Polymerization of Vinyl Acetate by High Energy Radiation

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Introduction

While extensive work has been carried out on the radiation polymerization of vinyl compounds, there has been comparatively little attention paid to that of vinyl acetate. One of the reasons for this seems to be that in the case of vinyl acetate the reproducibility was very poor as shown by the work of Chapiro[1]. It is, however, even more attractive for us to study the radiation polymerization of vinyl acetate, because the considerations on the degree of polymerization are done more easily from two sides as polyvinyl acetate and also as polyvinyl alcohol. Manowitz et al.[2] had recognized that the degree of polymerization increased during polymerization and this could be explained by the branching or the cross-linking of polymers. Attempts have now been made to clarify the chain transfer mechanism of polymer molecules in the radiation polymerization of vinyl acetate. This leads to some preliminary conclusion that the increase of the molecular weight during polymerization is coming from the branching at the acetyl side chain of polyvinyl acetate. The degree of polymerization of polyvinyl alcohol was found to be comparatively higher than that in the thermal polymerization. This reason, however, has not yet been clarified in this paper.

Experimental

Vinyl acetate (VAc), methyl acrylate (MA) and methyl methacrylate (MMA) were polymerized in sealed tubes, in which gas phase was replaced by vacuum and thereafter by nitrogen. Sources of gamma-rays were 20 and 0.5 curies of Cobalt-60, and its doses were measured by the method of Weiss[3]. X-ray from a 180 kV.-20 mA. apparatus were filtered by 0.3 mm. Cu and 0.5 mm. Al, and the dose rate at 12.5 cm. distance from target, that is at the middle point of reaction vessel, was 977 r/min. The average degrees of polymerization were calculated by the following equations,

PVAc in acetone: $\bar{P}_{AC}=(\text{antilog}\,\frac{[\eta]}{0.28}-1)\cdot 2000$

PMMA in chloroform: $[\eta]=2.52\cdot 10^{-3}\bar{P}^{0.80}$

PVA in water: $\log \bar{P}_A=1.613\log\frac{[\eta]\times 10^4}{8.87}$

Results

The rates of polymerization were shown in Figs 1 and 2. In both cases of gamma- and X-rays, the polymerization of MMA showed no induction period, that of VAc showed a moderate one and that of MA a long one. The order of the rates of polymerization was VAc>MA>MMA, in accordance with the results obtained by Chapiro[1]. Table I repre-

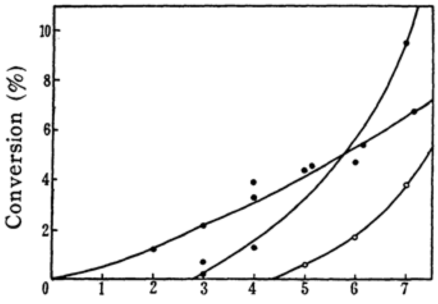

Fig. 1. Gamma-ray polymerization of VAc (●), MMA (⊙) and MA (○).
2 cm from 20 curie Co-60., 10±2°C, dose rate; about 15×10³ r/hr.

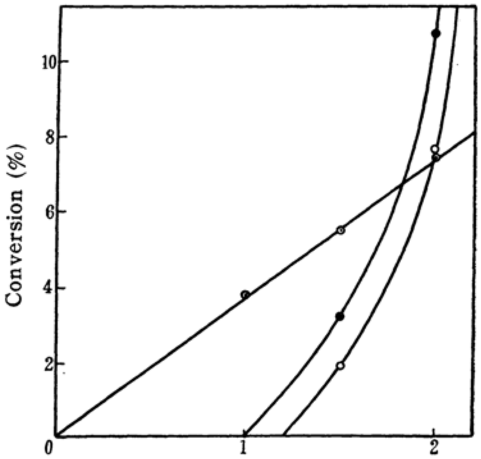

Fig. 2. X-ray polymerization of VAc (○ and ●) and MMA (⊙).
18±2°C, dose rate; 977 r/min.

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[1] A. Chapiro, *J. chim. phys.*, **47**, 764 (1950).

[2] D.S. Ballantine, P. Colombo, A. Glines and B. Manowitz, *Chem. Eng. Prog. Symp.*, **50**, No. 11, 267 (1954).

[3] J. Weiss, *Nucleonics*, **10**, (7), 28 (1952).

TABLE I

THE DEGREES OF POLYMERIZATION OF POLYVINYL ACETATE

Expt. No.	Condition of Irradiation	Polym. Time (hr.)	Polym. Yields (%)	Viscosity $[\eta]$	$\bar{P}_{AC}$	Huggins Constants k′
gamma-4	2 cm. from 20 curies Co-60	4	3.35	0.232	11480	0.28
gamma-5	〃 〃 〃	5	4.41	0.248	13370	0.31
gamma-7	〃 〃 〃	7	9.53	0.290	19710	0.37
X-1	X-rays	1.5	3.20	0.158	5330	0.30
X-2	〃	2	10.70	0.187	7190	0.32

sents the degrees of polymerization of polyvinyl acetate obtained by gamma- and X-rays.

As shown in Table I, the degrees of polymerization were found to increase rapidly during polymerization. In the case of MA, the intrinsic viscosities were measured as 0.38 and 0.73 at the polymerization yields of 1.7 and 3.9 respectively. The degrees of polymerization of PMMA were 6000–7000 independent of the polymerization yields in the range of 1–7. Table II shows the degrees of polymerization of polyvinyl alcohol obtained by the saponification of PVAc.

The degrees of polymerization of the polyvinyl alcohol were found to be very high compared with those obtained by the thermal polymerization. The content of 1,2 glycol bond in PVA, measured by the comsumption of periodic acid[4] was found to be 1.23% in the sample S–1.

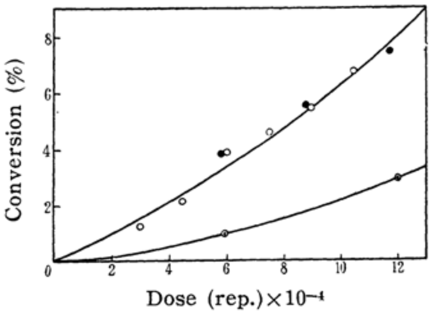

Fig. 3. The relationship between dose and conversion of gamma- and X-ray polymerization of MMA.

○; gamma-ray polym. (15000 r/hr. 10°C)

●; X-ray polym. (58600 r/hr. 18°C)

⊙; gamma-ray polym. (Manowitz et al.[2] 250000 r/hr. room temperature).

TABLE II

THE DEGREES OF POLYMERIZATION OF POLYVINYL ALCOHOL

Expt. No.	Condition of Irradiation	Polym. Time (hr.)	Polym. Yields (%)	Polym. Temp. (°C)	Viscosity $[\eta]$	$\bar{P}_A$	k'
gamma-7′	Same as gamma-7 in Table I	7	9.53	10	0.223	7440	0.77
gamma-15*	〃	15	95	〃	0.219	6710	0.75
gamma-24*	〃	24	100	〃	0.195	5990	0.63
X-2′	Same as X-2 in Table I	2	10.70	18	0.155	4140	0.90
S-1	at 3.5 cm. from 0.5 curies Co-60,	ca. 8 days	27	0–5	0.269	10070	0.82
S-2	〃	ca. 9 days	92	〃	0.234	7980	0.75
H-1*	Same as gamma-7	7	95.6	51	0.144	3680	0.80
L-III*	Upper of test tube at 1–6.4 cm. from 20 curies Co-60	15	Average 75	10	0.255	9230	—
L-M*	Middle	〃			0.232	7950	—
L-d*	Under	〃			0.202	6420	—

* Marks indicate that PVAc forms gel in acetone.

Discussion

The relationships between the rates of polymerization and the total doses of radiation are shown in Fig. 3. In these conditions, that was 15,000 r/hr., 10°C at gamma-rays and 58,600 r/hr. 18°C at X-rays respectively, just the same rates were obtained in both cases of gamma- and X-rays. The results of Manowitz[2] were considerably low, as shown in Fig. 3. It has been reported that the lower rates of polymerization were obtained at a higher dose rate in the same total doses[5].

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[4] I. Sakurada and G. Takahashi, Private communications. Sep., 10, 1955.

[5] I.A. Berstein, E.C. Farmer, W.G. Rothschild and F.F. Spalding, *J. Chem. Phys.*, **21**, 1303 (1953).

These situations were just the same as those shown in Fig. 3.

The degrees of polymerization of PVAc increase during polymerization, and the extrapolated values of degrees of polymerization to zero yields coincide well with that of PVA. This relation is just the same as in thermal or catalysed polymerization.

From the following equation[6], we could obtain the branching reactivity of polymer (k'_b/k_b) and that of monomer (k''_b/k_b).

$$\left(\frac{1}{\bar{P}_A}-\frac{1}{\bar{P}_{AC}}\right)$$
$$=-\frac{k'_b}{k_b}\left\{1+\frac{1}{X}\ln(1-X)\right\}+\frac{k''_b}{k_b}$$

where X was the polymerization yield, k'_b and k''_b were the branching velocity constants of polymer and of monomer respectively, and k_b was the propagating velocity constant.

As shown in Table III, the branching reaction by monomer is of the same order as the normal one $(k''_b/k_b \fallingdotseq 0.5\times10^{-4})$, but the branching by polymer (k'_b/k_b) occurs more rapidly than in the thermal or catalyzed polymerization $(k'_b/k_b \fallingdotseq 2.5\times10^{-4})$.

TABLE III

VELOSITY CONSTANTS RATIOS OF SECONDARY POLYMERIZATION BY GAMMA- AND X-RAYS

Conditions of polymerization	k'_b/k_b	k''_b/k_b
gamma-rays	$12.0\cdot10^{-4}$	$0.33\cdot10^{-4}$
X-rays	$13.9\cdot10^{-4}$	$0.36\cdot10^{-4}$

One of the observed complexities, hitherto reported in the case of styrene, methyl acrylate and so on, was found to be related to the branching reactions, which occurred during the radiation polymerization. Much further work, however, is of course necessary in these important points.

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[6] S. Okamura and T. Yamashita, *Bull. of the Institute for Chemical Research*, Kyoto University, **18**, 46 (1949).