# Photo-Polymerization of Vinyl Acetate Sensitized by Uranyl Ion

By

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It is recognized that vinyl acetate is easily photo-polymerized by the addition of an uranyl salt as sensitizer. Higher rates of polymerization and smaller temperature coefficients are found in this case, and the mechanism of the reaction is considered here. The polymerization seems to require a small amount of water and the initial mechanism is considered to be as follows : —

$$UO_2^{++}+2H_2O=U^{++++}+2OH\cdot+2OH^-$$
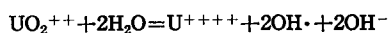
1. Introduction.

As uranyl oxalate has been known to be of use in actinometry, the uranyl ion may be an effective photo-sensitizer also in polymerization reactions. As already reported by H. W. Melville and his associates[1], acrylic acid has been polymerized in aqueous solution by using uranyl salt as a photosensitizer and it has been shown that the temperature coefficient of this reaction is very small i. e., the activation energy was very small (E=1.5 Kcal/mole). Since the mechanism of the polymerization of acrylic acid is very complicated, it was difficult to clarify the mechanism of its photo-sensitization reaction.

In this report vinyl acetate is polymerized at a low temperature and the characteristics of this reaction are considered also from the standpoint of the properties of polyvinyl alcohol[2] obtained from polyvinyl acetate.

2. Experimental.

i. Source of ultraviolet light : 400 W high pressure mercury lamp (the Nippon Denchi Co.)

ii. Materials ; Vinyl acetate, purified by a common method : Uranyl salts and ethyl alcohol and acetic acid, both of extra pure grades (the Wako Pure Chemical Industries.)

Diphenyl picryl hydrazil, synthesized in this Laboratory with its purity checked by absorption spectra.

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iii. Procedure; The rates of polymerization are determined by the dilatometric method. The degrees of polymerization are determined from viscosity measurements in acetone solutions.

3. Polymerization by uranyl nitrate in an aqueous solution.

When uranyl nitrate is dissolved in vinyl acetate, no polymerization has been observed even when the solution is irradiated with ultraviolet light. On the other hand if an adequate amount of w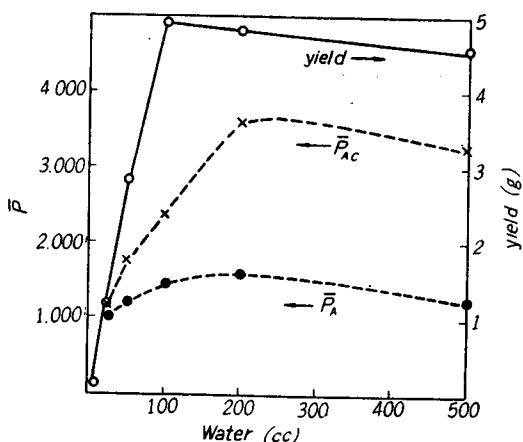ater is added to this system, polymerization takes place by irradiation and the polymer is formed on the walls of the vessel. It is known that when very small amounts of benzoqinone or nitrobenzene are dissolved into a monomer, polymerization is completety inhibited. It is clear from these preliminary results that the polymerization reaction with uranyl nitrate should proceed with a radical mechanism. The effect of water on the rates of polymerization is shown in Fig. 1. The concentration of sensitizer has a marked influence on the rates of polymerization, as shown in Fig. 2.

Fig. 1. The effect of water on the rates of aquous polymerization with uranyl nitrate.
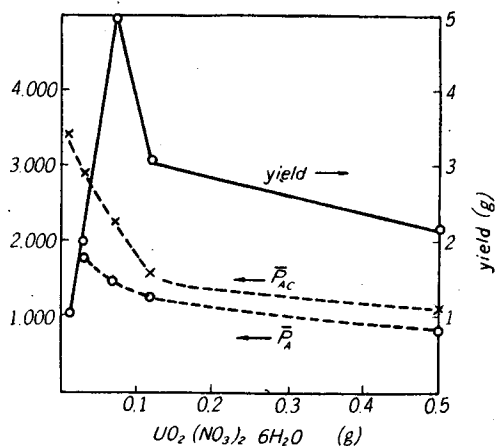
Fig. 2 The effects of the concentration of sensitizer on the rates of polymerization.

The P. H. of the polymerizing system is another variable influencing the rates as shown in Fig. 3. The yield of polymerization increases up to PH=6.4, but above ca. 6.6 no polymerization can be observed. It has already been reported[3] that UO_2^{++} changes to $[UO_2(OH)]^+$ at a high PH. Above PH 6.6, the sensitizer could have no effect on polymerization, for it was not present in the reaction phase due to precipitation. The absorption spectra of aqueous uranyl nitrats are shown in Fig. 4.

In the case of the aqueous polymerization mentioned above all polymers are formed in precipitation, and some suitable detergent such as polyethylene glycol-dodecylether or sodium dodecyl-sulphate acts effectively as emulsifiers for the formation of a stable emulsion.

4. Solution polymerization by uranyl nitrate.

It is difficult to provide a kinetic analysis of the aqueous polymerization as it proceeds heterogeneously. Therefore, solution polymerization in a homogeneous phase, is adopted for a kinetic study. Uranyl nitrate may be dissolved in the solution of acetic acid, vinyl acetate and polyvinyl acetate, but in these solutions no polymerization takes place. When water is added, polymerization proceeds very smoothly. Fig. 5 shows how the amount of water affects the rate (R_p) of the solution polymerization of vinyl acetate in this system.

Fig. 3. The effects of PH on the rates of aqueous polymerization.

Fig. 4. Absorption spectra of aqueous solutions of uranyl nitrate.

As the polomerization rate is expressed here in units of polymer mole/monomer l./sec, it is necessary to divide by about three as they appear in the figures for changing to the unit of polymer mole/total l. sec. Throughout all the experiments on this system, the degree of polymerization ($\bar{P}$) of polyvinyl acetate turned out to be equal to that of polyvinyl alcohol.

Fig. 6 shows the effect of the concentration ([I]) of the uranyl nitrate on the rate of polymerization at 30°C and Fig. 7 represents the relationship between R_p and $\bar{P}$. As shown in Fig. 7, no definite relation can be observed between R_p and $\bar{P}$. The reaction is frequently observed to stop when a large amount of uranyl nitrate is
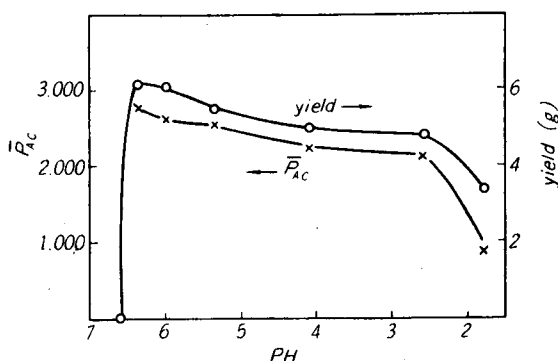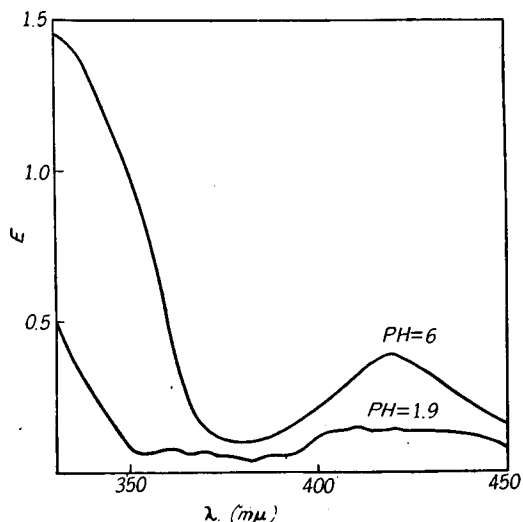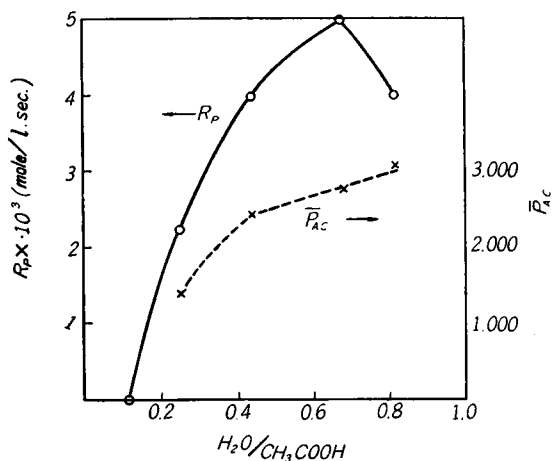
Fig. 5. The effect of water on the solution polymerization of vinyl acetate.
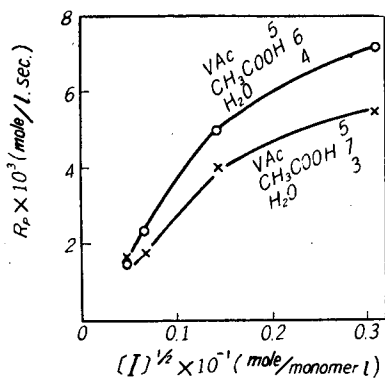

Fig. 6. The effect of uranyl nitrate concentration at 30°C.

used, and these results show that vinyl acetate seems to be hydrolysed perhaps by the strong acidity of uranyl nitrate. Because of the complexity of polymerization, due to other reactions, uranyl acetate (instead of uranyl nitrate) has been used in the following experiments.
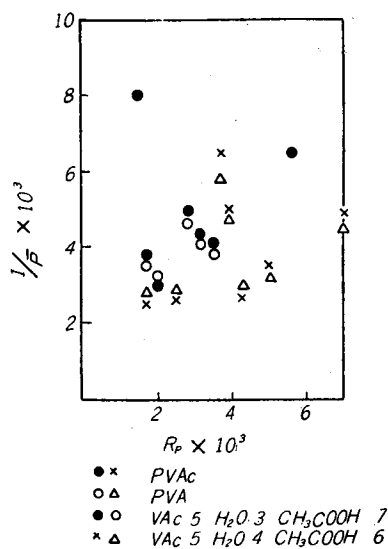

● × PVAc
○ △ PVA
● ○ VAc 5 H_2O 3 CH_3COOH 7
× △ VAc 5 H_2O 4 CH_3COOH 6

Fig. 7. Relations between R_p and $\bar{P}$.

5. Solution polymerization by uranyl acetate.

Vinyl acetate has been polymerized in an aqueous solution of acetic acid with uranyl acetate as sensitizer. As shown in Fig. 8 the rate of polymerization seems to be proportional to the square root of the concentration of uranyl acetate. The plots of R_p and $\bar{P}$ are shown in Fig. 9, from which $k_t/k_p^2 = 3$ and the transfer constant of [vinyl acetate + acetic acid + water $(5:6:4)$] $k_{tr}/k_p = 3 \times 10^{-4}$ are obtained.

The small influence of the temperature on the rate of polymerization may be characteristic of reactions in this type of system. As shown in Fig. 10, the activation energy of polymerization calculated from the rates of polymerization in an aqueous solution of acetic acid is found to be 1.5 Kcal/mole, and that in the ethanolic solution
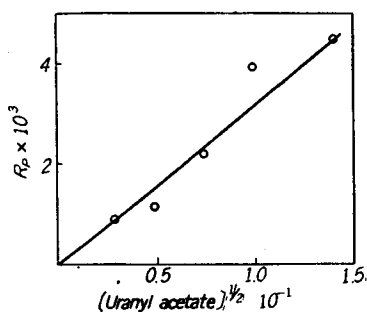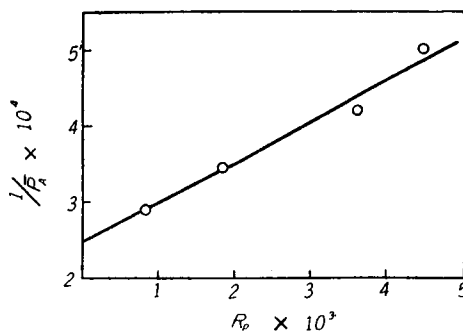
Fig. 8.

Fig. 9.

of acetic acid it is found to be almost zero. The activation energy required for normal photo-polymerization of vinyl acetate is reported to be 4–5 Kcal./mole, therefore, the activation energy of the initiation rate of the uranyl acetate sensitized photo-polymerization may be −2 to −5 Kcal./mole, and the initiation will be further discussed in chapter 9.

Meanwhile, uranyl acetate seems to be an effective sensitizer for a low temperature polymerization of vinyl acetate.

Fig. 10. The temperature dependency of solution polymerization.

6. The mechanism of the initiation of polymerization.

As shown in Figs. 1 and 5 it may be concluded that a small amount of water should be necessary for the sensitization of the photo-polymerization of vinyl acetate. During the polymerization in this system uranyl ion is found to change its color from yellow to green.

A mixture of 5 ml vinyl acetate, 4 ml acetic acid, 4 ml water and of 0.04 gr uranyl acetate is sealed in a test tube under vacuum and irradiated with ultraviolet light at 30°C for 10 hours. Absorption spectra taken before and after the
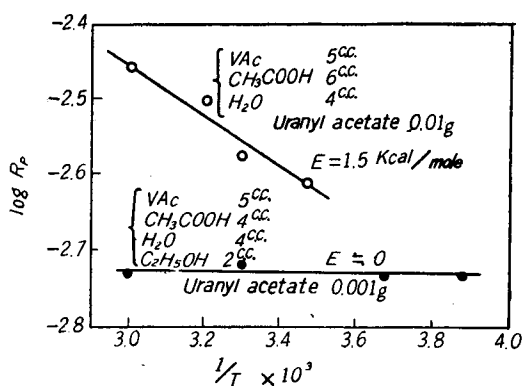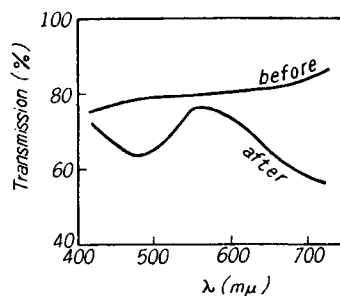

Fig. 11. Absorption spectra before and after the irradiation.

irradiation are shown in Fig. 11. Uranyl ion is recognized here to be changed to green, which shows the existence of urano ion (IV). If water is absent in this system, neither decoloration nor polymerization takes place. Water seems to be necessary for the change of UO_2^{++} into U^{++++} and the formation of that radical shall be accomplished through the following reaction:

$$UO_2^{++} + 2H_2O \longrightarrow U^{++++} + 2OH\cdot + 2OH^-$$
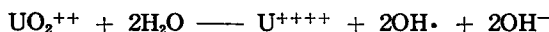
7. Polymerization in ethanolic solution.

As mentioned above, polymerization in acetic acid requires a small amount of water, but in the ethanolic solution polymerization is observed to occur even in the absence of water although the rate of polymerization may be very small. As shown in Fig. 12, the rate of polymerization in ethanol is about a fifth of that in the aqueous solution of acetic acid. The degree of polymerization is found to be about 300. From the result of estimation of radicals by diphenylpicrylhydrazil (DPPH) mentioned below, it may be concluded that the radical, perhaps the ethanolium radical, should be formed from ethanol, although its rate may be very slow.
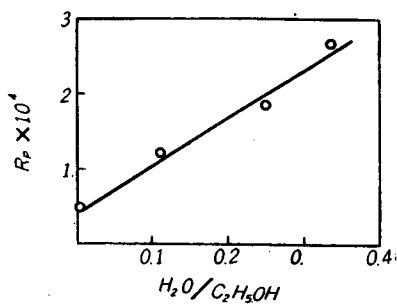

Fig. 12. Photo-polymerization in ethanol.

8. Thermal polymerization.

It has been observed that uranyl acetate initiates the thermal polymerization of vinyl acetate. The monomer is polymerized here in an aqueous solution of acetic acid and the rate of polymerization is estimated by the dilatometric method. From this experiment it is made clear that the rate of thermal polymerization is about a hundredth of that of photo-polymerization and its activation energy is estimated as 16 Kcal/mole, which is nearly the same as the referred value of 20 Kcal/mole. for thermal polymerization.
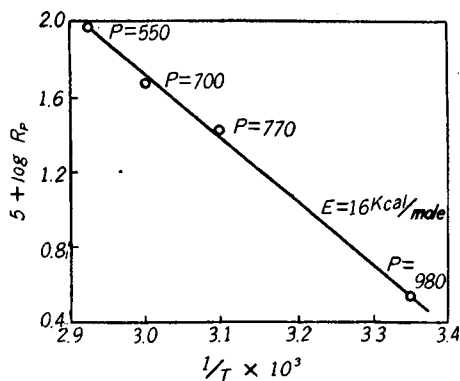
It has been also reported that ceric salt initiate the photo- and thermal-polymerization of vinyl monomers[4,5].

Fig. 13. Thermal polymerization with uranyl acetate.

9. Estimation of the rate of radical-formation
by the DPPH-method.

Because of the self decomposition of DPPH by irradiation, it may be very difficult to estimate the rate of radical formation by the DPPH method. In an aqueous solution of acetic acid DPPH is found to decompose very fast by irradiation so that its amount cannot be analysed exactly. But DPPH is recognized to decompose faster with than without uranyl acetate, as shown in Fig. 14. The initial rates of decomposition and the difference between the two cases of either with or without uranyl acetate are shown in Fig. 15.
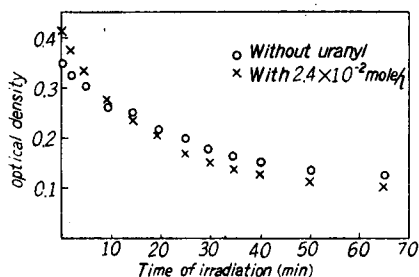

Fig. 14. Photo-decomposition of
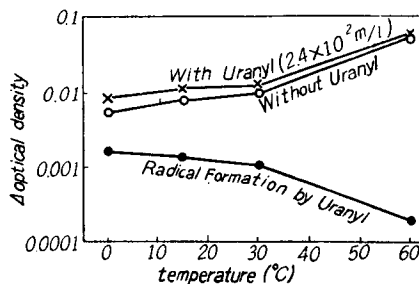DPPH in aqueous acetic acid.

Fig. 15. Effect of temperature on
the decomposition rate of DPPH
in aqueous acetic acid.

As shown in Fig. 15 it may be possible to evaluate roughly the consumption rate of DPPH caused by uranyl acetate. It is recognized that the radical formation by uranyl acetate is relatively faster at lower temperatures, which may be correlated with the negative activation energy on the rate of initiation mentioned already in chapter 5.

The consumption rate of DPPH in an ethanolic solution is measured as shown in Fig. 16. In this system the photo-self decomposition of DPPH is much slower, and therefore the consumption rate by uranyl acetate in this figure seems to be nearly equal to the rate of radical formation by the uranyl acetate. As shown in Fig. 16, the decomposition in ethanolic solution is about ten times faster than that in acetic acid. In spite of the faster decomposition the rate of photopolymerization in ethanolic solution is found to be very slow as mentioned above. The radical formed from the ethanol may be considered to change into an acetaldehyde and
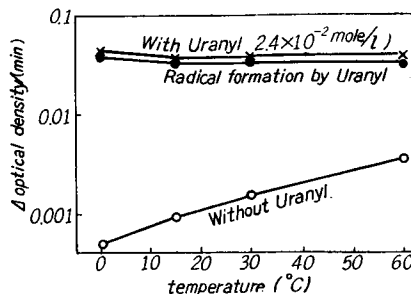

Fig. 16. Decomposition of DPPH
in ethanol solution.

then a very small amount of the radical seems to take part in the initiation of the polymerization. A large amount of acetaldehyde is actually detected after the poly-merization. In this connection, the photo-polymerization of vinyl chloride[6] sensitised with uranyl compounds, proceeds very fast, even in methanolic solutions.

$$C_2H_5OH \longrightarrow CH_3\text{-}\dot{C}H\text{-}OH \longrightarrow CH_3CHO$$
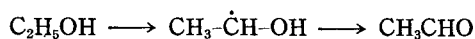
10. The number of 1.2 glycol linkages and the swelling properties of the polyvinyl alcohol obtained by low temperature photo-polymerization.

As previously reported[2], the number of 1.2 glycol linkages in the polyvinyl alcohol molecules determined by Flory's method and also the swelling degree of a polyvinyl alcohol film in water have both been decreased when the polymerization temperature was lowered. Vinyl acetate is polymerized at a low temperature. Vinyl acetate is polymerized here at $-40°C$. and sensitized by uranyl acetate; The poly-vinyl acetate obtained is saponified to polyvinyl alcohol as usual.

Mixture for polymerization: vinyl acetate 5 ml, acetic acid 2 ml, ethyl alcohol
    6 ml, water 2 ml, uranyl acetate 0.01 g.

Polymerization at $-40°C$ by ultraviolet rays.

Polymerization rate obtained: 0.212%/min.

Degree of polymerization as polyvinyl alcohol: 1065.

The results are shown in Figs. 17 and 18. As shown in the two figures, the experimental data obtained here are just on the curves mentioned (× marks in figures) in the previous report.
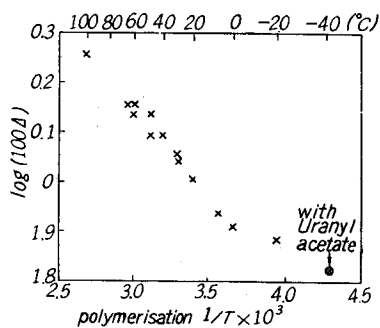

Fig. 17. Polymerization tem-
perature of vinyl acetate and
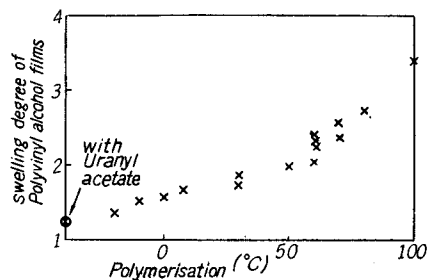1.2 glycol linkages in poly-
vinyl alcohol.

Fig. 18. Polymerization tempera-
ture of vinyl acetate and the
swelling of polyvinyl alcohol
films in water.

11. Polymerization of vinyl acetate by self-irradiation due to the radio-activity of uranyl acetate.

In the experiments mentioned above the possibility that vinyl acetate may be polymerized by self-irradiation due to the radioactivity of uranyl acetate may be taken into consideration. But by the calculations mentioned below, it is made clear here that polymerization by radioactivity can fully be neglected.

As hitherto known, natural uranium contains three isotopes ; U^{234}, U^{235} and U^{238}. The contents and radioactivities of these components are as follows :—

Components	Contents (%)	Radiation	Half life
U^{238}	99.274	α–rays (4.19 Mev	4.5×10^9 years
U^{235}	0.720	α–rays (4.39, 4.56 Mev)	7.07, 8.91×10^8 years
		γ–rays (0.17 Mev)	
U^{234}	0.006	α–rays (4.76 Mev)	2.3, 2.69×10^5 years
		X–rays	

It may be considered that the total energy of radiation will be absorbed in the system, so far as the α–rays are concerned.

Energy emitted may be estimated by the exponential equation as the following ;

$$1.0 \text{ g of } U^{238} \cdots\cdots\cdots 5.3 \times 10^4 \text{ mev/sec.}$$
$$0.00720 \text{ g of } U^{235} \cdots\cdots 0.2 \times 10^4 \text{ mev/sec.}$$
$$0.00006 \text{ g of } U^{234} \cdots\cdots 6.4 \times 10^4 \text{ mev/sec.}$$
$$\text{total} \qquad \cdots\cdots\cdots 11.9 \times 10^4 \text{ mev/sec.}$$

Assuming that 1 g of uranyl acetate may be dissolved into 100 g of monomer (extreme case), the content of uranium in this solution is estimated to be 0.56 g. When 0.56 g of uranium decays in this solution, the energy emitted is summed up to ;—

$$11.9 \times 10^4 \times 0.56 \text{ mev} = 6.67 \times 10^4 \text{ mev}$$
$$\doteqdot 11 \times 10^{-2} \text{ erg.}$$
$$\doteqdot 4 \times 10^{-3} \text{ r/hr.}$$

In the case of γ–ray polymerization of vinyl acetate the rate of polymerization is found to be 0.4%/min. at the dose rate 4×10^4 r/hr.

Assuming that the rate of polymerization may be proportional to the square root of the dose rate, the rate of polymerization contributed by the existence of radioactive uranium can be deduced, the rough estimate being 0.0001%/min.

This value is very small as compared to the rate of photo-polymerization and so these effects can be completely neglected.

References

1) H. W. Melville and R. B. Whyte ; J. Soc. Dye. Col. **65**, 703 (1949).
2) S. Okamura and T. Motoyama ; Kasen Koenshu **14**, 23 (1957).
3) R. Flatt and W. Hess ; Helv. chim acta **21**, 1506 (1938).
4) J. Weiss and D. Porret ; Nature **139**, 1019 (1937).
5) J. Saldick ; J. Polymer Sci. **19**, 73 (1956).
6) H. Watanabe, Y. Toyota and Y. Amagi ; KOGYO KAGAKU ZASSHI **61**, 893 (1958).