Conversion Distribution in Diffusion-Governed Chlorination of Poly(vinyl Chloride)

Conversion distribution in particles of chlorinated poly(vinyl chloride) (CPVC) is conceptually described based on balance equations involving mass transfer and chemical reaction. In the physical sorption of chlorine in poly(vinyl chloride) (PVC) as measured by the constant volume cell method, equilibrium concentration and diffusion rate obeyed Henry's law and Fick's law. The rate process of photo chlorination of PVC, which was investigated by the gravimetric method, could be well predicted by theoretical calculation of chlorine diffusion in PVC accompanying the infinitely fast chemical reaction. In a free grain of PVC synthesized by suspension polymerization, the chlorination rate was governed by the polymer-phase diffusion within agglomerates of coalesced primary particles.

To produce homogeneously chlorinated PVC, a periodic photo-irradiation method was theoretically proposed and experimentally demonstrated. The effect of the periodic operation on the thermal property of CPVC was evaluated by DSC.

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Introduction

The thermal stability of chlorinated poly(vinyl chloride) (CPVC) is greater than that of the source poly(vinyl chloride) (PVC): i.e., the glass transition temperature rises from 360 to 440 K depending on the chlorine content. This property improvement allows commercial application of CPVC for broad markets such as hot water delivery, fire sprinkler systems, and electrical and mechanical parts.

The dominant mechanism of the chlorination is generally assumed to proceed by a chain reaction where photo-initiated chlorine radicals preferentially substitute the hydrogens of the methylenic carbon (Berticat, 1967; Svegliado and Zilio-Grandi, 1969; Lukas *et al.*, 1981):

$$Cl_2 \xrightarrow{h\nu} 2\,Cl\cdot \tag{1}$$

$$Cl\cdot + \text{—}(CH_2 - CHCl)\text{—} \rightarrow \text{—}(\dot{C}H - CHCl)\text{—} + HCl \tag{2}$$

$$\text{—}(\dot{C}H - CHCl)\text{—} + Cl_2 \rightarrow \text{—}(CHCl - CHCl)\text{—} + Cl\cdot \tag{3}$$

The most probable termination step is the deactivation of chlorine radical rather than the deactivations of chloroethylenic radical immobilized on the solid surface or the coupling of radicals (Gambaretto *et al.*, 1974):

$$Cl\cdot \rightarrow \text{inactive products} \tag{4}$$

Thus, the maximum chlorine content reaches to 73.2 wt. % when one additional chlorine is inserted into every monomer unit of PVC.

In the industrial production of CPVC, the optimum content of chlorine is usually selected in the ranges of 60 to 70 wt. %, since the chlorination increases not only the thermal resistance but also the difficulty of the processability for extrusion, injection, etc. However, such property cannot be explained completely by the degree of chlorination. CPVC's with the same chlorine content can greatly differ in their properties (Trautvetter, 1966). A simple, low-cost process is the chlorination of PVC particles heterogeneously suspended in water (water-suspension process) or

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fluidized in gaseous chlorine (dry process) under UV irradiation. In the swelling process or solution process, PVC particles are swollen or homogeneously dissolved by a solvent. Ajroldi *et al.* (1971) showed that the swelling process can produce CPVC that is superior in both thermal and mechanical properties to the product of the dry process, and stated that the CPVC produced by the dry process was a mixture of various chlorine contents. Hosselbarth *et al.* (1979) showed that the chemical inhomogeneity in CPVC could be related to the slope of the glass transition curve. Komoroski *et al.* (1985) evaluated the heterogeneity of chlorine content from the observation of its average configuration by the NMR method, and indicated that, in the dry and water-suspension processes, PVC is chlorinated more heterogeneously than in the solution and liquid-chlorine processes. In the mixture of various chlorine contents, the low conversion component is thermally unstable and the high conversion component makes it difficult to process. Therefore, homogeneously-chlorinated PVC is industrially preferable.

The heterogeneity of chlorine content in CPVC presumably is caused by mass transfer resistance of chlorine in PVC particles. Gambaretto *et al.* (1974) suggested a mass transfer governed rate process from the kinetic study of PVC chlorination. Gianelos *et al.* (1979), on the basis of surface observation of CPVC particles by ESCA, noted that the chlorine content in the particle surface is almost at saturation in the early stage of PVC chlorination, while the average conversion is small. Decker *et al.* (1981), after investigating the chlorination of PVC film for various thicknesses from 5 to 100 μm, showed that the extent of chlorination decreased with increasing film thickness.

For proper recognition of the photo chlorination of PVC, the present study aims to clarify the effect of mass transfer on the rate process and the properties of CPVC produced. The conversion distribution in a particle of CPVC and its control by photoperiodic operation method were theoretically investigated. Physical sorption of chlorine and photo chlorination were experimentally observed using both films and powders of PVC. As for the rate process in the complicated structure of the PVC powder, both the gas-phase diffusion through intragrain pore and the polymer-phase diffusion within microparticle were considered based on the well known grain model. The photo-periodic operation was also conducted to evaluate the effect on the thermal property of CPVC produced.

Theory

Diffusion and chemical reaction of chlorine in a spherical particle of PVC are described by balance equations for chlorine and unreacted vinyl chloride monomer unit respectively as:

$$\partial C/\partial t = D\{\partial^2 C/\partial r^2 + (2/r)\partial C/\partial r\} - KCS \qquad (5)$$

$$\partial S/\partial t = -KCS \qquad (6)$$

In these equations, (1.1)-order dependency of chemical reaction kinetics on concentrations of chlorine and unreacted vinyl chloride monomer unit are derived from the mechanisms of Eqs. 1–4 based on the assumption of steady state for radical concentration. Photo intensity, which affects on the chemical reaction rate constant, is assumed to be constant within the reaction field. Fickian diffusion is also assumed, which will be experimentally evaluated in a subsequent section. Initial conditions and boundary conditions are given as:

$$\text{at } t = 0: \quad C = 0, \quad S = S_i \qquad (7)$$

$$\text{at } r = R: \quad C = C_o; \quad \text{at } r = 0: \quad dC/dr = 0 \qquad (8)$$

A numerical solution of the balance equations gives the concentrations of chlorine and unreacted vinyl chloride monomer unit as a function of both radial coordinate and time.

In the chemical reaction of polymer, conversion can be defined for each molecule as the ratio of reacted monomer unit to the total number of monomer units constituting a polymer molecule. Thus, local conversion in the chlorination of PVC is given as:

$$X(r) = 1 - S(r)/S_i \qquad (9)$$

Average conversion through a whole spherical particle is obtained as:

$$\mu_1 = (3/R^3)\int_0^R r^2 X dr \qquad (10)$$

Since the local conversion simply increases with the increase of radial coordinate, the population of the local conversion between $X(r)$ and $X(r + \Delta r)$ is determined as:

$$E = (3r^2\Delta r + 3r\Delta r^2 + \Delta r^3)/R^3/\{X(r + \Delta r) - X(r)\} \qquad (11)$$

Then, homogeneity or heterogeneity of the conversion distribution is quantitatively represented by variance as:

$$\mu_2 = \int_0^1 (\mu_1 - X)^2 E dX \qquad (12)$$

Figure 1 shows the calculated results of the variance of conversion distribution as a function of average conversion. Since the variance goes to zero at zero conversion and complete conver-

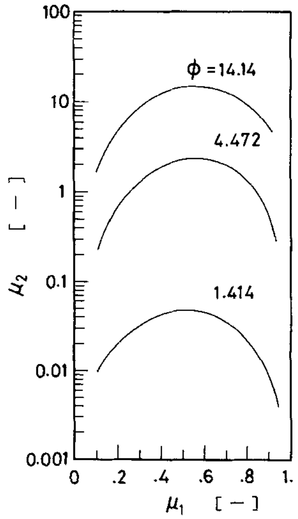


Figure 1. Variance of conversion distribution vs. average conversion.

Calculated at $R = 3 \times 10^{-6}$, $S_i = 2 \times 10^4$, $C_o = 100$, $D = 1 \times 10^{-14}$

sion, the technological importance of conversion distribution is only for the intermediately converted CPVC. In fact, industrial production of CPVC is usually in the intermediate chlorine content of 60 to 70 wt. %, that is the conversion of 0.2 to 0.8. The maximum value of the variance exists at an average conversion of around 0.5. When one assumes a quasisteady state of chlorine concentration, that is, $dC/dt = 0$ in Eq. 5, Eqs. 5–8 can be normalized by a dimensionless modulus, $\phi = R(KS_i/D)^{1/2}$, which was comprehensively reviewed by Szekely *et al.* (1976), and Ramachandran and Doraiswamy (1982). Indeed, this assumption of quasisteady state is almost satisfied at the calculated conditions in this study. The variance of conversion distribution increases with increasing modulus ϕ, since the value of the modulus represents the rate ratio of chemical reaction to diffusion. This means that small particle radius, small rate constant of chemical reaction, or large diffusion coefficient leads to the production of homogeneously converted CPVC.

From the viewpoint of industrial operation, another feasible method to control the conversion distribution is periodic photo irradiation. Chlorine can diffuse sufficiently during the intervals of no light, and it reacts homogeneously through a particle in a short period of photo-irradiation. In periodic operation, the time-dependent value of the chemical reaction rate constant is expressed as:

$$\text{at } n(T_{on} + T_{off}) < t < n(T_{on} + T_{off}) + T_{off}: \quad k(t) = 0 \qquad (13)$$

$$\text{at } n(T_{on} + T_{off}) + T_{off} < t < (n + 1)(T_{on} + T_{off}): \quad k(t) = K \qquad (14)$$

where $n = 0, 1, 2, \ldots$

The variances of conversion distribution at the average conversion of 0.5 were calculated and are shown in Figure 2 as a function of nonirradiation time with the parameter of photo-irradiation time. The nonirradiation time and photo-irradiation time are respectively rewritten to diffusion time, R^2T_{off}/D, and chemical reaction time, KS_iT_{on}. Study of Figure 2 shows that, when diffusion time is smaller than 0.01, the variance of conversion distribution nearly equals the value in continuous photo-irradiating operation and that, with increasing diffusion time the variance decreases, reaching the asymptote value at a diffusion time greater than 0.5. The shorter the photo-irradiation time becomes, the smaller the variance of conversion distribution involving the asymptote value.

Comparing the results of different values of dimensionless modulus as shown in Figure 2, the effect of nonirradiation time is almost normalized by the diffusion time through various values of the dimensionless modulus, whereas the effect of the chemical reaction time depends on the value of the dimensionless modulus. Then, under the condition of the average conversion of 0.5, the asymptote values of the variance at a diffusion time greater than 0.5 are shown in Figure 3 as a function of the chemical reaction time with the dimensionless modulus as parameter. When the chemical reaction time is greater than around 100, the variance almost equals the value in the operation of continuous photo irradiation at the same values of the dimensionless modulus. And the variance decreases simply with decreasing chemical reaction time.

Experimental

Material

Poly(vinyl chloride) (PVC) used was supplied by Kanegafuchi Chemical Industry (SC-16, DP = 600). It was synthesized by suspension polymerization as described elsewhere (Himei *et al.*, 1963; Shimizu, 1972). Figure 4 shows the scanning electron microscope photographs (SEM, Hitachi S-800). Several subgrains constitute a free grain of PVC, Figure 4a; and inside the subgrain, primary particles of around 1 μm in diameter are observed, forming intermediate agglomerates by coalescence of primary particles, Figure 4b. Average diameter of a free grain

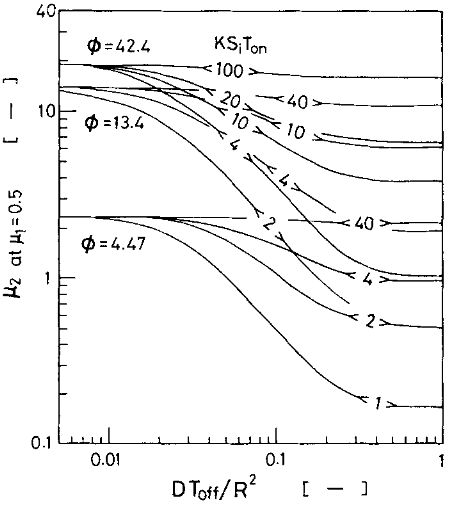


Figure 2. Effect of diffusion time in periodic operation on the variance of conversion distribution at average conversion of 0.5.

Calculated at $R = 3 \times 10^{-6}$, $S_i = 2 \times 10^4$, $C_o = 100$, $D = 1 \times 10^{-14}$

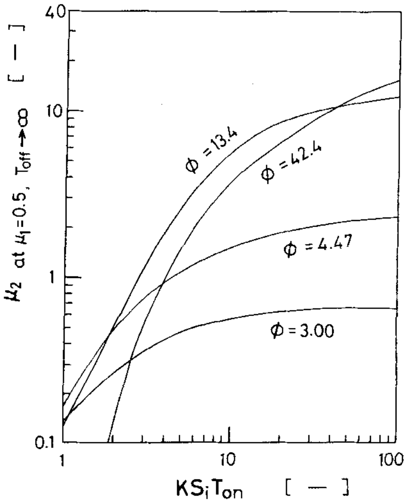
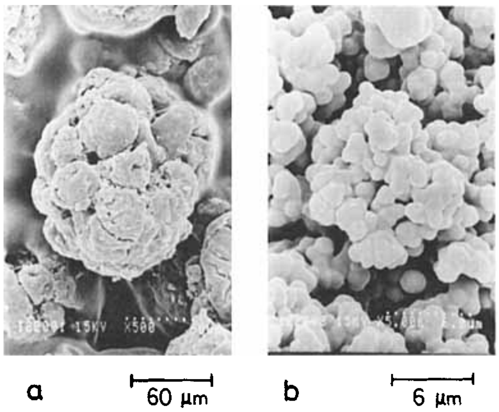


Figure 3. Effect of chemical reaction time in periodic operation with infinite diffusion time on the variance of conversion distribution at average conversion of 0.5.

Calculated at $R = 3 \times 10^{-6}$, $S_i = 2 \times 10^4$, $C_o = 100$, $D = 1 \times 10^{-14}$



a. free-grain;
b. agglomerate of coalesced primary particles.

Figure 4. SEM photographs of PVC:

determined by the Coulter-counter (Coulter Electronics, model TAII) was 105 µm. As measured by a mercury porosimeter (Micrometrics, Pore Sizer 9300), a porosity of 0.14 cm^3/g was detected in the pore diameter range of 0.5–5 µm, which corresponds to the size of voids between primary particles.

Films of PVC, around 30 µm thick, were prepared by casting from tetrahydrofuran (THF) solution.

Chlorine was supplied from a liquid chlorine cylinder (Kanegafuchi Chemical Industry).

Constant-volume cell method for physical sorption

The experimental apparatus for physical sorption is shown in Figure 5. The constant-volume cell, 20.6 mL in inside volume, was made of Pyrex glass. A pressure sensor (Toyoda-kouki PMS-5, 5H) was attached to the top of the cell. The cell was immersed in a water bath at constant temperature and was kept dark.

After setting the sample of PVC, the cell was evacuated by a pump. Gaseous chlorine was introduced into the cell to an appropriate pressure of less than 1 atm. Then the cell was closed and the time course of the pressure within the cell was recorded continuously.

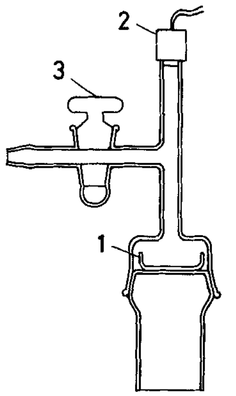


Figure 5. Experimental apparatus for constant-volume cell method.

1. sample holder; 2. pressure sensor; 3. stop valve

Gravimetric method for photo chlorination of PVC

The experimental apparatus for the photo chlorination of PVC is shown in Figure 6. The reactor, made of Pyrex glass, was 35 mm in diameter and 1.5 m high. A sample basket, made of quartz glass, was hung on a quartz glass wire connected to a metal core, covered by quartz glass, and to a quartz spring. The spring stretches 5.6 mm/g, and its motion is detected by a differential transformer due to the displacement of the core. The electrical signal of the differential transformer is amplified to 1 V/mm. A temperature sensor (thermocouple C.A.) was placed just below the sample basket. A super-high-pressure mercury lamp (Toshiba SHL-100UV, lamp output power of 75 W) and an elliptical reflector (long and short axes of 31 and 26 cm and 20 cm in height) were used. The light intensity of the lamp was 1.5×10^7 cd/m^2 in the wavelength ranges of 250–550 nm. The sample basket and the lamp were located at the focuses of the elliptical reflector. The radiation field of such experimental photo reactor has been comprehensively investigated (Cedrá *et al.*, 1973; Alfano *et al.*, 1986).

To maintain homogeneous photo intensity in the reaction field, a small amount of PVC powder (around 10 mg) was set in the sample basket under nitrogen atmosphere. Then the reaction was started by introducing gaseous chlorine and irradiating UV lamp. When the reaction was operated periodically, the UV lamp was manually shaded at regular intervals.

DSC measurement

A differential scanning calorimeter (Rigaku-Denki, DSC-10A) was used for the calorimetric study of CPVC. Sample weight was round 5 mg. Heating rate was 10 K/min.

Results and Discussion

Physical sorption of chlorine into PVC

In an experiment of physical sorption by the constant-volume cell method, the amount of chlorine sorped into the PVC sample was determined from the difference between initial and final pressure of gaseous chlorine. Figure 7 shows dissolved chlorine concentration vs. equilibrium chlorine concentration in gas

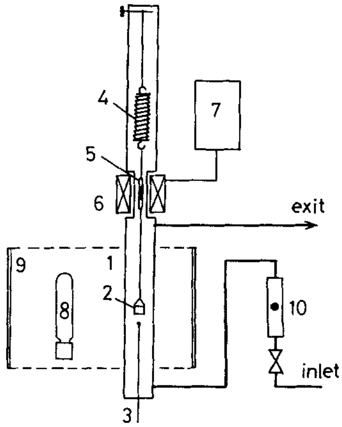


Figure 6. Experimental apparatus for gravimetric method.

1. reactor; 2. sample basket; 3. thermocouple; 4. spring; 5. core; 6. coil; 7. differential transformer; 8. lamp; 9. reflector; 10. flow meter

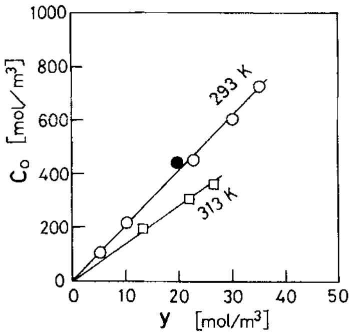


Figure 7. Sorption isotherms of chlorine to PVC.
○, □, PVC powder; ●, PVC film

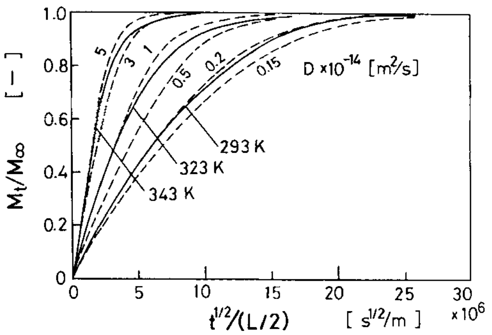


Figure 9. Chlorine uptake by PVC films in a constant-volume cell.
——, experimental; ------, calculation

phase. The concentration of chlorine dissolved in PVC polymer phase is proportional to the equilibrium concentration in gas phase:

$$C_o = Hy \tag{15}$$

PVC samples of powder and cast film showed the same values of Henry's solubility constant. As shown in Figure 8, the temperature dependency of the solubility is expressed by the following equation.

$$H = 0.280 \exp(10{,}480/R_gT) \tag{16}$$

Time courses of the amount of chlorine sorped in PVC film at 293, 323 and 343 K are shown in Figure 9 as solid lines. Assuming Fickian diffusion of chlorine in PVC film, the chlorine mass balance in PVC polymer phase is described (Crank, 1975) as:

$$\partial C/\partial t = D(\partial C^2/\partial x^2) \tag{17}$$

Boundary conditions are:

$$\text{at } x = 0: \quad C = Hy \tag{18}$$

$$\text{at } x = L/2: \quad dC/dx = 0 \tag{19}$$

A mass balance of gaseous chlorine in a constant-volume cell is:

$$\partial y/\partial t = AD(\partial C/\partial x)_{x=0} \tag{20}$$

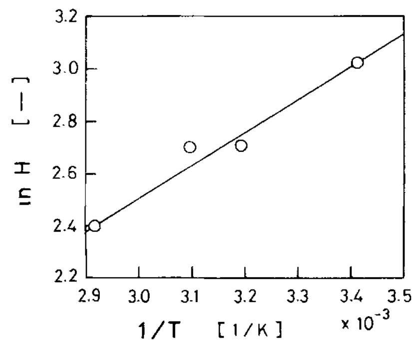


Figure 8. Temperature dependency of Henry's solubility constant for chlorine to PVC.

where A represents the surface area of PVC per unit volume of gaseous chlorine.

Initial conditions are:

$$\text{at } t = 0: \quad y = y_i, \quad C = 0 \tag{21}$$

Given a finite value of diffusion coefficient, Eqs. 17–21 are numerically solved to predict the theoretical curve of chlorine uptake at each experimental condition. Broken lines in Figure 9 are calculated theoretical curves for several values of diffusion coefficient. By choosing an appropriate value of diffusion coefficient, the experimental time course of chlorine uptake almost obeys the theoretical curve of Fickian diffusion. Thus, the values of diffusion coefficient were determined to fit the theoretical curve to the experimental one, and their temperature dependency was expressed as:

$$D = 9.19 \times 10^{-7} \exp(-49{,}100/R_gT) \tag{22}$$

An experimental time course of chlorine uptake by PVC powders is shown in Figure 10 by a solid line. Since a free grain of PVC powder is highly porous, the chlorine diffusivity in PVC of Eq. 22 should be adapted for a smaller scale of continuous PVC phase than the diameter of a free grain. This rate process could be interpreted by the well known grain model (Ramachandran and Doraiswamy, 1982), where chlorine gas has to diffuse through the intragrain pores to reach the microparticles of PVC. Then, chlorine diffusion in the spherical microparticle is de-

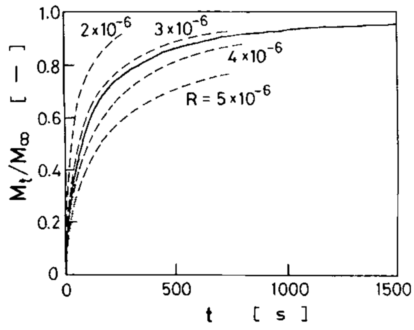


Figure 10. Chlorine uptake by PVC powders in a constant-volume cell at 293 K.
——, experimental; ------, calculation with $D = 2 \times 10^{-15}$

scribed as (Crank, 1975):

$$\partial C/\partial t = D\{\partial^2 C/\partial r^2 + (2/r)\partial C/\partial r\} \qquad (23)$$

Boundary conditions are:

$$\text{at } r = R\text{:} \quad C = C_o; \quad \text{at } r = 0\text{:} \quad dC/dr = 0 \qquad (24)$$

Mass balance of gaseous chlorine in a constant volume cell is:

$$\partial y/\partial t = -AD(\partial C/\partial r)_{r=R} \qquad (25)$$

Initial conditions are:

$$\text{at } t = 0\text{:} \quad C = 0, \quad y = y_i \qquad (26)$$

Broken lines in Figure 10 indicate the theoretical curves of chlorine uptake numerically calculated by Eqs. 23–26 for PVC spheres of various radii. Comparing experimental and theoretical chlorine uptake curves, the diffusion process is quantitatively explained by assuming a continuous PVC microparticle of 3.5 μm radius. The effect of intragrain gaseous diffusion through the pore within a free grain of PVC could be roughly estimated from the comparison between diffusion times of pore and microparticle as:

$$a^2/\{(\epsilon/\tau)D_g\} = (52.5 \times 10^{-6})^2/\{(0.2/5)(1 \times 10^{-5})\} = 6.9 \times 10^{-3}[\text{s}] \qquad (27)$$

$$R^2/D = (3.5 \times 10^{-6})^2/(2 \times 10^{-15}) = 6.1 \times 10^3[\text{s}] \qquad (28)$$

Thus, as the intragrain pore diffusion time is negligibly small in this experimental condition, the rate process of chlorine uptake is governed by diffusion in the microparticles of 3.5 μm in radius. This hypothetical microparticle seems to correspond to the actual form of tightly agglomerated primary particles, Figure 4b.

Photo chlorination of PVC

The increase of gravity during photo chlorination of PVC film at the experimental temperature of 343 K is shown in Figure 11 by a solid line. Diffusion of chlorine in PVC film accompanied by chemical reaction with the kinetics of (1,1)-order dependency on the concentrations of chlorine and unreacted vinyl chloride monomer unit is formulated as:

$$\partial C/\partial t = D(\partial^2 C/\partial x^2) - KCS \qquad (29)$$

$$\partial S/\partial t = -KCS \qquad (30)$$

Boundary conditions and initial conditions are:

$$\text{at } x = 0\text{:} \quad C = C_o; \quad \text{at } x = L/2\text{:} \quad dC/dx = 0 \qquad (31)$$

$$\text{at } t = 0\text{:} \quad C = 0, \quad S = S_i \qquad (32)$$

Theoretical time courses of PVC conversion can be calculated from Eqs. 29–32, which are shown in Figure 11 by broken lines for various values of chemical reaction rate constant. Up to 5×10^4 seconds, the theoretical line of $K = 10^{-7}$ fits the data, but after 10^5 seconds, that of $K = 2 \times 10^{-7}$ fits the data better. As a whole, however, it seems to be hard to determine the exact value of chemical reaction rate constant, for the experimental line is not so far from the theoretical lines of infinitely rapid chemical reaction. At the intensity of UV irradiation under this experimental condition, the chlorination of PVC film can be nearly represented by the diffusion-governed rate process.

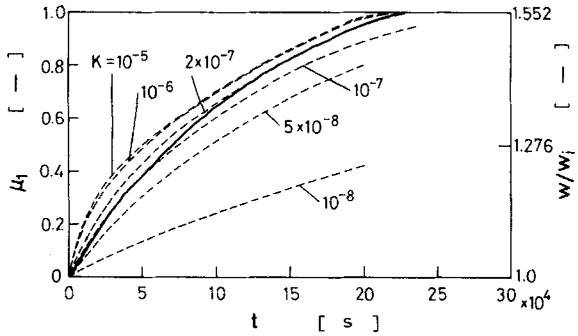
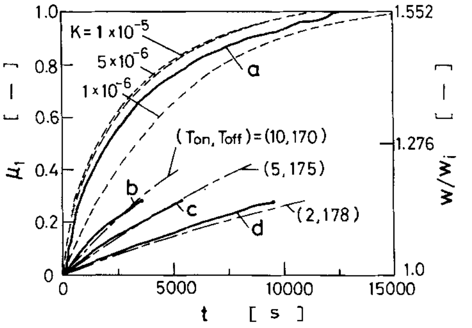


Figure 11. Kinetics of the photo-chlorination of PVC film at 343 K.

——, experimental; ------, calculation with $L/2 = 15.33 \times 10^{-6}$, $S_i = 23{,}480$, $C_o = 390$, and $D = 3.5 \times 10^{-14}$

PVC powder was also chlorinated in the gravimetric apparatus, as the solid line of Figure 12 shows. A theoretical expression of this phenomenon is given by Eqs. 5–8 by adapting the hypothetical sphere of 3.5 μm in diameter, from which curves of conversion vs. time were calculated for various values of chemical reaction rate constant, as shown in Figure 12 by broken lines. In this experimental condition, it was confirmed by the theoretical calculation of the grain model that the diffusion resistance through the intragrain pore was negligibly small. This fact is also supported by the rough estimation of Eqs. 27 and 28. It is interpreted from Figure 12 that chlorination of PVC powder is a diffusion-governed process accompanied by infinitely rapid chemical reaction within microparticles, while the time required for the conversion of PVC powder greatly differs from that of PVC film due to the difference in diffusion scale.

Experimental curves of conversion vs. time in the periodically photo-irradiated chlorination of PVC powder are also indicated in Figure 12 as the solid lines of b, c and d. The rate of chlorination in periodic operation is slower than that in continuous pho-



a. continuous operation: --------, calculations with $R = 3.5 \times 10^{-6}$, $S_i = 23{,}480$, $C_o = 495$, $D = 0.8 \times 10^{-14}$;
b, c and d. periodic operations: — - — - —, calculations with $K = 5 \times 10^{-6}$

Figure 12. Kinetics of the photochlorination of PVC powder at 323 K.

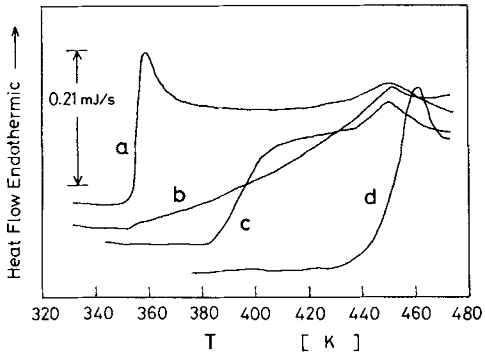
to-irradiating operation, and the chlorination rate decreases with the reduction of photo-irradiating time. Periodically operated chlorination of spherical PVC is theoretically described by Eqs. 5–8, 13 and 14. By choosing the value of chemical reaction rate constant as $K = 5 \times 10^{-6}$, the numerical calculation of these theoretical equations closely predicted the curves of conversion vs. time in periodic operations as shown in Figure 12 by dot-and-dash lines.

As the result of the above observation, the value of dimensionless modulus ϕ for the photo chlorination of PVC powder at this experimental condition is determined as

$$\phi = R(KS_i/D)^{1/2} = 13.4 \tag{33}$$

Therefore, as seen from calculations of Figures 1 and 2, the conversion distribution in the intermediately chlorinated PVC is predicted to be heterogeneous at the variance value of around 10. This phenomenon corresponds to the reported fact that the dry process produces heterogeneously converted CPVC (Ajroldi *et al.*, 1971; Komoroski *et al.*, 1985). As for the swelling process, since the chlorine diffusivity in the PVC polymer phase is presumably large to the maximum value of liquid-phase diffusivity, i.e. around 10^{-9}–10^{-10} m^2/s, the produced CPVC should be more homogeneously chlorinated than that of the dry process. At the case of large diffusivity, however, the effect of diffusion resistance through the intragrain pore should be considered. On the other hand, the periodic photo-irradiation method should produce the more homogeneously converted CPVC than the continuous photo-irradiation method of the dry process, where the variance of the conversion distribution is predicted from Figure 2 to be around one tenth of the continuous photo-irradiation method.

Figure 13 shows the results of DSC measurement for variously chlorinated samples of PVC powder. Increase of heat capacity is observed at the glass transition temperature of PVC or CPVC, followed by a melting peak down to the glass transition region. The glass transition temperature of PVC rises from 355 to 450 K by chemically saturating it with chlorine to the amount of 73 wt. %, curves a and d. In the DSC measurement of intermediately chlorinated PVC by the continuous photo-irradiating method, the heat capacity increased gradually in the temperature ranges of 355 to 450 K as shown by curve b. This means that the measured sample was a mixture of CPVC's of various glass transition temperatures due to the extent of chlorine introduction, as was suggested by Hosselbarth *et al.* (1979). Curve c shows the DSC measurement of intermediately chlorinated PVC by the periodic photo-irradiation method. The glass transition temperature in curve c is observed in relatively narrow ranges compared to that in curve b. Thus, periodic operation realized the production of homogeneously chlorinated PVC. These observations support the theories of mass transfer governing photo chlorination of PVC and its conversion distribution.



a. PVC;
b. CPVC at $w/w_i = 1.15$ by continuous operation;
c. CPVC at $w/w_i = 1.15$ by periodic operation; d. CPVC at $w/w_i = 1.552$ by continuous operation

Figure 13. DSC thermograms of PVC and CPVC.

Conclusions

In terms of mass transfer and chemical reaction in the photo chlorination of PVC, the concept of conversion distribution was theoretically investigated. The conversion distribution shows maximum variance at an average conversion of around 0.5. The value of the variance decreases simply with the reduction of the dimensionless modulus $\phi = R(KS_i/D)^{1/2}$. The periodic photo-irradiation method is effective in producing homogeneously chlorinated PVC by setting a longer diffusion time, R^2T_{off}/D, than around 0.5 and a shorter chemical reaction time, KS_iT_{on}, than around 1.

In the observation of physical sorption of chlorine in PVC by the constant-volume cell method, the equilibrium concentration of dissolved chlorine was proportional to the chlorine concentration in gas phase, and the diffusion rate obeyed the theoretical calculation of Fickian diffusion. The rate process of photo chlorination of PVC as measured by the gravimetric method was well predicted by the theoretical calculation of chlorine diffusion in PVC accompanied by infinitely rapid chemical reaction. As for a free grain of PVC synthesized by suspension polymerization, the rate process was governed by the polymer-phase diffusion within agglomerates of coalesced primary particles, while the diffusion resistance through intragrain pore was negligible. From observation of the reduced rate process in the periodic photo-irradiation method, the chemical reaction rate constant of the photo-chlorination of PVC was evaluated. The effect of periodic operation on the homogeneity of chlorine distribution in CPVC was confirmed from the observation of glass transition temperature by DSC measurement.

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Notation

a = radius of a PVC-free grain, m
A = surface area of PVC per unit volume of cell, 1/m
C = concentration of chlorine, mol/m^3
C_o = equilibrium concentration of chlorine to gas-phase chlorine, mol/m^3
D = diffusion constant in polymer phase, m^2/s
D_g = diffusion constant in gas phase, m^2/s
E = population function of conversion distribution
H = Henry's solubility constant
$k(t)$ = time-dependent chemical reaction rate constant, m^3/mol/s
K = chemical reaction rate constant, m^3/mol/s
L = thickness of a film, m
M_t = amount of chlorine sorped in PVC, mol
M_∞ = equilibrium value of M_t, mol
r = radial coordinate in a spherical particle, m
R = radius of a PVC microparticle, m
R_g = gas constant 8.31434, J/K/mol

S = concentration of unreacted monomer unit, mol/m^3
S_i = initial value of S, mol/m^3
t = time, s
T = temperature, K
T_{off} = nonirradiating time, s
T_{on} = photo-irradiation time, s
w = weight of PVC during chlorination, kg
w_i = initial weight of PVC, kg
x = coordinate in the direction of film thickness, m
X = local conversion
y = concentration of chlorine in gas phase, mol/m^3
y_i = initial value of y, mol/m^3

Greek letters

$\phi = R(KS_i/D)^{1/2}$, dimensionless modulus
ϵ = porosity of a PVC-free grain
μ_1 = average conversion
μ_2 = variance of conversion distribution
τ = tortuosity factor

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