

Polycondensation in Monomolecular Layers of Poly(*p*-vinylphenol), Formaldehyde, and Hexamethylenetetramine

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(Received May 29, 1979)

ABSTRACT: Two-dimensional polycondensation of the poly(*p*-vinylphenol) (PVP) monolayer and formaldehyde in subphase or hexamethylenetetramine in subphase was studied by a surface balance. The reaction product was successfully built up on a Ge prism as a multilayer characterized by ellipsometry and ATR-IR spectra. Polycondensation in two dimensions actually occurred together with a tremendous increase in surface viscosity in the monolayer. The rate constants of reaction between the PVP monolayer and formaldehyde or hexamethylenetetramine for a constant area and also at constant surface pressure were determined and discussed.

KEY WORDS Poly(*p*-vinylphenol) / Formaldehyde / Hexamethylenetetramine / Polycondensation / Condensation / Surface Balance / Monolayer / Built Up Film /

Recently, attention has been focussed on polymerization in organized systems, and especially the polymerization of vinyl monomers in monolayers at the gas–water interface has been studied by several authors and is summarized in ref 1. Two-dimensional polymerization and crosslinking reactions have been studied by Cubault, Casagrande, and Veyssie.² A polycondensation reaction in the monomolecular layer of octadecyl urea formaldehyde was reported by Rosilio and Ruaudel–Teixier.³

We found that poly(*p*-vinylphenol) forms a monomolecular layer at the air–water interface. Since the polycondensation reaction between phenol and formaldehyde or hexamethylenetetramine, which eventually leads to a three-dimensional polymer network, is a well known reaction, the chemistry of poly(*p*-vinylphenol) formaldehyde or hexamethylenetetramine in two dimension leading to a two-dimensional network polymer, *i.e.*, a polymeric sheet, is very interesting.

The present investigation is concerned with the chemical kinetics between poly(*p*-vinylphenol) and formaldehyde in the two dimensions studied by monolayer technique and also the formation of built up films of reacted poly(*p*-vinylphenol).

EXPERIMENTAL

Materials

Poly(*p*-vinylphenol) (hereafter abbreviated as PVP) was dissolved in tetrahydrofuran and precipitated by benzene. After repeating this procedure three times, the sample was dried in vacuum. The molecular weight of the sample was determined by intrinsic viscosity measurement in tetrahydrofuran at 30°C according to the viscosity equation

$$[\eta] = 3.45 \times 10^{-4} M_w^{0.60} \quad (1)$$

and the molecular weight was 10,000.

Formaldehyde (FA), hexamethylenetetramine (HMTA), NaHCO₃, and Na₂CO₃ were of analytical grade (Nakarai Chem. Co.). Water was doubly distilled from an all Pyrex apparatus.

Surface Balance

A teflon trough (0.16 × 0.91 × 0.01 m) and a Langmuir–Adam surface balance equipped with a paraffin coated mica float were used. The sensitivity of the balance was $2 \times 10^{-4} \text{ N m}^{-1}$. The pH of the substrate was adjusted by NaHCO₃–Na₂CO₃ Menzel buffer solution and HCl. 50 μl of a dilute 2-

propanol solution (1 mg ml^{-1}) of PVP was spread on the water surface as a monolayer by a Terumo microsyringe. After spreading the PVP solution and compressing it to the desired surface area, 50 ml of the reactants solution, *i.e.*, aqueous formaldehyde or hexamethylenetetramine solutions ($0.16 \text{ mol l}^{-1} \sim 8 \text{ mol l}^{-1}$), were injected beneath the water surface in the trough by a syringe. The reactant water mixture in the trough was gently stirred for five minutes by magnetic stirrer to ensure homogeneous mixing while avoiding ripple formation on the surface. The reaction rate between the PVP monolayer and the reactants was measured by following the increase in surface pressure (π) at a constant total surface area 0.5 m^2 , or the increase in the area (A) at a constant surface pressure $4 \times 10^{-3} \text{ N m}^{-1}$. Surface viscosity was measured by Joly's method⁴ using a platinum ring. The temperature of the water in the trough was kept $25 \pm 0.5^\circ\text{C}$ by maintaining the room temperature $25 \pm 2^\circ\text{C}$ by an air conditioner.

Built Up Film and ATR-IR Spectra

Built up multilayers of PVP or the reacted PVP were built up on a Ge prism by the Blodgett technique.⁵ A Ge prism was submerged in the trough on whose surface a monolayer was formed; the prism moved up and down by means of a micromanipulator, with the surface pressure maintained constant at $1.6 \times 10^{-2} \text{ N m}^{-1}$. The reacted or unreacted PVP monolayer was transferred onto the Ge prism successively. The thickness of the multilayer was measured by a Shimadzu ellipsometer using the NBS computer program.⁶ Experimental details of the ellipsometry were described by McCrackin *et al.*⁷ The ATR infrared spectra of built up multilayers on the Ge prism were measured by a Nihon Bunko IR G spectrometer.

RESULTS AND DISCUSSION

Surface Pressure–Area Isotherms of PVP

The surface pressure (π) vs. area (A) isotherms of PVP on the aqueous substrate at different pH are shown in Figure 1. It is clear that with increasing pH, the isotherms shift toward the larger area. However, from pH=4 to pH=6, the isotherms do not differ appreciably and the limiting area was about 0.07 nm^2 per monomer unit, which is almost identical to the molecular projection area of a

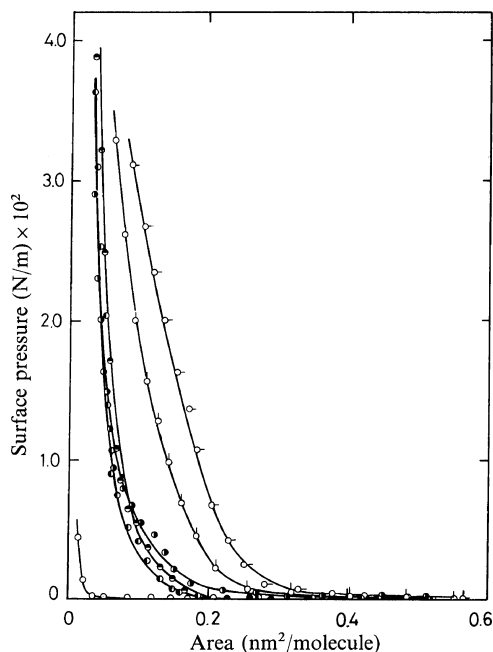


Figure 1. Surface pressure–area isotherms of the PVP monolayer at different pH.: \circ , pH=3; \bullet , pH=4; \circ , pH=5; \bullet , pH=6; \circ , pH=9; \circ , pH=11.

monomeric unit in which the benzene ring is in the vertical orientation.

At pH 3, the occupied area is quite small and it is considered that the contraction of monolayer was caused by the intra- and inter-molecular hydrogen bonds. At the highest pH, 11, the occupied area becomes large, and this expansion of the monolayer was caused by the electrostatic repulsive forces between dissociated phenol groups, since the pK value of phenol groups is 10. The two dimensional titration behavior of the PVP monolayer will be reported elsewhere.

Chemical Reaction of the PVP Monolayer with Formaldehyde and Hexamethylenetetramine

The chemical reactions between the PVP molecules at the surface with FA or HMTA cause an increase in surface pressure for a constant area. An example of PVP–FA reaction at pH=5 is shown in Figure 2. Both π and A steadily increase with the reaction time. The surface viscosity steeply increases after a reaction time of 100 min. For PVP–FA reactions at pH 4 and 6 and also for a PVP–HMTA

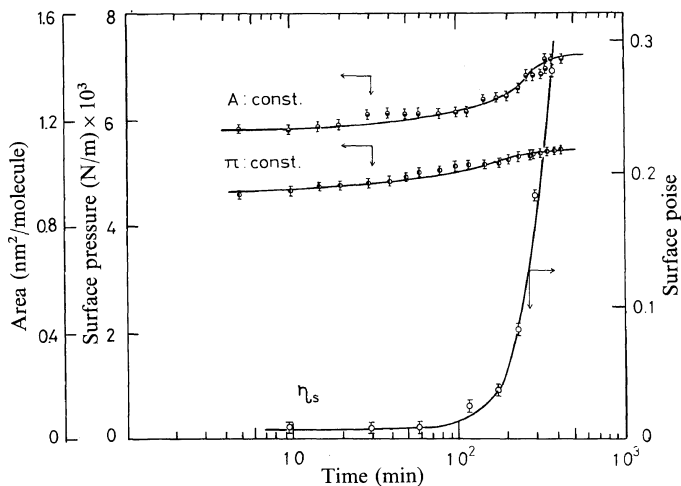


Figure 2. Reaction between the PVP monolayer and formaldehyde: ●, the change of π at constant area with time; ●, the increase of area at constant π ; ○, the change of surface viscosity η_s .

reaction at pH 6, almost the same results as shown in Figure 2 were obtained.

Characterization of Built Up Multilayers by Ellipsometry and ATR-IR Spectra

Both PVP and the reacted PVP monolayer were successfully built up on a Ge prism of the IR G spectrometer. 20, 70, and 100 multilayers of the reacted and unreacted PVP were formed. Their thicknesses, determined by ellipsometry, were 23, 70, and 100 nm, respectively. No difference was observed between the thickness of the reacted and unreacted PVP built up films of the same number of layers. Therefore, the thickness of the reacted and unreacted PVP monolayers in the built up multilayer is 1 nm which reasonably coincides with the thickness of a PVP molecule evaluated from molecular model spread as a monolayer. We concluded that preparation of a very thin film of PVP or reacted PVP of desired thickness at 1 nm interval could be carried out.

The ATR-IR spectra of the built up multilayers on the Ge prism were successfully obtained. Figure 3 shows the ATR-IR spectra of the built up multilayers of the PVP-HMTA reaction product for different reaction times; the transmission of phenyl groups does not change, but both CH_2 and NH peaks increase with time, indicating that chemical reactions took place. Taking the transmission of

phenyl or phenol as the standard, the change in the ratio of transmission of CH_2 with reaction time is indicated in Table I. However, it was difficult to measure quantitatively the amount of reacted FA or HMTA. The tremendous increase in surface viscosity is directly ascribed to the intermolecular two-dimensional crosslinking.

From both the ATR-IR spectra and the increase of the surface viscosity, we may conclude that two-dimensional crosslinking actually occurred.

Rate Constant

The chemical reactions between the PVP polymer and the FA or the HMTA occur at the surface phase. Therefore, both the reactant PVP polymers and the products, namely, the crosslinked PVP polymers do not dissolve in subphase and thus remain in the monolayer. In the chemical reaction of the PVP monolayer with FA and HMTA, both the FA and HMTA concentration bulk were in considerable excess, compared with the PVP concentration at the surface. The concentration of FA or HMTA *i.e.*, substrate reactants, was thus practically invariant for the chemical reaction. According to Adamson,⁸ for the chemical reaction occurring at a constant film pressure, assuming that the area is additive quantity, and moreover since the concentration of substrate reactant was invariant, the first-order rate law will thus be applicable as

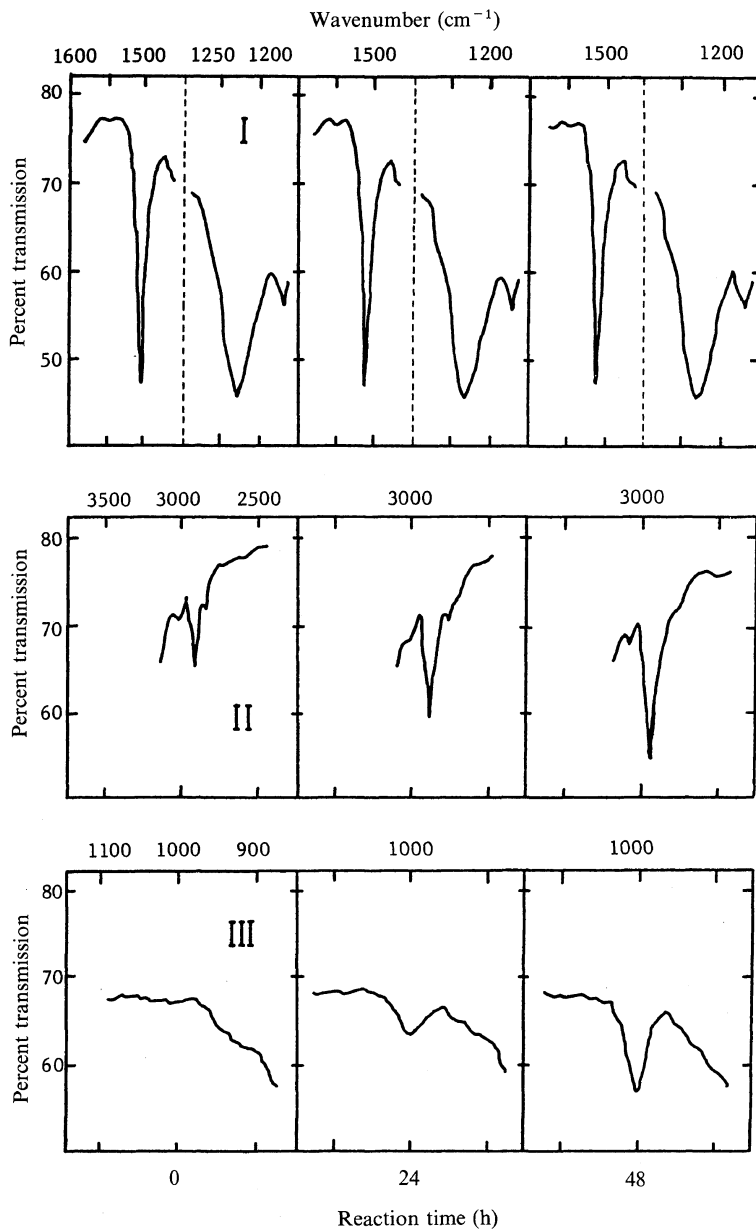


Figure 3. The ATR-IR spectra of built up multilayers of the PVP-hexamethylenetetramine reaction products: I, phenyl peak; II, CH₂ peak; III, NH peak.

follows

$$\frac{A - A^\infty}{A^0 - A^\infty} = e^{-k_\pi t} \quad (2)$$

where A^0 , A^∞ and A is total area at $t=0$, ∞ and $t=t$ and k_π is the reaction constant at a constant surface pressure. When a chemical reaction occurs at a constant total area, a similar equation may be

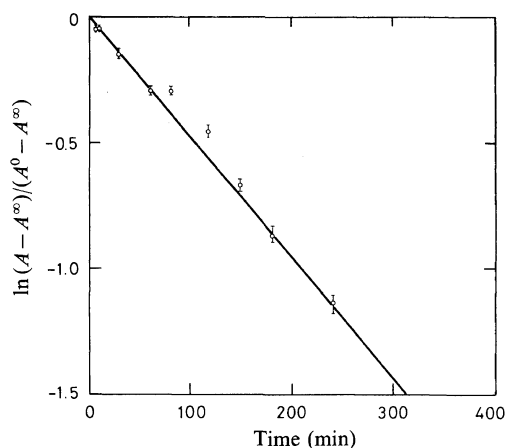
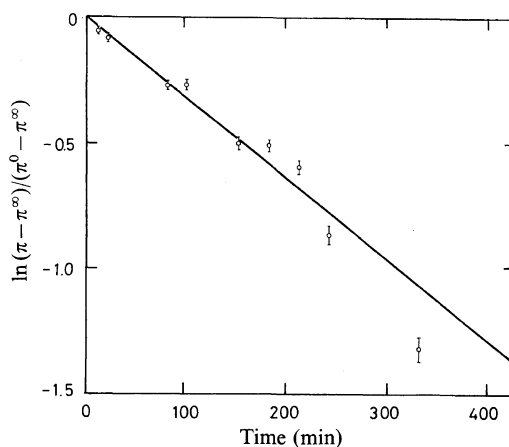
Table I. Results of "ATR-IR" measurements of built up multilayers, the ratio of transmission of CH₂ and phenol peaks

Reactant	Reaction time		$I_{\text{CH}_2}/I_{\text{ph-OH}}$	$I_{\text{CH}_2}/I_{\text{ph}}$
	h			
Formaldehyde (subphase pH=5)	0		1.00	1.00
	24		1.11	1.06
	48		1.17	1.19
Hexamethylene- tetramine (subphase pH=6)	24		1.54	1.87
	48		1.98	2.91

written as,

$$\frac{\pi - \pi^\infty}{\pi^0 - \pi^\infty} = e^{-k_A t} \quad (3)$$

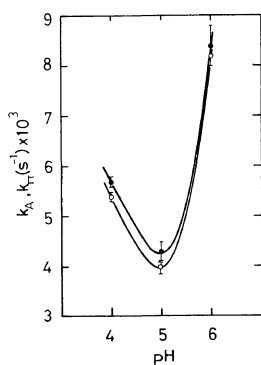
where π^0 , π^∞ , and π are the surface pressure at the reaction time $t=0$, ∞ and $t=t$ and k_A is the reaction constant at a constant total area. This implies that the film pressure is an additive function of composition at a constant total area. In Figure 4, $\ln(A - A^\infty)/(A^0 - A^\infty)$ is plotted against t for the PVP-HMTA reaction and in Figure 5, $\ln(\pi - \pi^\infty)/(\pi^0 - \pi^\infty)$ is plotted against t for the PVP-FA reaction. Both k_π and k_A were determined, and the results are summarized in Tables II and III. In Figure 6, both k_π and k_A of the reactions between PVP and FA are plotted against the pH of the substrate. It is clear that these rate constants show a minimum at pH 5. In three dimensional polyconden-

**Figure 4.** $\ln(A - A^\infty)/(A^0 - A^\infty)$ vs. t for the reaction between PVP monolayer and HMTA at 25°C.**Figure 5.** $\ln(\pi - \pi^\infty)/(\pi^0 - \pi^\infty)$ vs. t for the reaction between PVP monolayer and FA at 25°C.**Table II.** Rate constant k_A between the PVP monolayer and reactant at constant area (0.1 nm² per monomer) at 25°C

Reactant	pH of substrate	Concentration of reactant	Rate constant, $k_A \times 10^3$
		mol l ⁻¹	s ⁻¹
Formaldehyde	4	5×10^{-2}	5.4 ± 0.1
		5×10^{-2}	4.0 ± 0.1
	6	2.5×10^{-2}	4.0 ± 0.1
		5×10^{-2}	8.2 ± 0.2
Hexamethylenetetramine	6	1×10^{-3}	2.9 ± 0.1
		1×10^{-2}	3.0 ± 0.1
		5×10^{-2}	3.2 ± 0.2

Table III. Rate constant k_{π} between PVP monolayer and reactant at constant pressure (4×10^{-9} Nm⁻¹) at 25°C

Reactant	pH of substrate	Concentration of reactant	Rate constant, $k_{\pi} \times 10^3$
		mol l ⁻¹	s ⁻¹
Formaldehyde	4	5×10^{-2}	5.7 ± 0.1
		5×10^{-3}	4.7 ± 0.3
	6	5×10^{-2}	4.3 ± 0.2
		2.5×10^{-1}	5.5 ± 0.3
		5×10^{-2}	8.4 ± 0.4
Hexamethylenetetramine	6	1×10^{-3}	4.7 ± 0.1
		1×10^{-2}	6.8 ± 0.4
		5×10^{-2}	6.3 ± 0.4

**Figure 6.** Rate constant k_A (○) and k_{π} (●) of the reaction between the PVP monolayer and FA at 25°C vs. pH of the substrate.

sation of phenol and FA, it was reported that the rate constant of methylation has a minimum at pH 4.⁹ Direct comparison, however, between the polycondensation rate constant of phenol and FA in three dimensions and that of the present system is impossible, since in the former the second-order rate constant in methylation or of the consumption of FA has been measured, while in the latter, the overall rate constant, which is of the first order, was determined.

k_A is slightly smaller than k_{π} . The small rate constant indicates the difficulty with which the chemical reaction in the monolayer takes place. The occupied area 0.1 nm² per monomer unit is almost the same as the close packed area of the PVP monolayer. Therefore, the penetration of reactant

molecules into the PVP monolayer and rearrangement of the reactants to a suitable position in the transition state should encounter some difficulty. The low rate constant obtained at a constant area may be explained by the difficulty in penetration of the reactant into the monolayer, since the available area for FA or HMTA decreases with the reaction extent as a result of the total surface area's being kept constant. On the contrary, at a constant surface pressure, the penetration of the reactant into the monolayer is easier since the total surface area always increases with the reaction time. Therefore k_{π} is slightly larger than k_A .

CONCLUSION

A two-dimensional polycondensation reaction between the poly(*p*-vinylphenol) monolayer and formaldehyde or hexamethylenetetramine has been successfully studied by monolayer technique. The surface viscosity increased greatly with the reaction time indicating that the two-dimensional condensation actually occurred.

Built up multilayers of PVP or reacted PVP were successfully formed on a Ge prism. This indicates that multilayers or films of two dimensional reacted PVP of desired thickness can be formed. We believe that the evidence for the occurrence of a chemical reaction in the two dimension and the success in the formation of built up films should increase the possibility of preparing ultra thin polymer films.

Acknowledgement. We are indebted to Mr. M. Wada, Maruzen Petrochemical Co. for supplying

the poly(*p*-vinylphenol).

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