

Radiation-Induced Polymerization of Vinyl Acetate

Ichiro SAKURADA, Yoshito IKADA and Yasuko NISHIZAKI*

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The radiation-induced polymerization of pure vinyl acetate was studied in liquid-phase over the wide temperature range from $+62^{\circ}\text{C}$ to -78°C . The activation energy for overall polymerization was found to be 3.69 kcal/mole. The formation of branching from acetate groups was negligible in the conversion range below about 20%, and considerably high degrees of polymerization (about ten thousands) were obtained in the polymerization at about 0°C . The degree of polymerization-temperature curve was found to exhibit a maximum. This maximum was attributed to a very low activation energy for initiation at the radiation polymerization. The 1, 2-glycol content in the hydrolyzed polyvinyl alcohol decreased with decreasing temperature of polymerization and the 1, 2-glycol content-temperature curve was in accordance with those found for catalytic polymerizations. From the kinetic analysis of polymerization, the G_R -value of vinyl acetate was found to be between 1 and 2.

I. INTRODUCTION

It has been previously shown by Okamura and co-workers¹⁻⁵⁾ that the radiation-induced polymerization of vinyl acetate (VAC) leads to formation of linear polyvinyl acetate (PVAC) with a considerably high degree of polymerization such as about ten thousands. This fact seems of great importance, because by means of conventional catalytic polymerizations it is difficult to obtain PVAC of such a high degree of polymerization without hydrolyzable branches.

However, the radiation-induced polymerization of VAC has been investigated much less extensively than other monomers such as styrene and methyl methacrylate. In several points, the conclusions drawn by different investigators are frequently in disagreement with each other.⁶⁾

Therefore, to understand more deeply the radiation polymerization of VAC, further detailed studies are required. The present work was carried out for pure VAC in liquid-phase over a wide range of temperatures close to the melting point (-93°C), focussing the attention especially on the temperature dependence of the rate of polymerization, the degree of polymerization of PVAC's and the number of 1, 2-glycol bonds in polyvinyl alcohols (PVAL's) obtained by the hydrolysis of the PVAC's. The G_R -value of VAC is to be also discussed.

II. EXPERIMENTAL

1. Purification of VAC

The VAC monomer was purified by the method described by Matsumoto

* 桜田 一郎, 筏 義人, 西崎 靖子: Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Kyoto.

and Maeda.⁷⁾ Commercial monomer was washed with 40 % aqueous solution of sodium hydrogen sulfite and then with 20 % NaCl solution, dried over anhydrous calcium sulfate and distilled. The distillate was prepolymerized to a conversion of about 15 % using azo-bis-isobutyronitrile as initiator and the residual monomer was then re-distilled from the polymerizate, immediately before use. The middle, one third fraction (b. p. = 72–73°C) of the distillate was used for the radiation polymerization.

2. Polymerization Procedure

The purified monomer was taken into tubes, degassed by repeating cycles of freezing and thawing, and then sealed off under a pressure of 10^{-5} mmHg. The irradiation was performed with gamma-rays from a Co-60 source at temperatures from +62°C down to –78°C. The temperatures were maintained in a thermostat for 21°, 42° and 62°C. The temperatures below 0°C were kept at constant values by the help of the following refrigerants; pure ice for 0°C, ice-NaCl (100:29) for –21°C, ice-CaCl₂ (100:42.5) for –50°C and dry ice-methanol for –78°C.

The rate of polymerization was determined by isolating and weighing the polymer.

3. Measurement of Degree of Polymerization

Intrinsic viscosities $[\eta]$ of PVAC were measured in acetone at 30°C using an Ubbelohde-type viscosimeter and then converted to number-average degrees of polymerization $\bar{P}_n$ by means of the equation (1) derived for fractionated PVAC's from osmometry.⁸⁾

$$[\eta] = 7.94 \times 10^{-4} \bar{P}_n^{0.62} \quad (1)$$

4. Hydrolysis of PVAC and Acetylation of PVAL

Hydrolysis of PVAC's was carried out with sodium hydroxide in a medium of acetone-methanol-water (80:17:3 by vol.) mixture for 15 hrs. at room temperature. To ensure the complete hydrolysis, the PVAL precipitated was dissolved in pure water and hydrolyzed further by an addition of sodium hydroxide for 5 hrs. at room temperature.

Acetylation of the PVAL's thus obtained was effected in acetic anhydride-pyridine (1:2 by vol.) mixture under nitrogen atmosphere for 16 hrs. at 100°C. The reactant was poured into *n*-hexane to precipitate the PVAC's, which were then purified by repeated dissolution in acetone and precipitation in *n*-hexane.

5. Determination of the Content of 1, 2-Glycol Bonds⁹⁾

Excess of sodium periodate was added to the aqueous solution of PVAL and the oxidation of 1, 2-glycol bonds was allowed to proceed for 20 min. at 25°C. Then the solution was cooled to 1°C and the unreacted sodium periodate was titrated with *N*/10-NaOH, using thymolphthalein+1-naphtholbenzoin as indicator. The glycol content was calculated from the difference of the initial and final concentrations of sodium periodate.

III. RESULTS AND DISCUSSION

1. Rate of Polymerization

The mechanism of radiation polymerization of VAC in liquid-phase is known to be a typical radical process.^{1-6,10-13)} Most of the data are consistent with the assumption that the square-root relationship between the dose rate and the overall rate of polymerization is valid over a wide range of dose rates. The upper limit of dose rate, beyond which the square-root rule does not hold, is reported to be in the range of 3×10^5 r/hr.^{6,11)} In the present work the polymerization was carried out at a constant dose rate of 3.0×10^4 r/hr.

Fig. 1 shows time-conversion curves obtained at various polymerization temperatures. The polymer yield increases linearly up to about 15 % conversion with polymerization time. In every case the reproducibility of the result was good and no induction period was observed. The Arrhenius plot of the rate of polymerization was given in Fig. 2. From the slope of the straight line the activation energy for overall polymerization was found to be 3.69 kcal/mole, which is in good agreement with 3.7 kcal/mole reported in literatures.^{2,14)} In the case of non-sensitized photopolymerization of VAC it was 4.4 kcal/mole according to Burnett and co-workers.¹³⁾

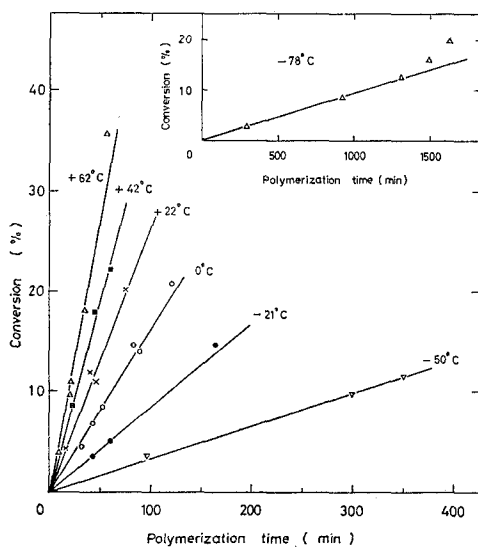


Fig. 1. Conversion curves of radiation polymerization of pure VAC at various temperatures.

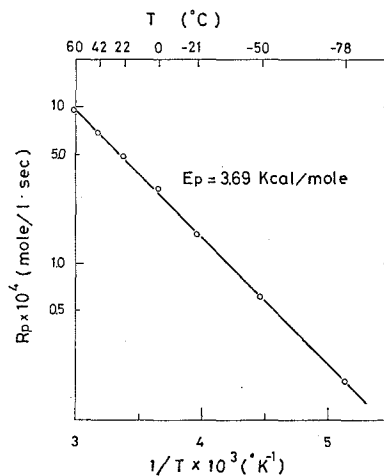


Fig. 2. Arrhenius plot of the overall rate of polymerization of VAC.

2. Formation of Branching from Side-Groups

As is well known, acetate side-groups of PVAC molecules are prone to be attacked by growing chain radicals and the resulting radicals may take up monomer molecules to give a branched polymer. The possibility of formation of such branching from acetate groups can be readily checked by comparing $\bar{P}_n$

of the original PVAC with that of the PVAL which is obtained by hydrolysis of acetate side-groups of the PVAC. In Fig. 3 the $\bar{P}_n$ values of the original PVAC and PVAL were plotted against the conversion of monomer. To avoid confusion owing to different equations correlating $[\eta]$ and $\bar{P}_n$ for PVAC and PVAL, the $\bar{P}_n$ of PVAL was calculated from the $[\eta]$ of the reacetylated PVAC using the same equation (1) which was applied to the original PVAC. It is seen from the figure that the $\bar{P}_n$ of the reacetylated PVAC agrees with that of the original PVAC within experimental error. Hence it follows that the branching from side-groups can be neglected in the conversion range investigated. A very slight increase in $\bar{P}_n$ with the conversion implies the gel-effect to be insignificant as far as the conversion is below about 20 %. This may be supported also by the fact that the time-conversion curves shown in Fig. 1 are approximately linear in the same conversion range.

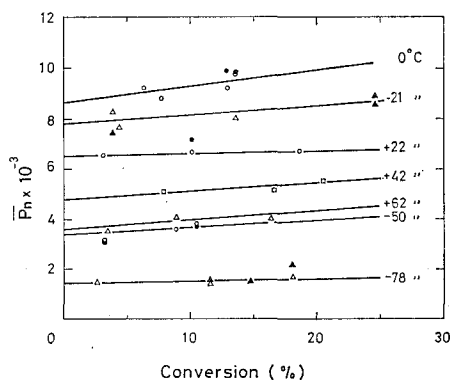


Fig. 3. Plot of the $\bar{P}_n$ of original PVAC and reacetylated PVAC as a function of conversion.
($\circ$, $\triangle$, $\square$...original PVAC. $\bullet$, $\blacktriangle$, $\blacksquare$...acetylated PVAC.)

Fig. 2 demonstrates further a noticeable feature that the nonbranched PVAC or PVAL with considerably high $\bar{P}_n$ is able to be obtained under certain suitable polymerization condition. This result is in accordance with that found by Okamura and co-workers.¹⁻⁵⁾

3. Temperature Dependence of $\bar{P}_n$

Fig. 4 shows the relationship between the polymerization temperature and the $\bar{P}_n$ which was obtained by extrapolation to 0 % conversion. It can be clearly seen that as the temperature is raised the $\bar{P}_n$ increases, passes through a maximum at about 0°C and then decreases. A similar trend was observed also by Okamura and co-workers.^{4,16)} In their case the temperatures where a maximum $\bar{P}_n$ was produced, were 0°C⁴⁾ and 20°C.¹⁶⁾ They pointed out that this may be ascribed to the predominant transfer reaction which is favored especially in the polymerization of VAC.

The maximum observed in the P_n -temperature curve is a remarkable unique feature which would justify a more detailed discussion. Provided that the termination reaction proceeds through disproportionation mechanism,¹⁷⁾ the re-

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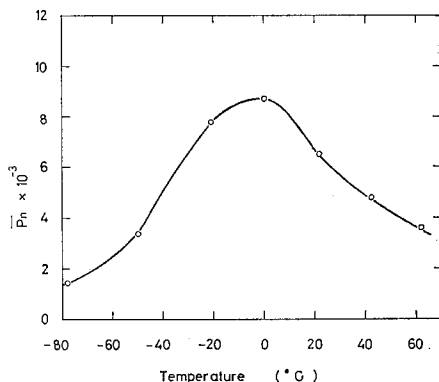


Fig. 4. Plot of the $\bar{P}_n$ at 0 % conversion as a function of polymerization temperature.

reciprocal $\bar{P}_n$ of polymer molecule formed is in our case given by the familiar equation (2), the radical transfer to polymer being neglected since consideration is here confined to low conversion of monomer,

$$\frac{1}{\bar{P}_n} = C_m + \frac{R_i}{R_p} \quad (2)$$

where C_m is the chain transfer constant for monomer, R_i is the rate of initiation, and R_p is the rate of propagation. The temperature dependence of C_m and R_p can be written by the following equations in a conventional fashion,

$$C_m = \frac{k_{tr}}{k_p} = \frac{A_{tr}}{A_p} \cdot \exp\{-(E_{tr}-E_p)/RT\} \quad (3)$$

$$R_p = \frac{k_p}{k_t^{1/2}} \cdot R_i^{1/2} \cdot [M] \quad (4)$$

$$= \frac{A_p}{A_t^{1/2}} \cdot \exp\{-(E_p-E_t/2)/RT\} \cdot R_i^{1/2} \cdot [M] \quad (5)$$

where T is the polymerization temperature, R is the gas constant, k , A and E are the rate constants, the frequency factors and the activation energies, and the suffixes p , t and tr denote the reactions of propagation, termination and transfer, respectively. R_i is usually assumed to be independent of temperature in the case of radiation-induced polymerization and is given by

$$R_i = \frac{d \cdot G \cdot I \cdot B}{100 \cdot N_L} \quad (6)$$

where I is the dose rate (r/sec), G is the G_R -value, that is, the number of monomer radicals produced per 100 eV absorbed, d is the density of monomer (g/l), B is the energy conversion factor (5.8×10^{13} eV/g·r), and N_L is Avogadro's number.

By substituting (3), (5) and (6) into (2), the equation (7) is obtained.

$$\begin{aligned} \frac{1}{\bar{P}_n} = & \frac{A_{tr}}{A_p} \cdot \exp\{-(E_{tr}-E_p)/RT\} \\ & + \frac{A_t^{1/2}}{A_p} \cdot \frac{1}{[M]} \cdot \left(\frac{d \cdot G \cdot I \cdot B}{100 \cdot N_L} \right)^{1/2} \cdot \exp\{(E_p-E_t/2)/RT\} \end{aligned} \quad (7)$$

The first term concerning the C_m was analyzed in detail by Clarke *et al.*¹⁸⁾ By recalculation of numerous data cited in literatures, these workers showed that the temperature dependence of C_m for VAC could be conformed to the following equation (8).

$$\log_{10} C_m = -1.59 - 6.70 T^{-1} \quad (8)$$

From this equation A_{tr}/A_p and $E_{tr} - E_p$ were estimated to be 2.54×10^{-2} and 3.1 kcal/mole, respectively. Furthermore, by substituting (6) into (5), we get

$$R_p = \frac{A_p}{A_t^{1/2}} \cdot \exp\{-(E_p - E_t/2)/RT\} \cdot \left(\frac{d \cdot G \cdot I \cdot B}{100 N_L}\right)^{1/2} \cdot [M] \quad (9)$$

where $d^* = 930$ g/l, $I = 3.0 \times 10^4/3,600 = 8.3$ r/sec, $B = 5.8 \times 10^{13}$ eV/r·g, $N_L = 6.023 \times 10^{23}$ and $[M]^* = 10.8$ mole/l. From the linear curve given in Fig. 2, it follows that $R_p = 0.252 \exp(-1,860/T)$, leading to $E_p - E_t/2 = 3.69$ kcal/mole and $A_p/A_t^{1/2} \cdot G^{1/2} = 2.69 \times 10^2$. As a result, the temperature dependence of $\bar{P}_n$ in the radiation polymerization of pure VAC can be represented by the equation (10).

$$1/\bar{P}_n = 2.54 \times 10^{-2} \cdot \exp(-1,540/T) + 1.63 \times 10^{-10} \cdot G \cdot I^{1/2} \cdot \exp(1,860/T) \quad (10)$$

As is seen from Fig. 5, where the $\bar{P}_n$ was plotted as a function of the polymerization temperature according to the equation (10) for various G -values, it is obvious that the maximum in the $\bar{P}_n$ -temperature curve appears as a result of counterbalance of the temperature dependence of the transfer, initiation, propagation and termination reactions. Therefore it is not correct to say that the phenomenon is specific to the radiation-induced polymerization. However, it is usually stated in the catalytic radical polymerization that an increase in the temperature of polymerization does lead to a reduction in $\bar{P}_n$. This apparent discrepancy between the catalytic and the radiation polymerization is due un-

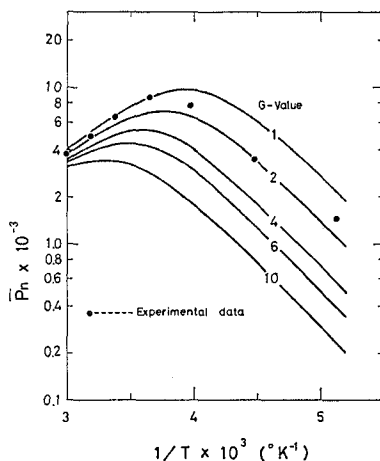


Fig. 5. Relationship between the $\bar{P}_n$ and the polymerization temperature calculated according to the equation (10) for the dose rate of 3.0×10^4 r/hr.

* These values are dependent of temperature, but as the temperature dependence is insignificant, the values at 15°C were adopted.

doubtedly to the large difference in the activation energy for initiation, as Sawada¹⁹⁾ and Perry²⁰⁾ also anticipated theoretically. According to Sawada, the maximum of $\bar{P}_n$ should be observed in the radical polymerization which proceeds through bimolecular termination mechanism, whenever the following condition is satisfied.

$$E_{tr} > E_p > E_i/2 + E_t/2 \quad (11)$$

Here E_i is the activation energy for initiation. In fact, if R_i given in (6) is assumed tentatively to have E_i as an activation energy, the same condition can be easily obtained by differentiating the modified equation of (7) with temperature and equating to zero. The value of E_i is about 30 kcal/mole in the radical polymerization initiated with conventional catalysts such as benzoyl peroxide, while the E_i is regarded nearly zero for the radiation polymerization. Furthermore, provided that E_t is negligibly small, E_p and E_{tr} are estimated to be 3.7 and 6.8 kcal/mole, respectively, from $E_{tr} - E_p = 3.1$ kcal/mole and $E_p - E_i/2 = 3.69$ kcal/mole. Therefore, it follows that in the conventional radical polymerization of VAC with a high value of E_i , the above condition is not satisfied. It is, however, possible that in some redox or photopolymerizations the $\bar{P}_n$ exhibits a maximum in a $\bar{P}_n$ -temperature relationship, because in these cases very low E_i is sometimes found. The phenomenon has been really observed for the photopolymerization of VAC.^{15,20)}

Now, we will discuss briefly the G -value of VAC. As is apparent from Fig. 5, the experimental data lie between the curves of $G=1$ and 2. The reported G -values are 1.4 (Okamura and Inagaki¹²⁾), 5.0, 7.5 (Nikitina-Bagdasaryan¹³⁾), 5.7 (Hardy-Allen²²⁾) and 12 (Chapiro⁸⁾). Our result is in good agreement with that of Okamura and Inagaki. It should be, however, emphasized that in the present case the evaluation of G -value was carried out using viscosity-average degree of polymerization and assuming that the termination occurs exclusively by disproportionation mechanism, irrespective of polymerization temperature.

4. Formation of 1, 2-Glycol Bonds

As is known, the PVAL obtained by hydrolysis of conventional PVAC has 1, 2-glycol bonds in the main-chain and the content decreases as the polymerization temperature of VAC becomes lower. The results found in the present work are given in Fig. 6, together with values of previous workers.^{5,23-25)} The 1, 2-glycol content is usually determined by either viscosity or titration method. Generally the content determined by the former method is somewhat lower than that determined by the latter one. Our data are in agreement with those determined by the titration method in the relatively high temperature range, verifying that the 1, 2-glycol bonds formation depends only on the polymerization temperature, but not on means to initiate the polymerization. It is not clear why a departure from linearity of the Arrhenius plot of 1, 2-glycol bonds formation occurs in the temperature range below about -50°C . It is interesting to note here that the PVAL's obtained by the polymerization at -78°C are colored light-yellowish, independent of the conversion. In Fig. 7 are given the ultraviolet spectra of the PVAL and a commercial one for comparison. It is seen that the

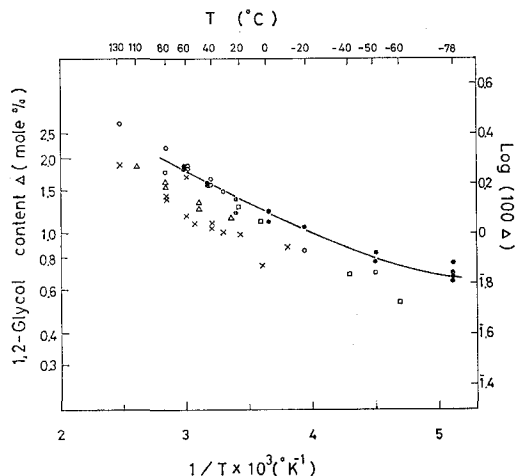


Fig. 6. Plot of 1, 2-glycol contents as a function of polymerization temperature. (By titration method: ●...the present work, ○...catalytic polymerization,²⁶⁾ □...photopolymerization. By viscosity method: ×...radiation polymerization,⁵⁾ △...catalytic polymerization.²⁵⁾

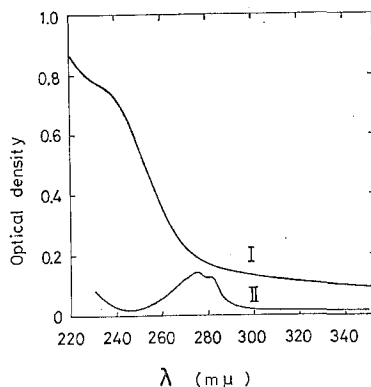


Fig. 7. Ultraviolet spectra of the PVAL obtained by the radiation polymerization at -78°C (I) and a commercial PVAL (II) (0.5% aqueous solution).

PVAL obtained by the radiation polymerization at -78°C shows no obvious absorption at $280\text{ m}\mu$, where, on the other hand, a distinct absorption is observed for the commercial PVAL. The absorption at $280\text{ m}\mu$ was assigned to carbonyl group.²⁶⁾ It seems probable that the coloration of the present PVAL is due to some functional groups, which are responsible for the strong absorption observed near $230\text{ m}\mu$.

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