# *Anionic Polymerization of Vinylidene Chloride. II. Homopolymerization Initiated by n-Butyllithium*

By Akio KONISHI

(Received May 10, 1961)

A number of attempts to polymerize various vinyl monomers by *n*-butyllithium have recently been reported on such monomers as butadiene[2-4], isoprene[5-9], styrene[10-16], methyl methacrylate[12,13], acrylonitrile[12,13], vinyl chloride[13,17], methyl and butyl acrylates[12], dimethyl maleate[12], vinyl acetate[12,13], allyl acetate[12] and vinyl *n*-butyl ether[13], though successful results have not yet been obtained in the last five monomers. From the copolymerization data it has been proposed that the polymerization initiated by this catalyst is of anionic mechanism[18,19].

An attempt to polymerize vinylidene chloride under anionic conditions by *n*-butyllithium has been made because the monomer is considered to be susceptible to anionic catalysis, as has been discussed in a previous paper[1].

## Experimental

A vinylidene chloride monomer produced by the Kureha Kasei Co. was repurified by drying it over calcium hydride and then distilling it under an argon atmosphere in the presence of copper stearate immediately before use. *n*-Hexane and *n*-butyl bromide were dried over calcium hydride and distilled immediately before use. Argon was freed from the oxygen by passing it through an alkaline solution of pyrogallol and drying it with concentrated sulfuric acid.

*n*-Butyllithium, prepared in *n*-hexane by the reaction of *n*-butyl bromide with lithium metal by a method similar to that of Gilman[20], was kept standing in the Schlenk apparatus and its concentration checked by titration[21] before use.

From half to one mole of monomer was used in every run. The addition of the reagents and the polymerizations were carried out under argon. Into

1) A. Konishi, This Bulletin, 35, 193 (1962).
2) A. A. Korotkov, *Angew. Chem.*, 70, 85 (1958).
3) V. A. Kropachev, B. A. Kolgolosk and N. I. Nikolaev, *Doklady Akad. Nauk, S. S. S. R.*, 115, 516 (1957).
4) I. Kuntz and A. Gerber, *J. Polymer Sci.*, 42, 299 (1960).
5) H. Hsieh and A. V. Tobolsky, ibid., 25, 245 (1957).
6) H. Hsieh, D. J. Kelley and A. V. Tobolsky, ibid., 26, 240 (1957).
7) H. Morita and A. V. Tobolsky, *J. Am. Chem. Soc.*, 79, 5853 (1957).
8) R. S. Stearns and L. E. Forman, *J. Polymer Sci.*, 41, 381 (1959).
9) A. A. Korotkov, N. N. Chesnokova and L. B. Trukhanova, *Visokomolekulyarnye Soedineniya*, 1, 46 (1959).
10) A. Zilkha, M. Albeck and M. Frankel, *J. Chem. Educ.*, 35, 345 (1958).
11) H. Sinn, C. Lundborg and K. Kirchner, *Angew. Chem.*, 70, 744 (1958).
12) M. Frankel, A. Ottolenghi, M. Albeck and A. Zikka. *J. Chem. Soc.*, 1959, 3858.
13) J. Furukawa, T. Tsuruta, K. Ito, I. Kashiuchi and A. Kawasaki, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), 63, 96 (1960).
14) K. F. O'Driscoll and A. V. Tobolsky, *J. Polymer Sci.*, 35, 259 (1959).
15) F. J. Welch, *J. Am. Chem. Soc.*, 81, 1345 (1959).
16) R. J. Kern, *Nature*, 187, 410 (1960).
17) S. A. Solvic, Belg. Pat. 566529 (Oct. 15, 1958).
18) K. F. O'Driscoll and A. V. Tobolsky, *J. Polymer Sci.*, 37, 363 (1959).
19) N. L. Zutty and F. J. Welch, ibid., 43, 445 (1960).
20) H. Gilman, J. A. Beel, C. G. Branner, M. W. Bullock, G. E. Dunn and L. S. Miller, *J. Am. Chem. Soc.*, 71, 1499 (1949).
21) M. Frankel, J. Rabani and A. Zilkha, *J. Polymer Sci.*, 28, 387 (1958).

a four-necked flask fitted with a stirrer, thermometer, and a gas inlet as well as an outlet for the argon, the required amounts of monomer and solvent were added. At above 30°C the polymerizations were carried out in a 150 cc. glass ampoule as a polymerization apparatus, and the reagents used were all added at −70°C under argon. The polymerization was stopped after the required time interval by adding methanol, followed by the pouring in of excess methanol. The polymer precipitated was filtered off with a glass filter, washed with methanol and water successively, and then dried to a constant weight in a vacuum-desiccator at 40°C. The rate of polymerization was determined gravimetrically.

Intrinsic viscosities were measured in cyclohexanone at 30°C, using an Ubbelohde dilution viscometer. The chlorine content of the polymer was measured by the combustion method with a Shimadzu universal micro determination apparatus type UM-2. The infrared spectra of the pressed potassium bromide disk containing the above samples were measured by a Perkin-Elmer model 13 infrared spectrophotometer.

## Results

Polymerizations were carried out with *n*-hexane as a solvent, and the influences of monomer concentration ($M$), catalyst concentration (BuLi) and polymerization temperature on the rate of polymerization ($R_p$), intrinsic viscosity [$\eta$] and chlorine content were investigated. The initial slope of conversion vs. time curve was taken as the rate of polymerization. The rate was markedly influenced by the method of the addition of the catalyst, as is illustrated in Fig. 1. In this paper, however, the author will report on the rate of polymerization induced by adding all the catalyst at the beginning of the reaction.

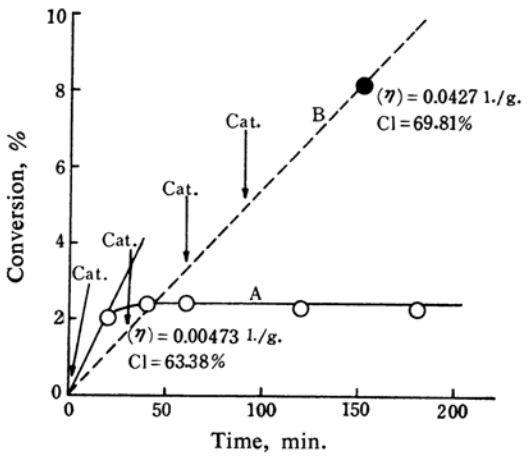


Fig. 1. Conversion vs. time curve.
Temp., 25°C ; A : ($M$) = 11.13 mol./l., (BuLi) = 0.111 mol./l., whole amount of the catalyst was added initially ; B : ($M$) = 11.44 mol./l., (BuLi) (final) = 0.0917 mol./l., each quarter of the whole amount of the catalyst was successfully added in every 30 min.

As listed in Table I, hydroquinone, a typical radical scavenger, showed little effect on the rate of polymerization, whereas dibenzoyl peroxide, a typical peroxide, reacted immediately with the catalyst and showed an inhibiting effect. This is thought to be an experimental evidence of the ionic character of the polymerization.

In Fig. 2 it is shown that, for a given monomer concentration, the rate is independent of the catalyst concentration above the critical

TABLE I. EFFECT OF INGREDIENTS
Temp., 25°C ; time, 30 min.; ($M$) = 5.00 mol./l., (BuLi) = 0.100 mol./l.

| Ingredient | Concn. mol./l. | Conv. % | [$\eta$] l./g. |
|---|---|---|---|
| None | — | 1.81 | 0.0064 |
| Hydroquinone | 0.050 | 2.06 | 0.0036 |
| Dibenzoyl peroxide | 0.050 | 0.017 | 0.0048 |

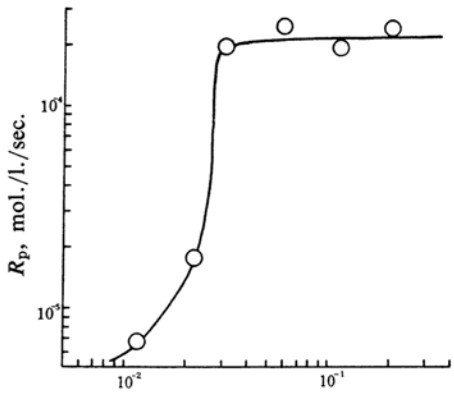


Fig. 2. The rate vs. catalyst concentration.
Temp., 25°C ; ($M$) = 10.0∼12.1 mol./l.

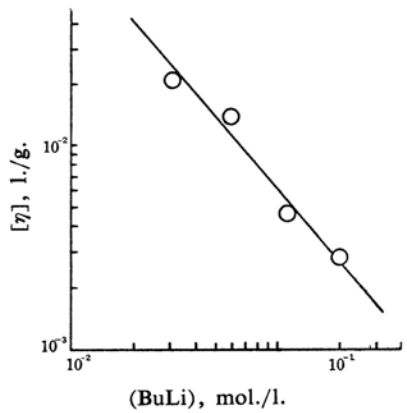


Fig. 3. Intrinsic viscosity vs. catalyst concentration. Condition, the same as in Fig. 2.

value (0.03 mol./l. in the case). The decrease in viscosity and chlorine content are inversely proportional to the increment of the concentration of the catalyst, as is shown in Figs. 3 and 4 respectively. Figure 4 also suggests that the polar chlorine atom reacted with the catalyst.

The rate of polymerization is proportional to the square of the monomer concentration, as in Fig. 5. Intrinsic viscosity decreases with the increasing monomer concentration, as in Fig. 6.

The effect of temperature on the rate was investigated in a range between −30 and +50°C, and the activation energy of the overall rate of polymerization was calculated to be 10.7 kcal./mol. from the Arrhenius plot, as is shown in Fig. 7. This relatively small value agrees with the activation energy found in methyl methacrylate (7.6 kcal./mol.)[13] and vinyl chloride (8.8 kcal./mol.)[13]. Intrinsic viscosity passed through a maximum at +10°C, as in Fig. 8. Chlorine content is almost independent of the temperature.

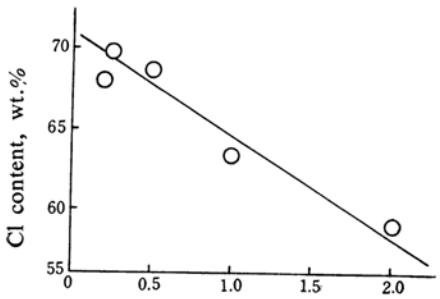


Fig. 4. Cl content vs. catalyst concentration. Condition, the same as in Fig. 2.

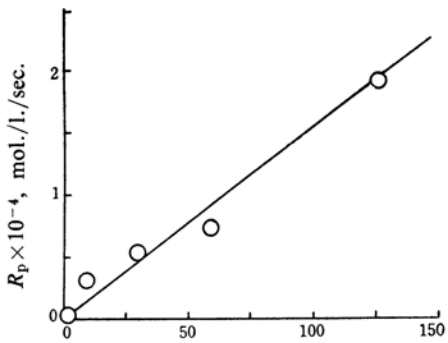


Fig. 5. The rate vs. monomer concentration. Temp., 25°C ; (BuLi) = 1.00 mol.% to monomer.

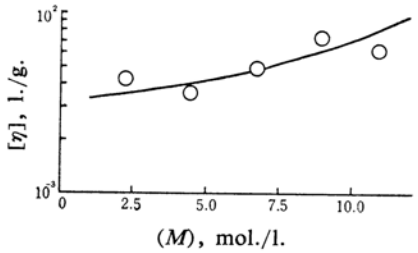


Fig. 6. Intrinsic viscosity vs. monomer concentration.
Temp., 25°C ; (BuLi) = 0.1086 mol./l.

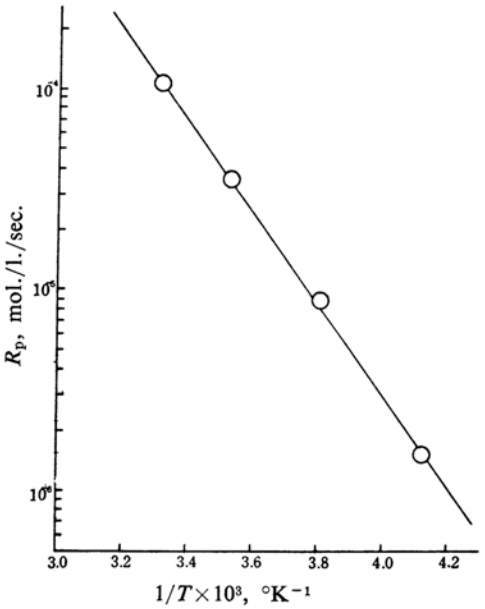


Fig. 7. The rate vs. temperature.
$(M) = 8.91$ mol./l.; (BuLi) = 0.0893 mol./l.

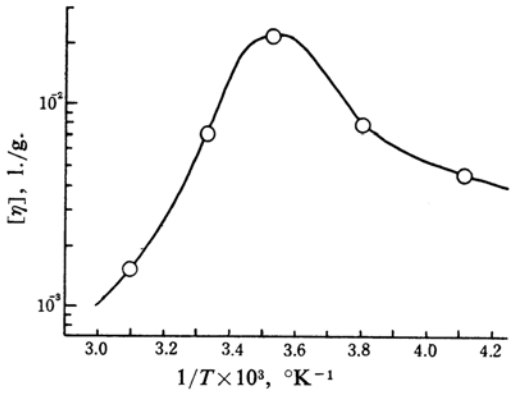


Fig. 8. Intrinsic viscosity vs. temperature. Condition, the same as in Fig. 7.

## Discussion

The kinetics of anionic polymerization of some other monomers initiated by *n*-butyllithium have been presented by O'Driscoll[14], Welch[15], Furukawa[13] and Korotkov[9], though they have not coincided with one another at

several points. The following mechanism is suggested:

$$(BuLi)_n \rightleftharpoons BuLi + (BuLi)_{n-1} \quad (1)$$

$$BuLi + M \xrightarrow{k_i} BuM^- + Li^+ \quad (2)$$

$$BuM^- + M + Li^+ \xrightarrow{k_p} \cdots \xrightarrow{k_p} Bu(M)_n^- + Li^+ \quad (3)$$

In a propagating step, the structure of the growing polymer chain seems to be not so simple as that expressed in an ion-pair form like 4, but it is assumed to be a complex one like cyclic structure 5 or like ionic quadrapole 6, as suggested by Cram[22] or Mark[23] in the stereospecific polymerization of methyl methacrylate or diene:

$$Bu\text{-}(\text{-}CH_2\text{-}CCl_2\text{-})_m\text{-}CH_2\text{-}\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{\overset{|}{\underset{|}{C}}}}{}^{-} : Li^+ \quad (4)$$

$$Bu\text{-}(\text{-}CH_2\text{-}CCl_2\text{-})_m\text{-}CH_2\text{-}\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{\overset{|}{\underset{|}{C}}}}{}^{-} \cdots Li^+ \quad (5)$$

$$Bu\text{-}(\text{-}CH_2\text{-}CCl_2\text{-})_m\text{-}CH_2\text{-}\underset{\displaystyle Li^+}{\overset{\displaystyle Li^+}{\overset{|}{\underset{|}{C}}}}{}^{-} : Bu^- \quad (6)$$

Since poly(vinylidene chloride) has no assymmetric centers, the problem of the tacticity of the polymer will not arise, the crystallinity of the polymer here obtained being similar to the polymer obtained by radical polymerization from X-ray study. It seems that structure 5 or 6 serves to stabilize the growing polymer anion. The termination probably occur by association reaction as follows:

$$Bu(M)_n^- + Li^+ + (BuLi) \xrightarrow{k_{t_1}} Bu(M)_nLi(BuLi) \quad (7)$$

or, less probably,

$$Bu(M)_n^- Li^+ \xrightarrow{k_{t_2}} Bu(M)_nLi \quad (8)$$

Since the elimination of chlorine is very remarkable, the following termination reactions are also suggested:

$$Bu\text{-}(\text{-}CH_2\text{-}CCl_2\text{-})_m\text{-}CH_2\text{-}\underset{\displaystyle Cl}{\overset{\displaystyle Cl^{\delta-}}{\overset{|}{\underset{|}{C}}}} : Li^+ \xrightarrow{k_{t_3}} Bu\text{-}(\text{-}CH_2\text{-}CCl_2\text{-})_m\text{-}CH_2\text{-}\underset{\displaystyle Cl}{\overset{|}{C}}{}^{-} + LiCl \quad (9)$$

then

$$\xrightarrow{H\text{-}R} Bu\text{-}(\text{-}CH_2\text{-}CCl_2\text{-})_m\text{-}CH_2\text{-}CHCl \quad (10)$$

or

$$\longrightarrow Bu\text{-}(\text{-}CH_2\text{-}CCl_2\text{-})_m\text{-}CH{=}CHCl \quad (11)$$

Other side reactions which induce the abstraction of chlorine from the polymer chain may be:

$$\text{-}CH_2\text{-}\underset{\displaystyle Cl}{\overset{\displaystyle Cl^{-\delta}}{\overset{|}{\underset{|}{C}}}}\text{-} + Li^+ \longrightarrow \text{-}CH_2\text{-}\underset{\displaystyle Cl}{\overset{|}{C}}{}^{+}\text{-} + LiCl \quad (12)$$

$$\xrightarrow{Bu} \text{-}CH_2\text{-}\underset{\displaystyle Cl}{\overset{\displaystyle Bu}{\overset{|}{\underset{|}{C}}}}\text{-} \quad (13)$$

$$\xrightarrow{H\text{-}R} \text{-}CH_2\text{-}CHCl\text{-} \quad (14)$$

The decrease in the chlorine content of the polymer can probably be attributed to reactions 9 and 12, in which the chlorine atom is eliminated as lithium chloride from the polymer chain.

Making the steady state assumption for the chain reaction:

$$k_i(M)(BuLi) = k_{t_1}(BuLi)(Bu(M)_n^-Li^+) + k_{t_2}(Bu(M)_n^-Li^+) + k_{t_3}(Bu(M)_n^-Li^+)$$
$$= (Bu(M)_n^-Li^+)\{k_{t_1}(BuLi) + k_{t_2} + k_{t_3}\} \quad (15)$$

$$(Bu(M)_n^-Li^+) = k_i(M)(BuLi)/\{k_{t_1}(BuLi) + k_{t_2} + k_{t_3}\} \quad (16)$$

$$R_p = k_p(Bu(M)_n^-Li^+)(M) = k_ik_p(M)^2(BuLi)/\{k_{t_1}(BuLi) + k_{t_2} + k_{t_3}\} \quad (17)$$

Supposing $k_{t_2}, k_{t_2} \ll k_{t_1}(BuLi)$ (18)

$$R_p \propto (M)^2 \quad (19)$$

Kinetic chain length $\overline{X}_n$ is written as

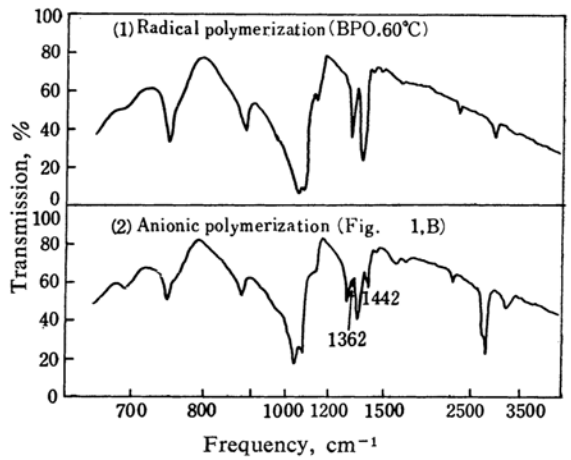


Fig. 9. Infrared spectrum of poly(vinylidene chloride).

23) S. Krim, *Fortschr. Hochpolym.-Forsch.*, **2**, 51 (1960).
22) D. J. Cram and K. R. Kopecky, *J. Am. Chem. Soc.*, **81**, 2748 (1959).

$$\overline{X}_n = R_p/R_t = k_p(\mathrm{Bu}(M)_n{}^-\mathrm{Li}^+)(M)/$$
$$(\mathrm{Bu}(M)_n{}^-\mathrm{Li}^+)\{k_{t_1}(\mathrm{BuLi}) + k_{t_2} + k_{t_3}\}$$
$$= k_p(M)/\{k_{t_1}(\mathrm{BuLi}) + k_{t_2} + k_{t_3}\} \quad (20)$$
$$\log[\eta] \propto \overline{X}_n \propto (M)/(\mathrm{BuLi}) \quad (21)$$

Namely, 19 and 21 accord with the experimental results qualitatively.

Infrared spectra of the polymer are compared with that of the polymer polymerized by dibenzoyl peroxide at 60°C, as is shown in Fig. 9. Characteristic differences observed at 1362 and 1442 $cm^{-1}$, are attributed to the methyl group in the terminal and pendant butyl groups of the polymer. These absorptions are thought to have been shifted by chlorine from the 1375 and 1457 $cm^{-1}$ which were observed in polyethylene[23].

**Summary**

The polymerization of vinylidene chloride initiated by *n*-butyllithium in *n*-hexane has been investigated. It has been found that the initial rate of polymerization is independent of the catalyst concentration above a critical value and is proportional to the square of the monomer concentration. The activation energy of the over-all rate was 10.7 kcal./mol. The chlorine content of the polymer decreased inversely with the increase of catalyst concentration. An anionic mechanism is suggested for the polymerization kinetics.

*Tokyo Laboratory*
*Kureha Kasei Co., Ltd.*
*Shinjuku-ku, Tokyo*