Polymerizations of Vinyl Acetate in Solution

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ABSTRACT

The polymerization of vinyl acetate in methanol, ethyl acetate and acetic acid is studied and the conversion-times are reported. Due to the importance of molecular weights of polymers from the solution and bulk methods, and their uses in optimization of polymerization, specially in controlling the properties of the polymer, the viscosity, molecular weight and molecular weight distributions are measured and reported. Statistical calculations and curve fittings of the data on the molecular weights and the solvent (methanol-monomer ratio) indicate a very low mathematical residues. The conversions are compared with bulk, and the effect of temperature on solution polymerization in ethyl acetate is used to show the importance of high activation energy of the initiator (benzoyl peroxide). Triethyl amine, being used as catalyst in solution polymerization of vinyl acetate (ethyl acetate and acetic acid), indicate a faster conversion.

Key Words: solution polymerization, vinyl acetate, statistical curve fitting, activation energy, triethyl amine

INTRODUCTION

Polymerization of vinyl acetate in bulk and in a number of organic solvents as solution have been studied in detail [1 and 2]. One of the special features of polymerization of vinyl acetate is the extensive chain transfer reactions and hydrolysis [3−6]. The chain transfer and hydrolysis take place mostly in solution and emulsion polymerizations [1 and 4]. The molecular weights in solution and bulk must be controlled. The molecular weight of a polymer is considered as one of the most important parameters of the polymerization reactions, as almost all properties (solubility, swelling, permeation, gellation, crystallinity, thermal properties,

tensile and dynamic properties or processing) of polyvinyl acetate are related to its structure and molecular weight. In the past, the effects of concentration and initiators have been used to determine primarily the molecular weights on the basis of the average degree of polymerization [1]. More recently, the effect of temperature and pressure have been considered in polymerization and copolymerization of vinyl acetate [7].

Therefore, important factors related to the rate must be considered with the effect of temperature or pressure of polymerization prior to optimization of the molecular weights of polymers. Because these relations are experimentally available, statistical calculations with known dependent

variables and specific effects can be used in determination of molecular weights and its magnitude with high level of confidence to the extent that the reaction procedure is designed [8].

The literature review shows that, optimization of polymerization reactions are based on the simplified kinetic relations rested on the isothermal condition of reaction [9]. However, to be more exact, these equations including Lagrange multiplier used in the final optimization of polymerization reaction, fail under nonisothermal conditions and dilute system where the monomer concentration is low, or when a low molecular weight polymer exists. The principle reason being, the diffusional effects both in solution polymerizations and its crucial importance in termination reactions. Hence, for more accurate results from the experimentation, statistical calculations may serve as an acceptable alternative to the optimization calculations of polymerization reactions [8].

In view of the earlier reasearch in this area, we have carried out the polymerization of vinyl acetate in methanol, ethyl acetate and acetic acid solutions and also in the bulk. The rates of conversion have been measured and compared [2].

The acetate content, viscosity, molecular weights, molecular weight distributions and the polydispersity ratios of polymers are measured and statistical calculations are used in model fittings of the molecular weights of polymers. The conversion rates at different temperatures have been used to calculate relative rates of conversions.

Furthermore, on the basis of thermodynamics, we have used a new catalyst for the increased rate of the polymerization.

EXPERIMENTAL

Vinyl acetate was purchased from Merck, $d=0.934$ g/cm^3. Benzoyl peroxide was obtained from Wako with 99.9% purity. Methanol was from BDH, $d=0.791$ g/cm^3 and purity of 99.9%. Other solvents employed were also 99.9% pure and used without further distillations or purifications. None of the starting materials were impure reagents. The

nitrogen gas was also 99.99% pure. The polymerization of the vinyl acetate in organic solvents were carried out at 50 °C under nitrogen in a 1L flask equipped with a condensor and stirrer. The polymerization reaction in ethyl acetate was also carried out at 60 °C. In each reaction the monomer solvent weight ratio (M/S) was based on 85/15, 67/33 or 50/50 weight percents. The weight percent of the initiator was calculated on the basis of the monomer (I/M). For 67 g vinyl acetate monomer, 0.15 g benzoyl peroxide was used (M/S=67/33, and I/M=0.22% or I=10 mmol/L). The polymer was separated by addition of water and used in the conversion time. The viscosity of the polymer was measured in acetone at 30 °C. The constants of the intrinsic viscosity and the molecular weight were $K=17.4\times10^{-5}$ and $a=0.68$. The molecular weight distributions were measured with GPC (Watkin Co.). The Oswald viscometer was used in viscosity measurements. The number, weight and viscosity average molecular weights and the polydispersity index of the polymers were measured with GPC. The column was calibrated with PS and all the tests were run in Polymer Department of National Institute of Petroleum, Ray. The polymer structure was studied with infrared spectrophotometer (Phillips), and the percent hydrolysis of polymers were measured according to ASTM D1396-73. In this method 2.15 g dried polymer was dissolved in 200 mL methanol and refluxed with 25 mL of 0.50 N KOH for 2 h, and it was finally titrated with 0.50 N HCl.

RESULTS AND DISCUSSION

Industrially the most important objective is to reduce the residual concentration, increase the output of polymerization and control the molecular weight for desired quality of the polymer. Because the control and its maximization is important in free radical polymerizations, molecular weight defined in terms of the initial monomer concentration (M_0), monomer molecular weight (W_m) and desired conversion (x_f) in eqn (1) can be used to relate the zero moment of the inactive polymer

(μ_f) to desired final number average molecular weight (M_{nf}) and kinetic equations of the rate of initiator decomposition (dI/dt) to monomer concentration (dM/dt) in the final time (t_f) needed for the polymerization. Eqns $(1-7)$ show the developments related to the optimization time of the free radical polymerization under isothermal condition. The time equation combined with the Lagrange multiplier (λ) for concentrations of monomer can form a new function (J) (eqn (8)) that is used in minimization of the reaction using an initiator and a temperature for a desired molecular weight.

$$dI/dt = -k_d I \tag{1}$$

$$dM/dt = -k_p \sqrt{(2fk_dI/k_t)}(M-M_e) \tag{2}$$

where, M_e is the equilibrium monomer concentration.

$$d\mu_0/dt = 2fk_d I \tag{3}$$

At constant temp.: $I_f = I_0 \exp(-k_d t_f)$ $\qquad(4)$

$$\mu_{0f} = 2fI_0[1-\exp(-k_d t_f)] \tag{5}$$

where, μ_{0f} is the desired final value for μ_f.

$$t_f = -1/k_d \ln(1 - \mu_{0f}/2fI_0) \tag{6}$$

$$\mu_{0f} = W_m(M_0 x_f)/M_{nf} \tag{7}$$

The optimality condition is expressed in eqn (8). This equation may be differentiated with respect to the initiator or the temperature. However, in our work, the statistical calculations of system performance is considered independent of the details related to kinetics or energetics.

$$J = -1/k_d \ln(1-\mu_{0f}/2fI_0) + \lambda\{\ln(M_0/M_f-M_e)-$$

$$2(k_0I_0)^{1/2}[1-(1-\mu_{0f}/2fI_0)^{1/2}]\} \tag{8}$$

where, M_f is the final monomer concentration (mol/L). Our system performance is dealt with response surface (a single factor (x_1) for single
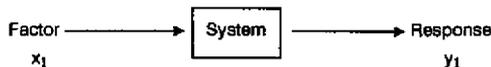

Figure 1. A single factor system.

response (y_1)), as depicted in Figure 1.

The statistical calculations are basically unimodal and the optimizations are expressed in terms of minimum or maximum. The linear or nonlinear relations are used to express the response of the system. Eqns (9) and (10) describe the behaviour commonly seen in these systems:

$$y_{1i} = \beta_0 + \beta_1 x_{1i} + r_{1i} \tag{9}$$

$$y_{1i} = \beta_0 + \beta_1 x_{1i} + \beta_{11} x_{1i}^2 + r_{1i} \tag{10}$$

Notice that r_{1i} in these equations is the residues that is calculated from the variance. Eqn (9) is clearly very similar to regression equation in which the linear relation shows slope β_1 and the intercept β_0. To use these equations in statistical calculations of the modelling of polymerization reaction or the optimization; these equations can be written in terms of n distinct set of conditions for known variables expressed in terms of vectors in a matrix. Matrix X is used to show the experimental conditions and information (x_{ij}), and matrix Y shows the measured response (y_{ij}). The matrix $\hat{B}$ (eqn 16) indicates the coefficients of the linear or nonlinear equations. Eqns (11 and 12) show the above mentioned matrices used in the statistical calculation of the system based on three level of experiments (quadratic model).

$$X = \begin{vmatrix} 1 & x_{11} & x_{11}^2 \\ 1 & x_{12} & x_{12}^2 \\ 1 & x_{13} & x_{13}^2 \end{vmatrix} \qquad Y = \begin{vmatrix} y_{11} \\ y_{12} \\ y_{13} \end{vmatrix} \tag{11}$$

$$XX' = \begin{vmatrix} n & \Sigma x & \Sigma x^2 \\ \Sigma x & \Sigma x^2 & \Sigma x^3 \\ \Sigma x^2 & \Sigma x^3 & \Sigma x^4 \end{vmatrix} \qquad X'Y = \begin{vmatrix} \Sigma y \\ \Sigma xy \\ \Sigma x^2 y \end{vmatrix} \tag{12}$$

In the polymerization reaction; free radical

Table 1. The effect of methanol on the percent conversion, molecular weight and degree of polymerization of vinyl acetate with I/M=0.23% in 12 h.

No	M/S	Conversion (%)	Molecular weight average, $\bar{M}_w$
1	85/15	59.5	513944
2	67/33	53.51	385074
3	50/50	10.85	261928

polymerization of vinyl acetate in solution or bulk is considered as the system, and its performance is the polymerization under the single factor like the initiator concentration or time and the response is the change in molecular weight or the conversion.

In statistical calculations and optimization of the system, the important factors involved in response surfaces are used without any specific details regarding the assumptions or approximations involved in kinetic equations. The time eqn (6) for free radical polymerization uses equilibrium monomer concentration, M_e, of reaction used in eqn (2) on the assumption that $M_0 > > M_e$. This assumption may not hold for all reactions and simplified version of the calculations may be difficult:

$$M_n^0 + M \xrightarrow[k_{dp}]{k_p} M_{n+1}^0 \qquad (13)$$
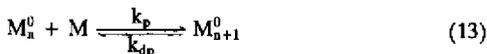
Statistical Calculations of the Polymerization of Vinyl Acetate

The statistical calculations are based on the

following observations:

The Effect of Solvent (Methanol) on the Molecular Weight of the Polymer

The data on the effect of solvent on the molecular weight in Table 1 was used in a linear equation of molecular weights and solvent-monomer ratios to calculate eqn (15). The mid-point combination model of three point experiments once coded according to matrix of the eqn (11) indicated a far more acceptable result than the simple linear regression analysis (Figures 2 and 3).

$$\bar{M}_W = 5.55004 \times 10^5 - 3.00765 \times 10^5 \, (S/M) \quad (14)$$

$$\bar{M}_W = 5.67047 \times 10^5 - 3.05824 \times 10^5 \, (S/M) \quad (15)$$

Table 2 shows the statistical calculations of y_i, $\hat{y}_i$ and r_i.

The Effect of Initiator Concentration

The effect of the initiator concentration in methanol (M/S=77/33) is shown in Table 3. The viscosity and molecular weight are expected to decrease with the initiator concentration.

The Effect of Solvents

The effect of solvent on the molecular weight of the polymer is shown in Tables 1−4. The viscosity and molecular weights decrease with the increasing solvent concentration, and polymer conversion may increases after 12 h. Because the experimental
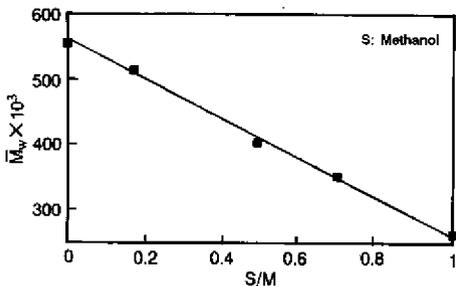
Figure 2. The linear regression equation of the molecular weight of polyvinyl acetate with different S/M ratios.
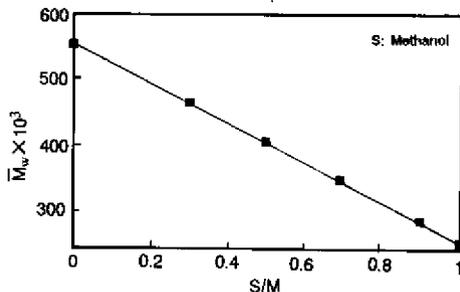
Figure 3. The modelled fittings of the molecular weight of polyvinyl acetate with different S/M ratios.

Table 2. The mathematical r_i of the solvent-monomer ratio (S/M) of the polymerization of vinyl acetate.

No	x_i (S/M)	y_i ($\overline{M}_w$)	$\hat{y}_i$	r_i
1	0.176	513944	51322	722
2	1.000	261928	261223	725

points are few and the concentrations of the initiator and solvent are very close, it is not possible to clear the linear or nonlinear relation of these factors in the polymerization reaction of the vinyl acetate.

In the statistical calculations and the equations similar to (9) and (10) the residual part r_{li} is the mean response y_i subtracted from each individual response y_{1i}. Since r_{1i} consists of the differences, the square root of variance is used to measure RR' [9].

$$\begin{vmatrix} b_0 \\ b_1 \end{vmatrix} = \hat{B} \text{ and } R = Y - X\hat{B} \text{ where } s_r = (s^2)^{1/2} = RR' \tag{16}$$

Where b_1 and b_0 are the slope and intercept and s_r is the standard deviation, and s^2 is the variance.

The conversion of vinyl acetate in bulk is shown in Table 4. Figure 4 shows the conversion-time curves of the vinyl acetate in the bulk. The conversion in bulk is twice the polymerization conversion in the solution (acetic acid). Since the rate of polymerization in bulk is dependent on $(k_p/k_t^{1/2})k_{in}^{1/2}$ then the rate of reaction in solution is expected to be several times slower than the bulk (literature value is about 5) [2]. This is mainly due to diffusional effect on termination in the bulk and

Table 3. The effect of I/M weight percents on the viscosity and the weight average molecular weight of the polymer (M/S=67/33).

No	I/M (wt.%)	$[\eta]$	$\overline{M}_w$
1	0.0504	1.1105	394057
2	0.2300	1.0963	380210
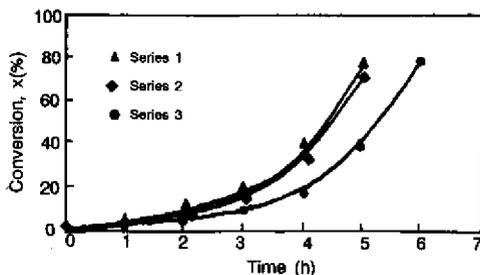
Figure 4. The polymerization percent conversion versus time of polyvinyl acetate in bulk.

solvent effect leading to lower viscosity and molecular weight in the solution polymerization.

The molecular weight distribution of polyvinyl acetate in solution and bulk is shown in Figure 5. The polydispersity of polymers in bulk and solution are about 2.

The molecular weights of polymers in solution and bulk are closer in acetic acid. The viscosity average molecular weight of polyvinyl acetate in bulk is slightly higher compared to the polymer obtained in ethyl acetate.

The Percent Hydrolysis of Acetate and the Structure of Polyvinyl Acetate

The percent vinyl acetate hydrolyzed with base was measured for the polymers from the solution polymerizations in methanol and acetic acid. The percent hydrolyzed acetate in polymer was measured from the titration of the blank sample and polymer, using S g sample, and 0.5 N HCl with the known volume of HCl for the blank (B) and sample (V) according to eqn (17):

$$\text{Acetate } (\%) = [(B-V) \times N \times 8.6/S] \tag{17}$$

The hydrolyzed acetate group obtained is 94.4% for polymer prepared in methanol and 95.2% for polymer prepared in acetic acid. This indicates that polymer chain is mostly made of acetate.

The structure of the polymers indicate

Table 4. Polymerization conversions of vinyl acetate in methanol (I/M=0.15 %), ethyl acetate (I/M=0.15 %), acetic acid (I/M=0.18 %), and the bulk.

| Solvent						Bulk	
Methanol		Ethyl acetate		Acetic acid			
t (h)	x (%)	t (h)	x (%)	t (h)	x (%)	t (h)	x (%)
3	1.57	5	0.96	6	0.21	1	2.82
5	2.19	7	6.00	8	0.39	2	6.28
7	8.82	8	10.15	8	3.00	3	13.97
10	35.29	9	15.90	10	11.79	4	31.07
11.5	54.12	10	23.17	11	25.27	5	69.09
14	65.34	11	41.72	12	62.43	–	–
–	–	12.5	58.20	13	–	–	–
–	–	14	70.12	–	–	–	–

$\nu(C=O)$ for the ester carbonyl absorption at 1700 cm^{-1}, and $\nu(CH_2)$ bending of $-CH_2-$ at 1450 cm^{-1}, the $\nu(-C-O-)$ absorption for ether was also at 1080 cm^{-1} [10]. The IR of polyvinyl acetate from methanol is shown in Figure 6.

Thermodynamics of the Polymerization

Recent studies show that, free radicals and ion radicals strongly localized as unpaired electrons, are capable of interacting with the polymer chain. The interaction in polyvinyl acetate is strongly dependent on temperature [6]. During the polymerization the temperature is expected to affect almost all thermodynamic parameters (ΔH, ΔS and ΔG).

Recently, higher temperatures and pressures
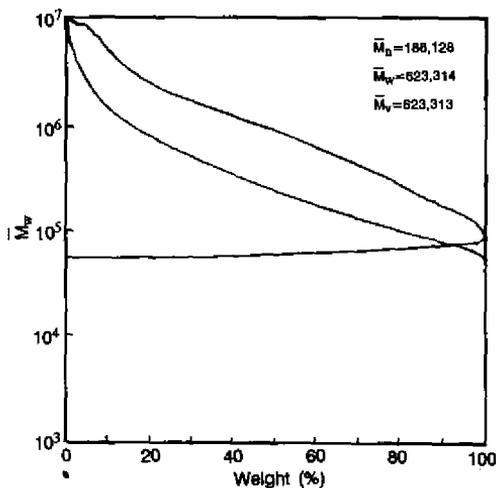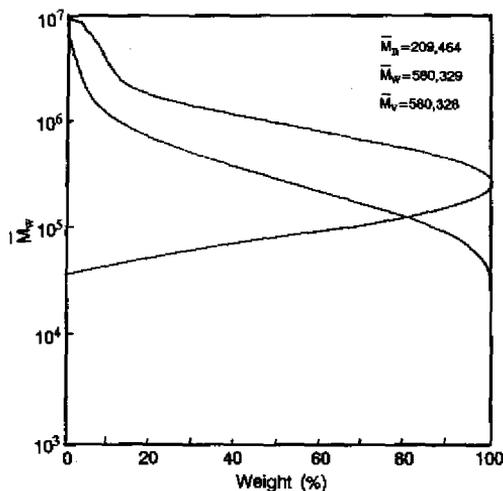
Figure 5. The molecular weight distributions from polymerization in (a) bulk and (b) ethyl acetate solution.
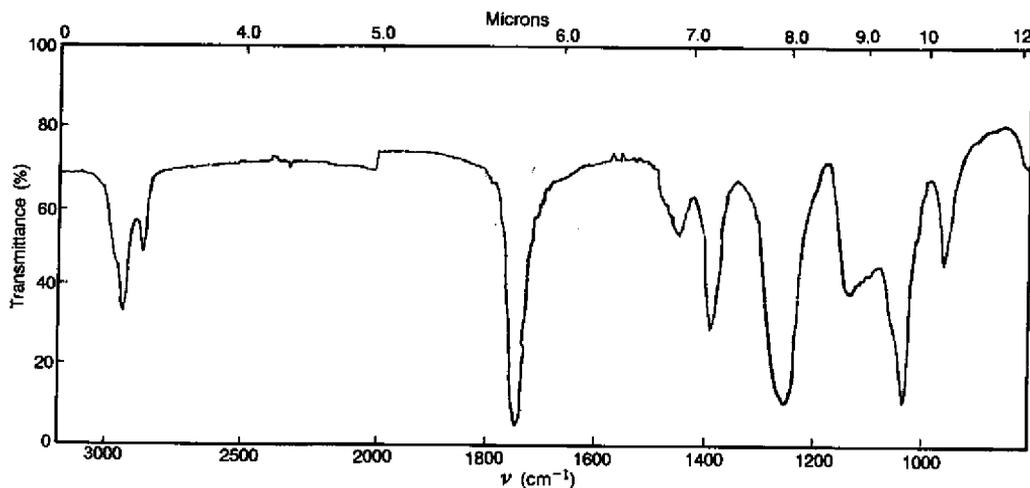
Figure 6. The infrared spectrum of polyvinyl acetate from methanol.

have been used in the copolymerization of vinyl acetate with ethylene [7]. Based on the new information and complexation of tertiary amines with benzoyl peroxide in the polymerization of unsaturated polyesters we have selected triethyl amine as a catalyst to explore the lower temperature and shorter reaction times [11 and 12]. Table 5 shows the catalytical effect of triethyl amine in reducing

Table 5. Effect of triethyl amine catalyst on the conversion of the vinyl acetate in acetic acid and ethyl acetate (M/S=85/15 and I/M=0.23 %).

No	Solvent[a]	Catalyst[b]	Time (h)	Conversion (%)
1	Acetic acid	–	6	33.52
		–	14	62.28
		Et₃N	5	68.51
2	Ethyl acetate	–	6	10.75
		–	12.5	50.23
		Et₃N	4	53.36

a: Et₃N and Co(Naphthenate) show no effect in methanol.

b: 10 percent catalyst is used.

the conversion time to more than half. An effect very similar to temperature, where one expects a lower thermodynamic stability, but a higher reactivity of catalyst in the polymerization reaction.

The Effect of Temperature

The effect of temperature on polymerization of vinyl acetate in ethyl acetate at 50 and 60 °C is shown in Table 6. The results show that for every 10 °C increase the conversion time has decreased 2.5 times. We have explained this effect with the activation energy of polymerization. If the effective activation energy of the solution polymerization of vinyl acetate is written according to eqn (18), then Arrhenius equation and rate of the reaction at two

Table 6. Effect of temperature on the polymerization of vinyl acetate conversion in ethyl acetate (M/S=85/15, I/M=0.25).

No	T (°C)	Time (h)	Conversion (%)
1	50	12.5	58.23
2	60	5	60.48

different temperatures can be calculated [12]:

Effective activation energy = $(E_p + E_d/2 - E_t/2)$

(18)

E_d=29.7 kcal/mol with benzoyl peroxide initiator
E_p=5.606 kcal/mol
E_t=5.509 kcal/mol

E_{eff} = -17.601 kcal/mol (19)

r_p = $C \exp(-(E_{eff})/RT)$ (20)

$\ln r_p(T_2)/r_p(T_1) = -(E_{eff})/R (1/T_2 - 1/T_1)$ (21)

$\ln r_p(T_2)/r_p(T_1) = 0.7960$ (22)

$r_p(T_2) = 2.216(T_1)$ (23)

The same calculation shows that the number average molecular weight changes for every 10 °C increase in temperature.

CONCLUSION

The polymerization of vinyl acetate in solution is commercially very important, and the material serves as adhesives and gums. The polymerization of vinyl acetate is carried out in the same equipments as the emulsion polymerizations. The poly-vinyl acetate obtained from the solution polymerization is relatively lower in molecular weight than the polymer obtained from the bulk. The effect of temperature and pressure on the bulk polymerization is different than the solution polymerization reaction of vinyl acetate.

The conversion times are usually reduced in the solution polymerization at a lower temperature. The increased temperatures and pressures are the parameters that are industrially important in the copolymerization of vinyl acetate.

Catalysts are, therefore, considered to be important in the polymerization reactions, where there is a need for a shorter reaction time, lower temperatures and higher conversions. In this work, we have used triethylamine as catalyst for the conversion of vinyl acetate in solution which may be industrially attractive in polymerizations and copolymerization of vinyl acetate with other monomers and specially with ethylene.

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