Polymerization of β-Propiolactone Initiated by Sodium Chloroaurate

By

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Bulk polymerization of β-propiolactone (β-PL) initiated by sodium chloroautae (NaAuCl$_4$·2H$_2$O) at 30°C. was investigated. The polymerization initiated by NaAuCl$_4$·2H$_2$O is accelerated by photoirradiation similar to the polymerization of N-vinylcarbazole as mentioned in a previous paper.[3]

The time-conversion curve of the polymerization under photoirradiation reaches a dead end, particularly when the polymerization is carried out in a quartz vessel. The intial rate of polymerization is proportional to $[Au^{III}]^{\sim 1}$ in the light and $[Au^{III}]^{\sim 2}$ in the dark. From the effects of additives and solvents, and electronic spectroscopies, it is concluded that the polymerization is cationic initiated by charge transfer process from β-PL to the Au^{III} and/or the Au^{II} species on other decomposition products of Au^{III}.

Introduction

β-Propiolactone (β-PL) is an interesting cyclic monomer since the monomer is polymerizable by both anionic and cationic mechanisms. In addition, neutral salts such as alkali halide can also induce the polymerization by some undefined mechanism.[1] One example of photopolymerization of β-PL using uranyl nitrate as sensitizer was presented by Sakamoto.[2] Since the monomer is not capable of being polymerized by radical mechanism, the photopolymerization of β-PL was claimed to be an example of photosensitized ionic polymerization. Although photochemical reaction has been believed to proceed by radical mechanism, radical process is not necessarily the only one possible mechanism if the reaction is initiated by a photoredox process which often involves the formation of ion-radicals as transient species, or if ionic catalysts are produced by photochemical process.

As has been published in a letter,[3] we have several examples of photosensitized charge transfer polymerization which are most likely to proceed by cationic mechanism. This is an example of marked acceleration of polymerization of β-PL in bulk initiated by sodium chloroaurate under photoirradiation.

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Experimental

Materials:

β-Propiolactone kindly provided by Dainippon Celluloid Co. Ltd., was dried by passing through a layer of anhydrous calcium chloride[4] twice and distilled in vacuo immediately before use.

Sodium chloroautate (Nakarai Chemicals Co. Guaranteed Reagent) and ascorbic acid (Nakarai Chemicals Co. G.R. Grade) were used without further purification.

Acetonitrile (G.R. Grade) was dried over phosphorous pentaoxide and distilled twice through a 50 cm Widmer column at the atmospheric pressure.

Nitrobenzene (G.R. Grade) was repeatedly washed, dried over calcium chloride, then over calcium hydride and distilled twice in vacuo.

Polymerization:

The polymerization was carried out in a hard glass ampoule or a quartz ampoule. For the polymerization in vacuo, the monomer and the catalyst were introduced into different arms of a reaction vessel and the two components were mixed after degassing and sealing off the reaction vessel. The polymerization mixtures were precipitated in methanol and the conversion to polymer was determined by weighing polymer.

When the polymerization system was to be irradiated, a 300 W high pressure mercury lamp was the light source.

The viscosity of polymer was measured at 30°C. as chloroform solution.

Spectroscopy:

A Shimazu SV 50A spectrometer was used for electronic spectroscopy.

Results and Discussion

Effects of Photoirradiation on the Polymerization Intiated by NaAuCl$_4$ ·2H$_2$O.

Effects of light on the time-conversion curve are shown in Figure 1. Acceleration of polymerization by photoirradiation is obvious. At high Au^{III} concentration (Figure 1a) the effect of photoirradiation is not so prominent as in the system with lower Au^{III} concentration (Figure 1b), indicating the higher order of dependence of R_p on catalyst concentration in the dark than in the irradiated system. The dependence of the rate of polymerization (R_p) on catalyst concentration is shown in Figure 2. The values of R_p were taken as the initial slope of time-conversion curve. The R_p is approximetely proportional to the catalyst concentration for the
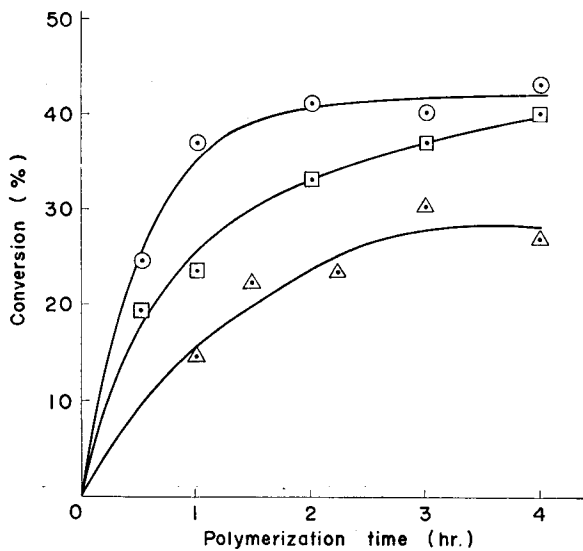
a) $[Au^{III}]=4.4\times10^{-2}$ M,
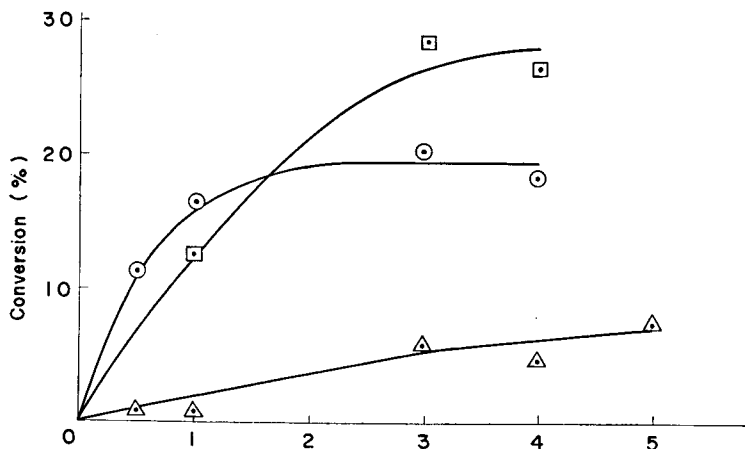
b) $[Au^{III}]=2.0\times10^{-2}$ M.

Fig. 1. Conversion curve of β-PL -NaAuCl₄·2H₂O system irradiated from 7 cm in air at 30°C.

⊙ : in quartz vessel
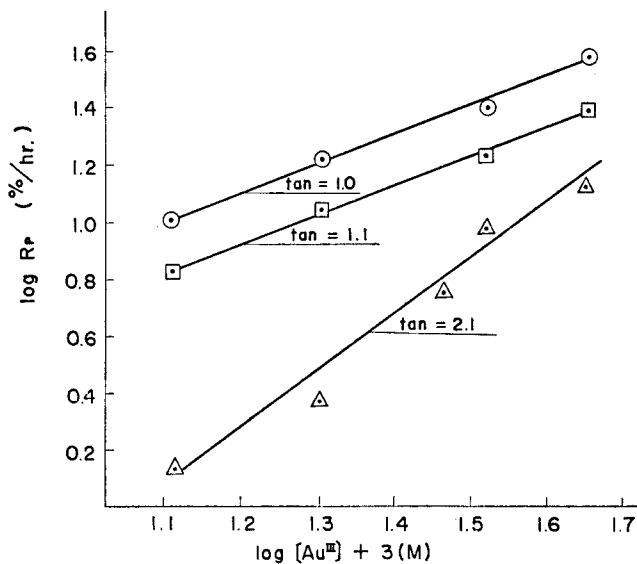▣ : in hard glass vessel
△ : polymerization in dark

Fig. 2.   Dependence of R_p on [Au^{III}]
⊙ : irradiated in a quartz vessel
▣ :   //   a hard glass vessel
△ : polymerization in dark

irradiated system using either hard glass or quartz reaction vessels, and to the
square of catalyst concentration for the polymerization in the dark.

The characteristic difference between the photopolymerization in quartz and
hard glass reaction vessels is the fact that the former system shows the faster initial
rate and the dead end tendency at the earlier period than the latter system.   The
hard glass cuts off light below the wavelength of $\sim$320 mμ.   The gold salt has its
maximum absorption at this wave length region (Figure 6) which has been considered
as a charge transfer band[5].   If photoabsorption at this charge transfer band is re-
sponisible for the acceleration of polymerization, it is readily understandable that
the difference in transmission of light through hard glass and quartz would affect
the initial R_p.   The dead end of polymerization would be due to the rapid con-
sumption of catalyst by photochemical processes and the low efficiency of initiation.
Consequently, when high intensity of light is supplied as for the polymerization in
a quartz vessel, a high concentration of active apecies may be attained during the
very initial period and soon after it will dissipate by further side reactions competing
with initiation.   In support of this view of photoreduction of catalyst, the initiator
activity of the gold salt was found to decrease when the gold salt dissolved in
nitrobenzene was irradiated from a distance of 5 cm for 15 minutes prior to addition

of monomer, and was completely inactivated by prolonged irradiation over 40 minutes.

The reaction products of Au^{III} seem to disturb the polymerization since further polymerization does not occur when additional monomer or catalyst is added after the saturation of polymer yield (Figure 3).
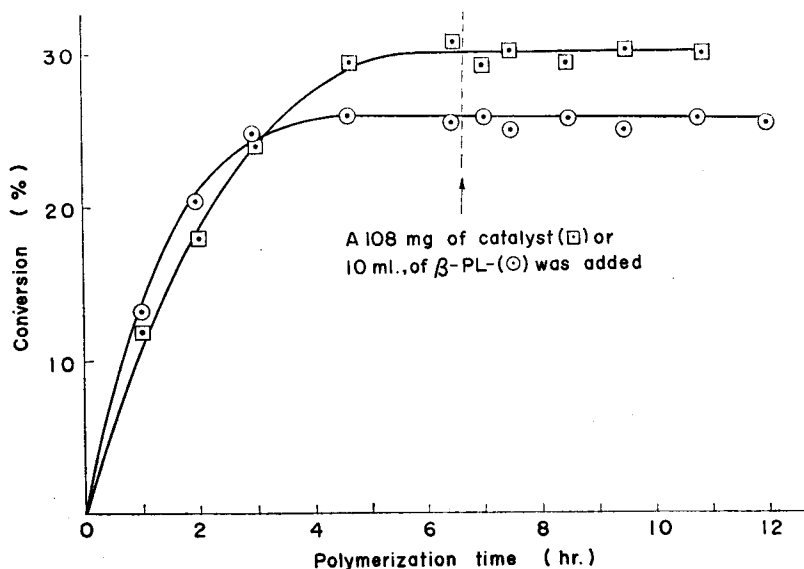

Fig. 3.   Addition of monomer and catalyst after saturation of conversion.
irradiation in a quartz vessel from the distance of 11 cm in air
at 30°C.   [NaAuCl$_4$·2H$_2$O] = 3.0 × 10^{-2} M
initial volume :   10 ml for ⊙, 20 ml for ⬤.

Conversion-Viscosity Relation

As often observed in ring opening polymerization, the viscosity of polymer increases with conversion as shown in Figure 4.
Differences between systems are small.

Effects of Additives

Since the redox process involving the Au^{III} species is definitely important, several redox reagents are examined for their effectiveness as cocatalyst.

As shown in Figure 5, ascorbic acid (insoluble in β-PL) accelerates the polymerization.   Ascorbic acid accelerated the polymerization of N-vinlycarbozole as well,[3),6)] and the effect was attributed to the reduction of Au^{III} to active Au^{II}. Since ascorbic acid alone is not capable of initiating polymerization of β-PL the same mechanism of acceleration would be considered for the polymerization of β-PL.
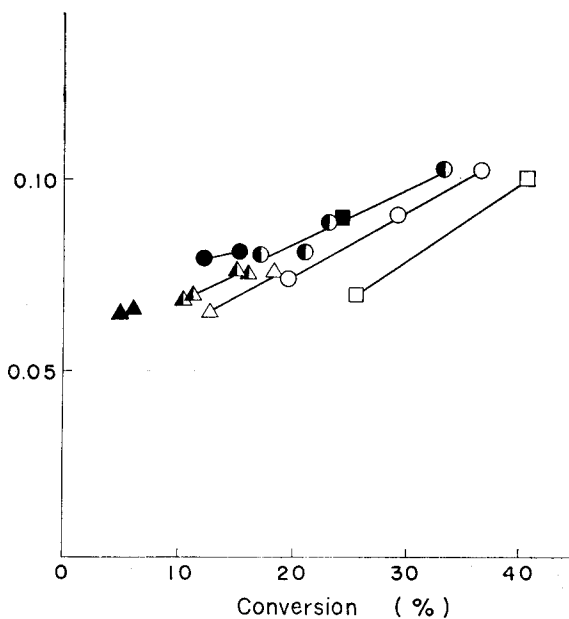
Fig. 4.   Dependence of viscosity of polymer on conversion and catalyst
concentration.
    irradiation in air at 30°C in quartz vessel
        $[NaAuCl_4 \cdot 2H_2O] = 3.4 \times 10^{-2}$ M ($\square$), 1.2×10^{-2} M ($\blacksquare$),
    irradiation in air in a hard glass vessel
        $[NaAuCl_4 \cdot 2H_2O] = 3.4 \times 10^{-2}$ M ($\bigcirc$), 3.0×10^{-2} M ($\leftmoon$),
        1.2×10^{-2} M ($\bullet$)
    Polymerization in dark
        $[NaAuCl_4 \cdot 2H_2O] = 3.4 \times 10^{-2}$ M ($\triangle$), 3.0×10^{-2} M ($\blacktriangle$),
        2.1×10^{-2} M ($\blacktriangle$)
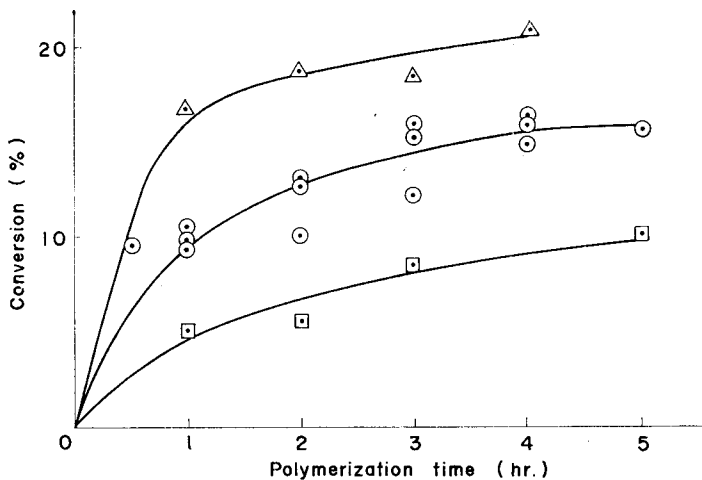
Fig. 5.   Effect of additives on polymerization in dark at 30°C.
    $[NaAuCl_4 \cdot 2H_2O] = 3.0 \times 10^{-2}$ M.
    $\odot$: in air $\boxdot$: in vacuum $\triangle$: ascorbic acid added in air.

Importance of oxygen has also been found in the polymerization of β-PL by uranyl nitrate,[2] but the origin of oxygen effect is no elucidated at present.

Effect of Solvents

When acetonitrile or nitrobenzene is added, polymerization occurs only in the latter solvent as shown in Table 1. This result would indicate that the polymer-, ization is of cationic nature.

Table I. Effect of Solvent on Polymerization at 30°C.

Solvent (ml)		Light or dark	NaAuCl₄· 2H₂O (mg)	β-PL (ml)	Polymerization time (hr.)	Conversion (%)
CH₃CN	0.5	light	12.5	2	5	0.04
"	0.5	dark	12.3	2	5	0
C₆H₅NO₂	1	light	26	3	5	22.9
"	1	dark	26	3	5	14.7

Spectrosocopy

Changes in absorption spectra during photoirradiation are shown in Figures 6 and 7. The absorption by Au^{III} at ~320 mμ decreases rapidly by photoir-radiation and the system becomes once colourless. Then, after prolonged irradiation a new absorption appears at about 550 mμ. The results of spectroscopy indicate two step decomposition of the Au^{III} salt. Since the experimental conditions
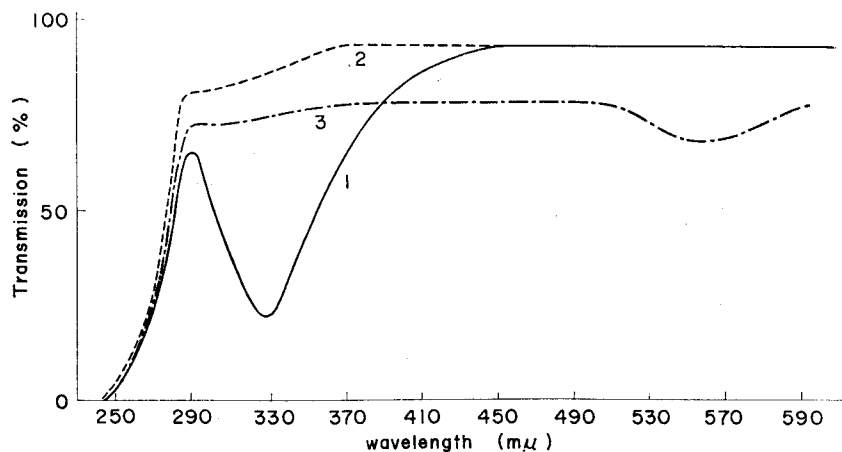

Fig. 6. Electronic spectra of the β-PL-NaAuCl₄·2H₂O system.
[Au^{III}] =9.0 × 10⁻⁴ M.   Optical length : 1 mm
irradiation from 28 cm.
1 : before irradiation
2 : irradiation for 243 min.
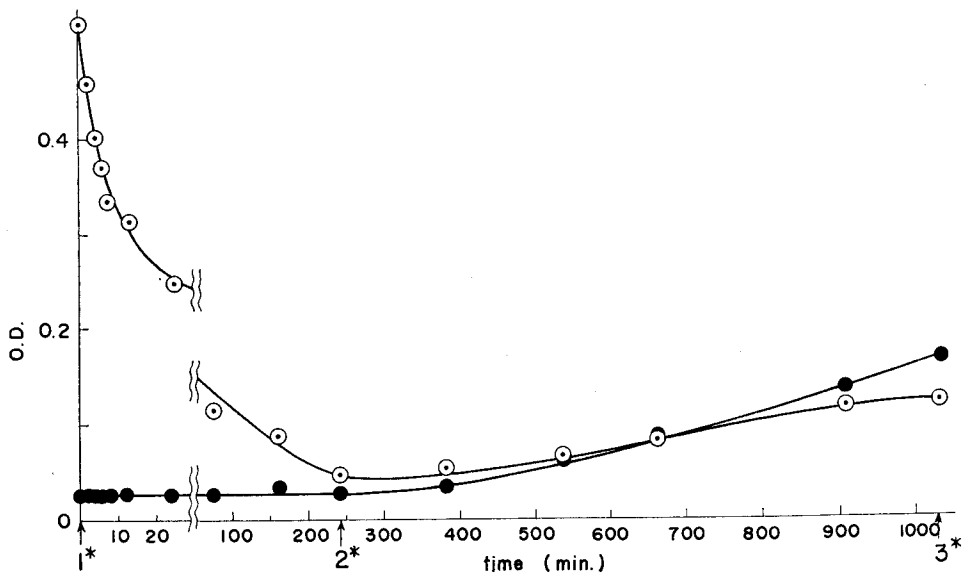3 : irradiation for 1035 min.

Fig. 7. Change in optical density of the β-PL-NaAuCl$_4$·2H$_2$O
system as a function of irradiation time.
　　Conditions for measurements are same as Fig. 6.
* corresponds to the numbers in Fig. 6.
⊙: O.D. at 324 mμ, ●: O.D. at 550 mμ.

for spectroscopy are not the same as those for polymerization experiments, it is
not possible to compare quantitatively the decomposition curve of the Au^{III} salt
(Figure 7) with the time-conversion curves.　The initial rapid fall of the absorption
at 320 mμ seems to correspond to the initial fast rate of photopolymerization in a
quartz vessel.

Comparison with the Polymerization of N-Vinylcarbazole (VCZ) initiated by NaAuCl$_4$·2H$_2$O

　　The polymerization of β-PL initiated by NaAuCl$_4$·2H$_2$O is comparable to that
of VCZ using the same initiator in view of the acceleration by photoirradiation and
also in the presence of ascorbic acid.　The time-conversion curve of the present
system could not be interpreted kinetically as clear as the VCZ-NaAuCl$_4$·2H$_2$O
system.　Similar as the polymerization of VCZ, it is difficult to consider initiation
mechanisms other than those involving redox processes between β-PL and Au^{III} and/
or Au^{II} or other decomposition products of Au^{III}.　If one assumes that NaAuCl$_4$·
2H$_2$O acts as an ordinary cationic initiatior, namely as an acid, the photochemical
acceleration as well as the effect of ascorbic acid could not be explained.

　　Differences in behaviours of β-PL and VCZ such as the dead end nature of time-

conversion relation and the increase in molecular weight of polymer with conversion of β-PL could be attributed to the lower reactivity of β-PL in initiation by the gold salt, to the slower rate of propagation of β-PL in comparison with VCZ and to the instability of the gold salt in oxygenated solvents. The facts that the gold salt looses the initiating activity quickly in THF[6] and the polymerization of vinyl ethers initiated by $NaAuCl_4 \cdot 2H_2O$ gets to the saturation yield at the early stage[6] would indicate the spontaneous decomposition of the gold salt in oxygenated solvents or monomers. The saturation of polymerization yield of β-PL would be in part due to the spontaneous decomposition of initiator which will not contribute to the intiation of polymerization.

References

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