Vinyl Polymerization. LXVII. The Polymerization of Vinyl Acetate in the Presence of Zinc Chloride

By Minoru IMOTO, Takayuki OTSU and Toshio ITO

(Received October 31, 1962)

In the previous paper[1], we have found that photopolymerization of vinyl acetate initiated by azobisisobutyronitrile (AIBN) in the presence of zinc chloride proceeds in the heterogeneous system. The present paper deals with the effect of zinc chloride on the radical polymerization of vinyl acetate and on the properties of the resultant polymers.

Experimental

Materials.—Vinyl acetate was purified as follows: Commercial vinyl acetate was washed successively with 5% sodium thiosulfate solution and dilute sodium hydroxide solution and then dried over calcium chloride. Pure vinyl acetate was obtained by distillation in the presence of 2% azobisisobutyronitrile in a nitrogen atmosphere. Commercial grade zinc chloride was used without further purification and dehydrated according to the method described in a previous paper[1]. Azobisisobutyronitrile and other reagents were purified by the usual method.

Polymerization Procedure.—In a 100 ml. hard glass tube, a given amount of zinc chloride was placed and the tube was heated at about 300°C for 15 min. under vacuum. Pure vinyl acetate was then added and the tube was shaken to make a solution. The resulting solution was rapidly transfered by pipetting into the polymerization tubes. The tubes were then degassed and sealed under vacuum.

Polymerizations were allowed to take place on shaking in a thermostat. Photopolymerizations were carried out in a thermostat, irradiating by the Madzuda SHL type high pressure mercury lamp. After a given time, the tube was removed from the thermostat and the content of the tube was rapidly filtered to separate the monomer-insoluble polymer. Then the filtrate was poured into a large amount of petroleum ether to precipitate the polymer. Both polymers were washed with dilute hydrochloric acid and then purified by the reprecipitation method with petroleum ether from acetone solution. Conversion was calculated from the weight of the dry polymer obtained.

Treatment of the Polymer.—Intrinsic viscosity of polyvinyl acetate was determined by viscosity measurement of its dilute acetone solution at 30°C. Hydrolysis of polyvinyl acetate was performed as follows: 2 g. of polyvinyl acetate was dissolved in 100 ml. of methanol and 3 ml. of 5% aqueous sodium hydroxide solution was added. After standing overnight at room temperature and then refluxing for an hour, polyvinyl alcohol was isolated. Intrinsic viscosity of polyvinyl alcohol was determined from the viscosity measurement in water solution. Reacetylation was carried out by heating polyvinyl alcohol in pyridine-acetic anhydride at 95°C for 3 hr.

Experimental Results

Polymerization of Vinyl Acetate (VAC) with Zinc Chloride.—Results of the polymerization of VAC with zinc chloride are shown in Table I.

As can be seen from Table I, the polymerizations of VAC with zinc chloride proceeded with a slow rate to yield the colored polymer which was insoluble in the VAC monomer. Tho resulting dried polymer melted at 106∼108°C and was a low molecular weight polymer. Carbon and hydrogen contents of this polymer were 61.39 and 7.40%, respectively and these values widely differ from those calculated for pure polyvinyl acetate (C, 54.54; H, 9.09%). This polymer was easily soluble in most organic solvents, such as methanol and acetone, to make a colored solution which was decolorized by the addition of bromine. Infrared spectra of this polymer showed the absorption bands of hydroxyl, carbonyl and carbon-carbon double bonds.

It was also found that the polymerization could not be retarded by the addition of hydroquinone. Accordingly, it might be considered that the polymerization of VAC with zinc chloride proceeded with the carbonium ion mechanism and the resulting polymer then reacted with zinc chloride to yield the colored polymer having a complexed structure.

Table II shows the results of the polymerization of VAC by the system AIBN and zinc chloride. Although AIBN is a typical radical initiator, the yields of polymer were approximately equal to those obtained by zinc chloride alone. It was assumed that the polymerization with both initiator and zinc chloride proceeded with carbonium-ion mechanism and the resulted colored polymer served as an inhibitor for the radical polymerization of VAC by AIBN.

---

[1] Part LXVI of this series: M. Imoto, T. Otsu and S. Shimizu, *Makromol. Chem.*, in press.

TABLE I. BULK POLYMERIZATION OF VAC WITH ZINC CHLORIDE FOR 20 hr.

Exp. No.	$[ZnCl_2]$ mol./l.	[VAC] ml.	Temp. °C	Conversion %	Color of polymerization mixture
1.1	0.081	10	50	2.19	Blackish-brown
1.2	0.161	10	50	2.28	Blackish-brown
1.3	0.242	10	50	2.92	Blackish-brown
1.4	0.081	10	40	1.20	Reddish-brown
1.5	0.081	10	30	0.33	Reddish-brown

TABLE II. POLYMERIZATION OF VAC INITIATED BY THE SYSTEM AIBN AND ZINC CHLORIDE AT 50°C

Exp. No.	$[AIBN]\times10^3$ mol./l.	$[ZnCl_2]$ mol./l.	[VAC] ml.	Time hr.	Conversion %	Color of polymerization mixture
2.1	0.244	0	10	3	35.60	Colorless
2.2	0.244	0.063	10	20	4.42	Pale-yellow
2.3	0.244	0.126	10	20	3.25	Yellowish-brown
2.4	0.244	0.189	10	20	2.71	Reddish-brown
2.5	0.244	0.252	10	20	2.26	Blackish-brown

TABLE III. PHOTOPOLYMERIZATION OF VAC WITH AIBN-ZINC CHLORIDE $[AIBN]=6.1\times10^{-3}$ mol./l.

Exp. No.	$[ZnCl_2]$ mol./l.	[VAC] ml.	Temp. °C	Time hr.	Conversion, %	
					Insolu. Pt.	Solu. Pt.
3.1*	0	10	50	3	0	35.6
3.2*	0.252	10	50	20	0	2.26
3.3	0	10	10	20	0	2.60
3.4	0.218	10	10	20	5.13	1.64
3.5	0	10	−10	20	0	0.59
3.6	0.218	10	−10	20	1.67	0.20
3.7	0	10	−30	20	0	Trace
3.8	0.218	10	−30	20	0.57	Trace
3.9	0	10	−50	20	0	Trace
3.10	0.218	10	−50	20	0.011	Trace

* In these cases, polymerizations were carried out by AIBN (2.44×10^{-3} mol./l.) in the absence of light.

TABLE IV. PHOTOPOLYMERIZATION OF VAC WITH AIBN-ZINC CHLORIDE $[AIBN]=6.1\times10^{-3}$ mol./l.

Exp. No.	$ZnCl_2$	[VAC] ml.	Temp. °C	Time min.	Conversion, %		$[\eta]$ in C_6H_6	
					Insolu. Pt.	Solu. Pt.	Insolu.	Solu.
4.1	None	10	30	5	0	1.70	—	1.68
4.2	Added*	10	30	5	0.49	1.02	0.88	1.33
4.3	None	10	−30	45	0	Trace	—	—
4.4	Added*	10	−30	45	3.31	Trace	0.98	—

* The concentrations of zinc chloride were about 0.2∼0.5 mol./l.

Effect of Zinc Chloride on the Photopolymerization of VAC Sensitized by AIBN.—Results of the photopolymerization of VAC sensitized by AIBN are shown in Tables III and IV.

As can be seen from Tables III and IV, the rates of polymerization of VAC at rather high temperatures (> 30°C) decreased with the addition of zinc chloride. However, at lower temperatures below 10°C, the rates increased with the addition of zinc chloride and the resulting polymer contained the VAC-insoluble polymer which was dissolved in most organic solvents after purification. The amount of the VAC-insoluble polymer increased with decreasing the polymerization temperature. It is also proved from these tables that at rather high temperatures, cationic and radical polymerizations occured simultaneously and the resulting colored polymer served as inhibitor for the radical polymerization.

Since the low-temperature photopolymerization of VAC sensitized by AIBN in the presence of zinc chloride proceeded in a heterogeneous system, it was difficult to study kinetically this polymerization. As can be seen from Fig. 1, however, the time-conversion curve of the polymerization showed a straight line at the initial stage of the polymerization. Accordingly, it may be possible to investigate kinetically this polymerization.

Figure 1 shows time-conversion curve for the photopolymerization of VAC sensitized by AIBN in the presence of zinc chloride at $-30°C$. Time-conversion curve shows a straight line up to 2% conversion, but in general the rate decreased with the proceeding of the polymerization. Figure 2 shows the relationship between the rate of polymerization (R_p) and the concentration of zinc chloride. At lower concentrations of zinc chloride, it was clear that R_p is proportional to the concentration of zinc chloride. Figure 3 shows the relationship between R_p and the concentration of AIBN at constant concentration of zinc chloride. From this figure, it was deduced that R_p was proportional to the square root concentration of AIBN.

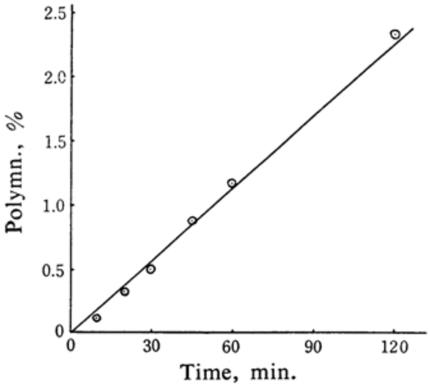

Fig. 1. Time-conversion curve for the photopolymerization of VAC with AIBN-$ZnCl_2$ at $-30°C$: $[AIBN]=6.1\times10^{-3}$, $[ZnCl_2]=0.215$ mol./l.

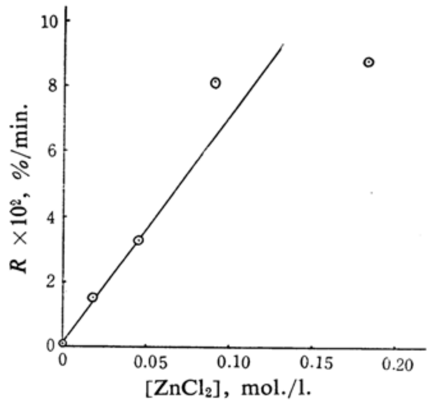

Fig. 2. Relationship between R_p and $[ZnCl_2]$ for the photopolymerizations of VAC at $-30°C$: $[AIBN]=6.1\times10^{-3}$ mol./l.

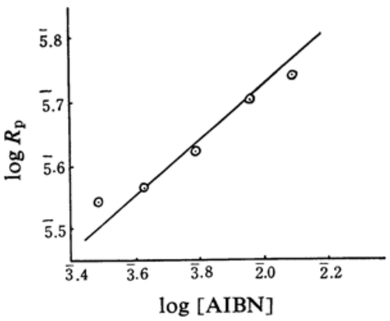

Fig. 3. Relationship between R_p and [AIBN] for the photopolymerizations of VAC at $-30°C$: $[ZnCl_2]=0.341$ mol./l.

Properties of the Resulting Polymer.—A large amount of zinc chloride was detected in the crude VAC-insoluble polymer obtained by the photopolymerization of VAC in the presence of zinc chloride at $-30°C$. For example, 0.245 mol./l. of zinc chloride was occluded in the polymer isolated at 3.32% conversion, using $[ZnCl_2]=0.413$ mol./l. This crude polymer was very hygroscopic, but the polymer purified through the reprecipitation method to remove zinc chloride was soluble in VAC, methanol, acetone, ethyl acetate and benzene. Accordingly, it was clear that the formation of the VAC-insoluble polymer was due to a complex formation of PVAC with zinc chloride.

Elementary analysis and infrared spectra also showed that the pure polymer had the structure of ordinary polyvinyl acetate. Intrinsic viscosities of these polymers were lower than those of polymers obtained in the absence of zine chloride, as indicated in Table IV. The result suggested that zinc chloride served as a chain transfer agent for the polymerization.

Experiments of the hydrolysis of this polymer to yield polyvinyl alcohol and of further reacetylation were carried out. During these treatments, it was confirmed by infrared spectra that these reactions proceed completely. Viscosity changes of the polymers are shown in Fig. 4. As understood from this figure, intrinsic viscosities and k'-values of polyvinyl acetates did not change during the hydrolysis and then reacetylation. This fact indicated that PVAC obtained by the polymerization in the presence of zinc chloride had no long chain branch of the ester type which is capable of scission by hydrolysis. Solubilities in hot water, phenol and dimethyl sulfoxide and the crystallinities by X-ray analysis of these polyvinyl alcohols coincided almost with the ordinary polyvinyl alcohol.

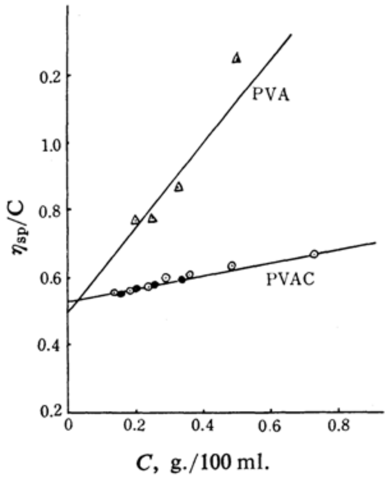

Fig. 4. Relationship between η_{sp}/C and C for polyvinyl acetate (PVAC) and polyvinyl alcohol (PVA) obtained from the photopolymerizations with AIBN-$ZnCl_2$: ⊙ before hydrolysis, ● after hydrolysis and then reacetylation for PVAC.

The Complex Formation of VAC with Zinc Chloride.—In order to isolate the complex of VAC with zinc chloride, a required amount of zinc chloride was dissolved by shaking in an excess of VAC and then the excess of VAC was rapidly removed by vacuum distillation. Pale yellow viscous liquid was obtained. From the weight and chlorine analyses it was proved that the complex was composed of 1 : 1 molar ratio of VAC to zinc chloride.

This complex was very hygroscopic and unstable. When the complex was allowed to stand in a sealed tube at room temperature, the cationic polymerization occured explosively after standing about 20 hr. to produce the colored polymer.

Discussion

It has been generally known that zinc chloride can initiate the cationic polymerization. In polymerization of vinyl acetate, it was observed in the present paper that zinc chloride could also initiate the cationic polymerization. In this case, however, the polymerization was accompanied by side reactions such as hydrolysis, deacetylation or dehydration and the resultant polymer was a yellow or reddish brown powder with a low molecular weight. These results agreed with those obtained by Higashimura and Okamura(2) that tin(II) chloride could initiate the cationic polymerization of vinyl acetate.

The rate of cationic polymerization of vinyl acetate was so slow that it hardly proceeded at rather low temperatures. Therefore, when AIBN as an initiator for radical polymerization was used together with zinc chloride, both radical and cationic polymerizations proceeded at the same time at higher temperatures ($>30°C$).

The polymer obtained in the latter reaction served as an inhibitor for the radical polymerization. At lower temperatures ($<10°C$), however, no inhibition of polymerization was observed, since the cationic polymerization might be retarded and only the polymerization proceeded through the radical mechanism.

The presence of zinc chloride may characterize the photopolymerization of vinyl acetate at lower temperatures using AIBN as photosensitizer, in two respects: acceleration of polymerization and progress of polymerization in a heterogeneous system. Although the rate of decomposition of AIBN could not be affected by the presence of zinc chloride(1), the effect of zinc chloride in the polymerization system might be considered as follows: (1) Complex formation with the monomer (VAC), (2) interaction with the growing radical and the monomer at the transition state of the propagation step, and (3) influences on the transfer and termination reactions. If the interaction of (2) was the most important among them, a stereoregular polymer should be obtained as Kargin et al.(3) pointed out. In fact, this effect of zine chloride could be neglected, since no stereoregular polymers were obtained through radical polymerizations as shown in a previous(1) and in the present paper. As for influences of (3), Table IV showed that smaller values of intrinsic viscosity were obtained in the presence of zinc chloride, indicating that zinc chloride served as a chain transfer agent.

The present authors(4) observed that zinc chloride could readily form a complex with methyl methacrylate or acrylonitrile. It was

---

(2) T. Higashimura and S. Okamura, *Chem. High Polymer, Japan*, **17**, 635 (1960).

(3) V. A. Kargin, V. A. Kabanov and V. P. Zubov, *Vysokomol. Soed.*, **2**, 765 (1960).

(4) M. Imoto, T. Otsu, Y. Harada and M. Nakabayashi, Presented at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962; *Makromol. Chem.*, in press.

reported by Matsumoto⁵⁾ that vinyl acetate made a complex in a molar ratio of 1 : 1 with $Cd(C_2H_5)_2$. A complex of zinc chloride with vinyl acetate in a molar ratio of 1 : 1 could also be isolated in the present work. However, since the complex was so unstable that the cationic polymerization proceeded explosively on standing. Since it was hygroscopic, the present authors could not determined infrared absorption spectra. Nevertheless, both the results of Matsumoto⁵⁾ and of the present authors⁴⁾ have almost made it clear that the carbonyl group of vinyl acetate might contribute to the complex formation with zinc chloride.

The probable formation of such a complex might cause polarization of double bands. As the e value for vinyl acetate was -0.3, the reactivity of uncomplexed vinyl acetate radicals with complexed vinyl acetate was considered to be increased. Therefore, as Bamford et al.⁶⁾ pointed out, the acceleration by zinc chloride might be explained in terms of copolymerization of complexed and uncomplexed vinyl acetate. It was confirmed by the fact that a large amount of zinc chloride was detected in the resultant polymer which was insoluble in the monomer, or that polymerization begins in a heterogeneous system.

Summary

A study of the effect of zinc chloride on the polymerization of vinyl acetate has been made. Zinc chloride can initiate the cationic polymerization of vinyl acetate at above room temperatures to yield the colored low-molecular weight polymer. However, in the low-temperature photopolymerization of vinyl acetate initiated by azobisisobutyronitrile, zinc chloride accelerates the radical polymerization and the colorless polymer which is insoluble in the monomer is obtained. Elementary analysis, infrared spectra and X-ray analyses show that the structure of this polymer after purification does not differ with that of ordinary polyvinyl acetate and polyvinyl alcohol obtained through the hydrolysis of this polymer has no crystallinity superior to that of the ordinary sample.

Faculty of Engineering
Osaka City University
Kita-ku, Osaka

---

5) S. Matsumoto, *Chem. High Polymer, Japan*, **16**, 467 (1959).

6) C. H. Bamford, A. D. Jenkins and R. Johnston, *Proc. Royal Soc.*, **A241**, 364 (1957).