol/dm³.

Table 3 Results of estimation

Parameters	A	B	C	n	$V_{\sigma 11}$	$V_{\sigma 22}$	$k_0(\text{dm}^3/\text{mol}\cdot\text{s})$
Value estimated	1.109	0.497	0.889	1.0	0.108	0.78	4.08×10^6

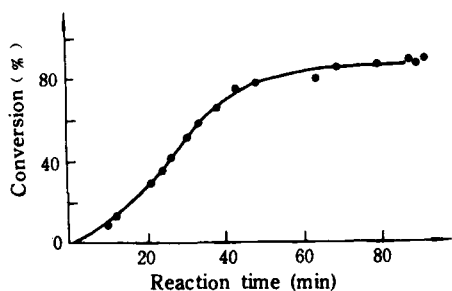


Fig. 4 Conversion-time curve of VP-MMA

The curve is the result of computer simulation

"■" experimental points

Copolymerization condition:

VP:MMA = 43:57(mol), ABIN = 0.06wt%, 70°C.

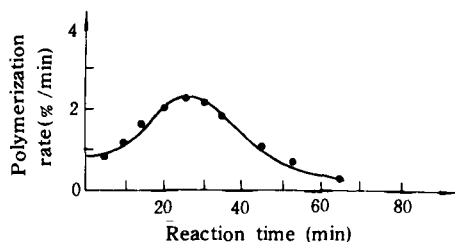


Fig. 5 Copolymerization rate-time curve

copolymerization can not be estimated through equation (1). But with the particularity of the VP-MMA copolymerization system, after a series of reasonable assumption and simplification, the total activation energy of the copolymerization can be estimated through this equation.

The monomer reactivity ratio is the ratio of two propagation rate constants and its variation with temperature will depend on the difference in propagation activation energy according to $d \ln r_1 / dT = (E_{11} - E_{12}) / RT^2$, where E_{11} and E_{12} are the propagation activation energy for M_1 radical adding M_1 and M_1 radical adding M_2 respectively. Since the activation energy of propagation is generally less than 41.8 KJ/mol, $E_{11} - E_{12}$ is even less than 10 KJ/mol for most pairs of monomers, the effect of temperature on r is not large. This effect can be ignored as the variation of reaction temperature is limited in a narrow range. Under the prerequisite of this hypothesis, for a definite copolymerization system with a fixed feed composition, the composition of the copolymer and the monomer at certain conversion P will be the same even if the copolymerization is carried out at two different temperatures. That is: $[M_1]_{T_2} = [M_1]_{T_1}$, $[M_2]_{T_1} = [M_2]_{T_2}$

It is supposed that, M_1 and M_2 represent MMA and VP respectively. Two copolymerization processes are carried out at T_1 and T_2 respectively, the copolymerization rates at a certain conversion P are R_{p1} and R_{p2} respectively. Since $[M_1]_{T_1} = [M_1]_{T_2}$, $[M_2]_{T_1} = [M_2]_{T_2}$, the following equation can be got.

$$\frac{R_{p1}}{R_{p2}} = \left(\frac{R_{i1}}{R_{i2}} \right)^{\frac{1}{2}} \left(\frac{k_{t1}}{k_{t2}} \right)^{\frac{1}{2}} \left[\frac{r_1[M_1]_{T_2}/(k_{11})_{T_2} + r_2[M_2]_{T_2}/(k_{22})_{T_2}}{r_1[M_1]_{T_1}/(k_{11})_{T_1} + r_2[M_2]_{T_1}/(k_{22})_{T_2}} \right] \quad (13)$$

Since $r_1 = 4.06$, $r_2 = 0.00772$, $r_1 \gg r_2$, so those terms containing r_2 can be ignored. If $R_i = 2k_d[I]$, equation (13) can be simplified as follows:

$$\frac{R_{p1}}{R_{p2}} = \left(\frac{[I]_1}{[I]_2} \right)^{\frac{1}{2}} \left(\frac{k_{d1} \cdot k_{t2} (k_{11})_{T_1}^2}{k_{d2} \cdot k_{t1} (k_{11})_{T_2}^2} \right)^{\frac{1}{2}} \quad (14)$$

Using Arrhenius equation, we have

$$\frac{R_{p1}}{R_{p2}} = \left(\frac{[I]_1}{[I]_2} \right)^{\frac{1}{2}} \exp \left(-\frac{E_G}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \right) \quad (15)$$

where E_G is the total activation energy of the copolymerization $E_G = E_d/2 + E_{11} - E_t/2$. If $[I_1]/[I_2] \approx 1$, taking logarithm to equation (15), it gives the following equation:

$$\ln(R_{p1}/R_{p2}) = -E_G/R(1/T_1 - 1/T_2) \quad (16)$$

the total activation energy E_G can be obtained by a plot of $-\ln(R_{p1}/R_{p2})$ vs. $(1/T_1 - 1/T_2)$.

Three copolymerization processes of MMA/VP at a fixed monomer ratio (VP:MMA=43:57 (mol)) are carried at 65°C, 70°C and 80°C respectively, when their conversion all reach 40% (weight), they are all in the middle of autoacceleration. The copolymerization rates measured at this conversion are listed in Table 4. From Table 5, the monomer concentrations at this conversion are as follows: $[M_1]=0.396$ $[M_2]=0.604$. According to the k_{11} and k_{22} values reported by the literature, we know that $k_{22} > k_{11}$ and $r_2[M_2]/k_{22} \ll r_1[M_1]/k_{11}$, so those terms containing r_2 can be ignored. Through calculating, $[I]_1/[I]_2 \approx 1$ is fulfilled, therefore the activation energy of copolymerization can be calculated with equation (16) in this case. Fig.6 is the plot of $-\ln R_{p1}/R_{p2}$ vs. $(1/T_1 - 1/T_2)$. From the slope of the straight line $E_G=88.6$ KJ/mol is obtained.

Table 4 Copolymerization rate

Copolymerization temperature (°C)	65	70	80
Copolymerization rate %(min)	1.43	2.36	5.68

Table 5 f_{vp} and F_{vp} at various conversion

Conversion %	10	20	30	35	40	50	60	70	75
f_{vp}	0.462	0.500	0.546	0.573	0.604	0.678	0.775	0.910	0.992
F_{vp}	0.149	0.166	0.187	0.201	0.216	0.257	0.320	0.433	0.641
$r_1=4.06$, $r_2=0.00772$, $f_{vp}=0.43$ (at 0% conversion)									

According to the equation $E_G = 1/2 E_d + E_p - 1/2 E_t$ and the data of the activation energy of copolymerization, E_G equals to 84.6. This value is close to the value calculated with the above method.

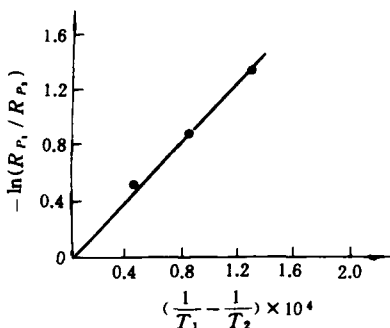


Fig.6 $-\ln(R_{p1}/R_{p2})$ vs $(1/T_1 - 1/T_2)$ plot

Acknowledgement The authors wish to thank associate professor Ruan Zhu for her help in the FTIR experimental work.

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