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Base-Catalyzed Polymerization of Vinyl Acetamide and Allyl Cyanide

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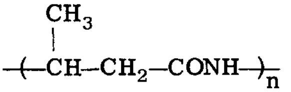
Summary

The base-catalyzed polymerizations of vinyl acetamide and allyl cyanide have been studied. It was found by chemical and spectroscopic analyses that the polymer obtained from vinyl acetamide was poly(2-methyl-β-alanine),



$$-\!\left(-\begin{array}{c}CH_3\\|\\CH\end{array}-CH_2-CONH-\right)_n$$

which was the same structure as the polymer prepared by base-catalyzed polymerization of crotonamide. It is concluded, therefore, that vinyl acetamide was polymerized through the isomerization of allyl group and the proton transfer reaction from amide group. The gas-chromatographic analysis of the polymerization system showed that vinyl acetamide was consumed faster than crotonamide. This fact suggests that an intermediate other than crotonamide might be present in the process of isomerization of vinyl acetamide. On the other hand, in the base-catalyzed polymerization of allyl cyanide, the allyl group was isomerized, but the reaction of cyanide group hardly occurred.

It is well known that the proton transfer reaction occurs in the base-catalyzed polymerization of acrylamide and its derivatives, in which amide group combines directly with a olefinic double bond. It has been found in the previous papers that the rate of proton transfer polymerization to vinyl polymerization depends on the polymerization conditions and there are two types of the proton transfer reactions: intra- and intermolecular reaction [1–3].

Also, proton transfer polymerization of vinyl benzamide [4–6] and vinyl acetamide [7] has been observed in which an amide group combines indirectly with an olefinic double bond. As for vinyl acetamide, it was reported that the polymer obtained by an Na metal catalyst had an amide group in the polymer backbone [7]. Vinyl acetamide is an interesting monomer, because vinyl acetamide has two kinds of active protons, in the amide group and in the active methylene group. In the polymerization of vinyl acetamide, therefore, the proton transfer step might occur from a methylene group; such a reaction does not exist in the polymerization of acrylamide.

In this paper the polymer structure and kinetics in the base-catalyzed polymerization of vinyl acetamide are studied, and the proton transfer reaction in vinyl acetamide is discussed. Furthermore, the base-catalyzed polymerization of allyl cyanide containing an active methylene as well as vinyl acetamide is briefly studied.

EXPERIMENTAL

Materials

Vinyl acetamide was synthesized from allyl bromide through hydrolysis of allyl cyanide and amidation of vinyl acetic acid. The crude product was recrystallized three times from benzene to give the plate-form crystal, m.p. 74°C (lit. [8] 72–72. 5°C). It was indicated by the gas-chromatographic analyses that the product consisted of 95% vinyl acetamide and 5% crotonamide. No other impurity was found by this method.

Crotonamide obtained commercially was recrystallized three times from acetone to give needle-form crystal, m.p. 161°C (lit. [9] 159. 5–160. 0°C).

Allyl cyanide was obtained by redistillation of the product on the way to synthesis of vinyl acetamide: b.p. 116. 8–119. 0°C, $n_D^{16.4}$ 1. 4059 (lit. [10] b.p. 116–121°C, n_D^{20} 1. 4060). The purity of allyl cyanide was more than 98% by gas-chromatographic analysis.

n-Butyllithium was prepared in benzene solution by the method described previously [1].

Sodium-tert-butoxide obtained commercially was dried at 40°C in vacuum before use.

Polymerization of Vinyl Acetamide

Polymerization was carried out in two methods. For the formation of polymer, catalyst was added to a test tube containing monomer, solvent, and the inhibitor for radical polymerization (N-phenyl-β-naphthylamine 20 mg/100 ml), and the test tube was sealed under a nitrogen atmosphere. The reaction mixture were heated for a definite time and then the mixture was poured into the acetone (ca. 10 times of volume of the mixture) containing a small amount of hydrochloric acid. The polymer was obtained by filtration, washed with acetone, and dried at 40°C for 48 hr in vacuum.

On the other hand, for the measurement of the rate of reaction, polymerization was carried out in a three-necked flask (200 ml). The reaction was carried out with stirring under a nitrogen atmosphere. A part of reaction mixture was picked out by a syringe in the specified interval and the residual monomer concentration was measured by gas chromatography [3] [column, poly(ethylene glycol) (6000); column temperature, 185°C; carrier gas, H_2 (70 ml/min)].

Indentification of the Polymer Structure

One half gram of the polymer prepared from vinyl acetamide was dissolved to 10 ml of 50% sulfuric acid and was heated at 110°C for about 10 hr. Then the solution was neutralized with barium hydroxide. After removal of the barium sulfate by filtration, the filtrate was evaporated. The residue was submitted to thin-layer chromatography (TLC) to compare with β- and γ-amino-n-butyric acid. A sample was developed with the mixture of chloroform, methyl alcohol, and 17% aqueous ammonia (2:2:1 volume ratio) on a silica gel layer and subsequently the amino acid developed was detected by ninhydrin test.

IR spectra were measured by KBr disk with a Shimadzu Model IR-27 or Japan Spectroscopic Model DS-402G infrared spectrometer.

NMR spectra of the polymers were measured in formic acid (7% w/v) with a JNM 3H-60 proton resonance spectrometer operating at 60 Mc at room temperature, and tetramethylsilane was used as the internal reference.

Polymerization of Allyl Cyanide

A monomer and a solvent were redistilled into the reaction vessel connecting with the glass tube, which contained a catalyst solution in vacuum. Sealing off these tubes in vacuum, the reaction vessels were held at reaction temperature and polymerization was started by mixing a monomer solution with a catalyst solution. After the desired time, the reaction mixture was poured into a large amount of methanol containing a small amount of hydrochloric acid. The product was removed by filtration and dried at 40°C for 48 hr in vacuum. The concentration of allyl cyanide in the reaction mixture was determined by gas-chromatographic analysis (column, poly(ethylene glycol) (6000); column temperature, 85°C; carrier gas, H_2 (70 ml/min)].

The molecular weight of polymer was measured by the ebullioscopic method in acetone solution.

RESULTS AND DISCUSSION

Polymerization of Vinyl Acetamide by n-BuLi

The change of the monomer concentration during polymerization of vinyl acetamide in toluene was measured at various temperatures. Figures 1–3 show that crotonamide is formed during the consump-

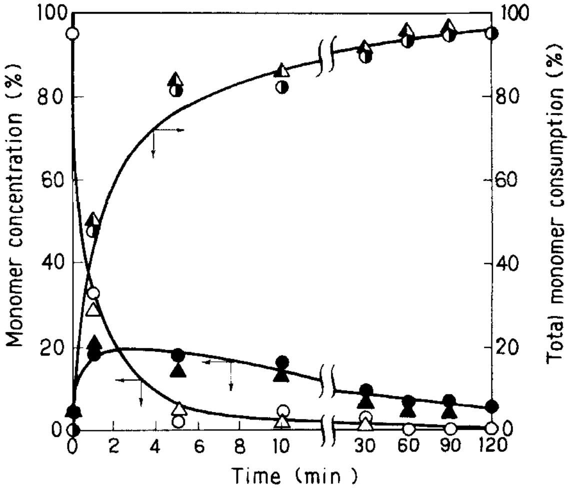


FIG. 1. Rate of monomer consumption in the polymerization of vinyl acetamide in toluene at 100°C: ○△, concentration of vinyl acetamide; ●▲, concentration of crotonamide in reaction mixture; ◑▲, total monomer consumption; $[M]_0$, 0.29 mole/liter; [n-BuLi], ○●◑, 48, △▲◭, 24 mmoles/liter.

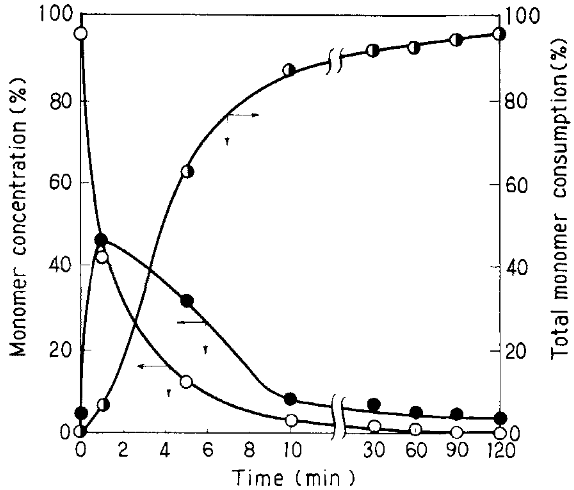


FIG. 2. Rate of monomer consumption in the polymerization of vinyl acetamide in toluene at 80°C: $[M]_0$, 0.29 mole/liter, [n-BuLi], 48 mmoles/liter. (Key the same as Fig. 1.)

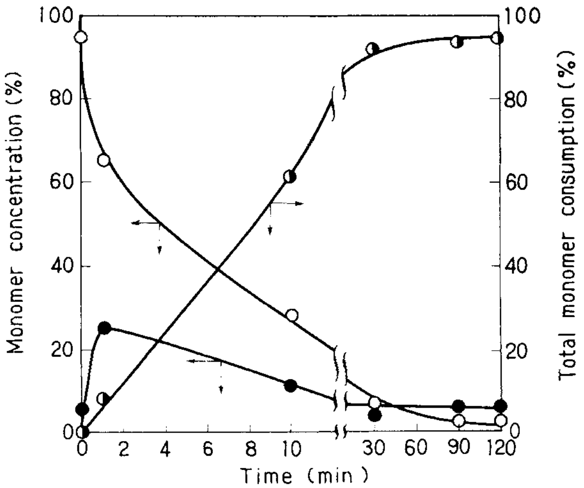
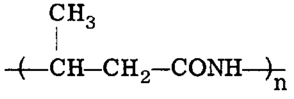


FIG. 3. Rate of monomer consumption in the polymerization of vinyl acetamide in toluene at 60°C: $[M]_0$, 0.29 mole/liter; [n-BuLi], 48 mmoles/liter. (Key the same as Fig. 1.)

tion of vinyl acetamide and that its concentration decreases through the maximum value with increasing the reaction time. A large amount of crotonamide was produced at 80°C. The total monomer consumption, that is, the sum of vinyl acetamide and crotonamide consumed, is also shown in Figs. 1–3. As shown in Fig. 1, the rate of monomer consumption was independent of the catalyst concentration in the range 24–48 mmoles/liter.

The total amounts of consumed monomer were compared with the yield of polymer. Table 1 shows that the amount of polymer is smaller than that of monomer consumption and the yield of polymer decreases with lowering polymerization temperature although the monomer was consumed almost completely, even at 60°C.

As described later, the polymer, that is, the acetone-insoluble products in the polymerization of vinyl acetamide were poly(2-methyl-β-alanine) (1).



$$\left(-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-CONH-\right)_n \qquad (1)$$

On the other hand, the low molecular product was obtained by ether extraction of monomers from the acetone-soluble part of the polymerization mixture, and its yield was nearly equal to the difference between monomer consumption and polmer yield. IR spectrum of

TABLE 1. Polymerization of Vinyl Acetamide by n-BuLi in Toluene ($[M]_0$, 0.29 mole/liter; [n-BuLi], 48 mmoles/liter; time, 2 hr)

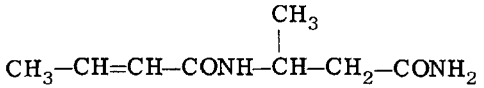
Temp., °C	Total monomer consumption, %	Polymer yield, %	η_{sp}/c of polymer[a]
100[b]	93	57	0.05
100	95	80	0.05
80	97	61[c]	0.05
60	96	2	—

[a] Measured in formic acid solution (1% w/v) at 30°C.

[b] n-BuLi; 24 mmoles/liter.

[c] Yield of acetone-soluble and ether-insoluble product was 31%.

the acetone-soluble and ether-isoluble products was similar to that of crotonamide monomer, but showed new —CONH absorptions in addition to $-CH_3$, —C=C—, and $-CONH_2$ groups. In view of this fact and the results in the previous paper that the acetone-soluble and ether-insoluble products in polymerization of acrylamide [3] and methacrylamide [7] are mainly the dimer, it was estimated that the acetone-soluble product in the polymerization of vinyl acetamide would consist of mainly crotonamide dimer (2):



$$CH_3{-}CH{=}CH{-}CONH{-}\overset{\overset{\displaystyle CH_3}{|}}{C}H{-}CH_2{-}CONH_2 \qquad (2)$$

It has been observed in the polymerization of acrylamide [3] that the large amount of dimer was obtained under the condition that the intermolecular proton transfer reaction occurred more easily than the intramolecular reaction. In view of the fact that dimers were obtained and the molecular weights of polymers were low, it may be concluded that proton transfer is dominantly due to the intermolecular reaction.

The polymerization of vinyl acetamide was carried out in pyridine, because it is not only strongly polar but also a good solvent for monomers in comparison with toluene. Time-conversion curves in polymerization of vinyl acetamide and crotonamide in pyridine are shown in Fig. 4. This figure shows that crotonamide was formed in the polymerization of vinyl acetamide and a small amount of

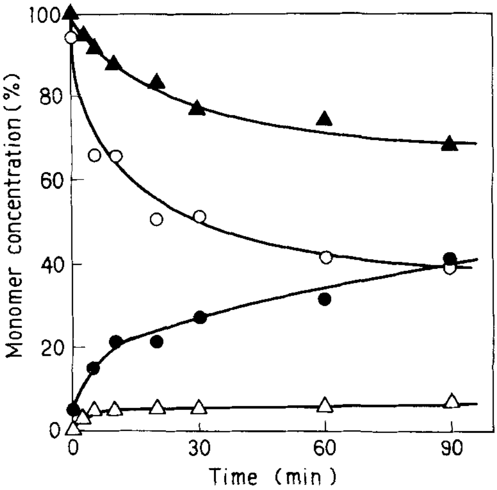


FIG. 4. Rate of monomer consumption in the polymerization of vinyl acetamide (VAAm) and crotonamide (CAm) in pyridine at 100°C: ○, concentration of VAAm in the polymerization of VAAm; ●, concentration of CAm in the polymerization of VAAm; ▲, concentration of CAm in the polymerization of CAm; △, concentration of VAAm in the polymerization of CAm. (VAAm contains 5.0% CAm.)

vinyl acetamide was formed in that of crotonamide. In both cases, the polymer yields for 2 hr were only 2–3%, although the monomer consumption (the amount of consumed vinyl acetamide and crotonamide) was 20% or more. It may be estimated that a monomer would be consumed mainly to prepare a dimer, since the intermolecular proton transfer was favorable in the polymerization of acrylamide in pyridine.

In Fig. 5 the rate of consumption of the total monomer in the polymerization of various monomers was compared. The monomer consumption in the polymerization of vinyl acetamide was faster than in that of crotonamide.

On the basis of the previous result that crotonamide was formed and consumed during the polymerization of vinyl acetamide, it is tentatively proposed as one of the mechanisms that vinyl acetamide is isomerized into crotonamide by a base catalyst and then polymers are obtained by the polymerization of crotonamide. However, the result that monomer consumption of vinyl acetamide was faster than that of crotonamide cannot be explained by this mechanism. Therefore, it seems reasonable to assume as follows. Vinyl ace-

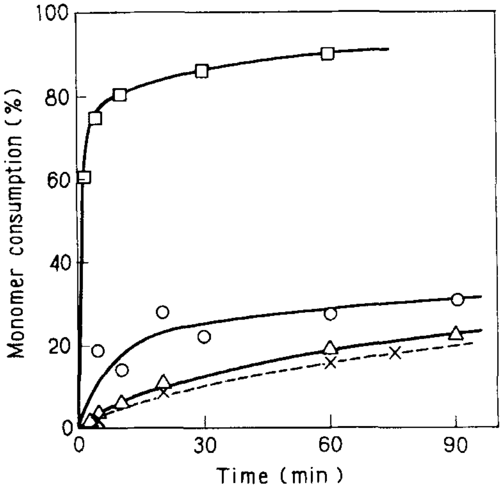


FIG. 5. Comparison of the rate of monomer consumption: Solvent, pyridine; temp., 100°C.

	$[M]_0$, moles/liter	[C], mmoles/liter
□ Acrylamide	0.56	9
○ Vinyl acetamide	0.56	15
△ Crotonamide	0.56	15
× Methacrylamide	0.47	26

tamide might be isomerized through the active intermediate such as isocrotonamide (cis isomer) into crotonamide (trans isomer) and a more unstable intermediate would be polymerized faster than crotonamide. However, the active intermediate cannot be confirmed at present.

Polymerization of Vinyl Acetamide by t-BuONa

The results of polymerization of vinyl acetamide and crotonamide by t-BuONa are shown in Table 2. In toluene the monomer consumption and polymer yield in polymerization of vinyl acetamide were larger than those of crotonamide at the same condition. Otherwise, in pyridine, the amount of the acetone-insoluble part obtained from vinyl acetamide was smaller than that from crotonamide. IR and NMR spectra of the acetone-insoluble polymers obtained by t-BuONa were the same as the spectra of that obtained by n-BuLi.

TABLE 2. Polymerization of Vinyl Acetamide (VAAm) and Crotonamide (CAm) by t-BuONa ($[M]_0$, 0.29 mole/liter; [t-BuONa], 0.10 mole/liter; time, 2 hr; temp., 100°C)

Monomer	Solvent	Residual monomer concentration, %		Total monomer consumption, %	Polymer yield, %	η_{sp}/c of polymer[a]
		VAAm	CAm			
VAAm	Toluene	4	21	75	56	0.05
VAAm	Pyridine	12	44	44	6	—
CAm	Toluene	0	57	43	41	0.05
CAm	Pyridine	7	60	33	21	—

[a] Measured in formic acid solution (1% w/v) at 30°C.

Structure of Poly(Vinyl Acetamide)

IR spectra of the polymers obtained by base-catalyzed polymerizations of vinyl acetamide and crotonamide are shown in Fig. 6.

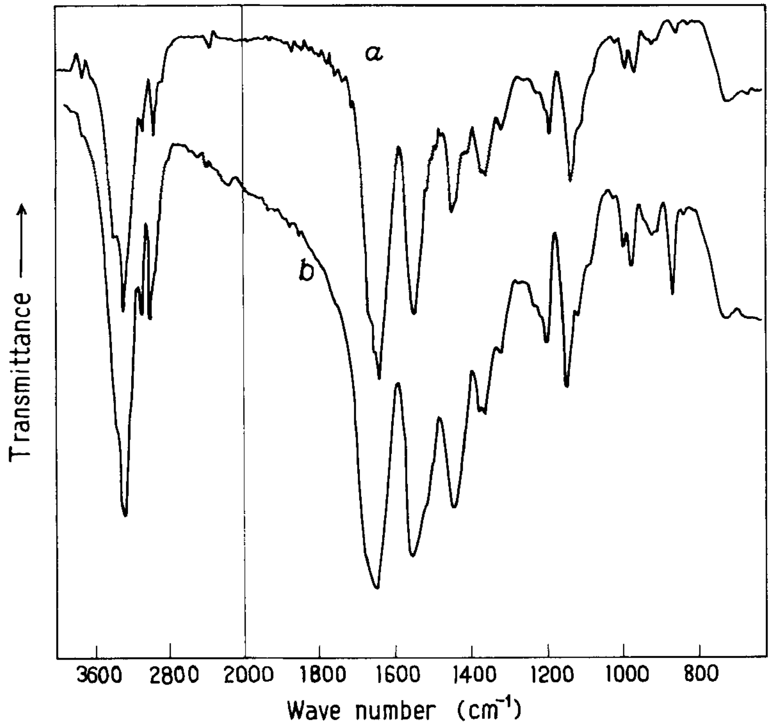


FIG. 6. IR spectra of poly(vinyl acetamide) (a) and polycrotonamide (b).

These spectra were quite similar and exhibited absorptions due to methyl groups at 2960 and 1442 cm^{-1} and a characteristic band of secondary amide at 1535 cm^{-1}. These facts indicate that both polymers have amide groups in their backbones and pendant methyl groups.

By TLC analyses, β-amino-n-butyric acid [$CH_3CH(NH_2)CH_2COOH$] was detected and γ-amino-n-butyric acid was not observed in the hydrolyzates of polymer obtained from vinyl acetamide and crotonamide. The results also show that both polymers would consist of the same repeating unit.

NMR spectra of poly(vinyl acetamide) and polycrotonamide are compared in Fig. 7. Apparently, these spectra were the same and

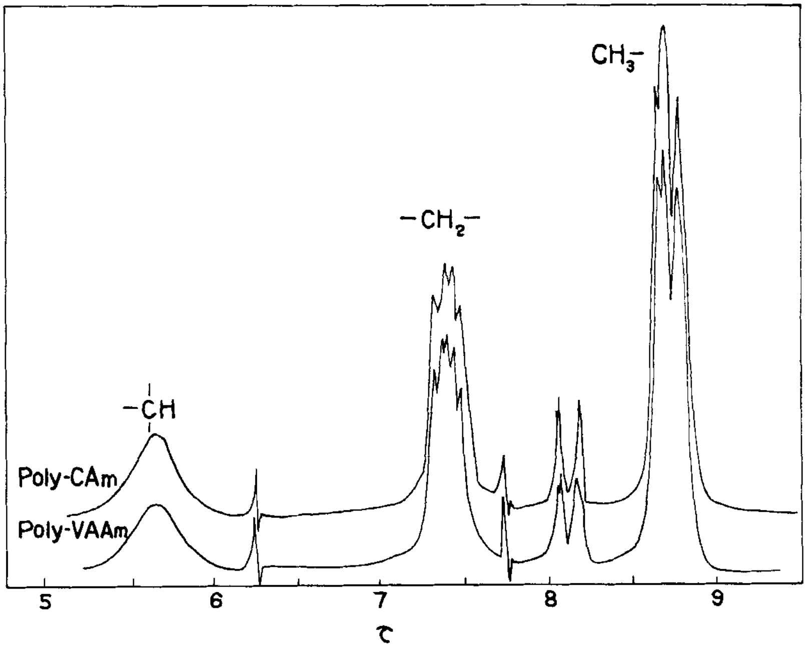
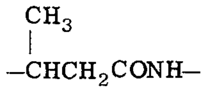


FIG. 7. NMR spectra of poly(vinyl acetamide) and polycrotonamide.

characteristic peaks at 8.75, 7.40, and 5.65τ were assigned to methyl, methylene, and methine protons, respectively. The area ratio of these peaks was about 3:2:1 [e.g., 3.05:2.12:1.00 in the case of poly(vinyl acetamide) shown in Fig. 7]. These facts suggest that the repeating unit of poly(vinyl acetamide) was the structure



$$-\overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2CONH-$$

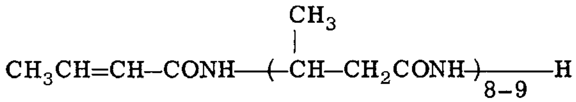
the same as poly(crotonamide).

Moreover, the NMR spectra of polymers showed doublets at 8.10, 4.00, and 3.05τ, respectively. These peaks were distinctly observed in the spectra of crotonamide monomer, and from the area ratio and coupling constants the doublets at 4.00, 3.05, and 8.10τ were identified to correspond with α-, β-, and γ-hydrogen in crotonamide (3), respectively.

$$\underset{\gamma}{CH_3}\text{—}\underset{\beta}{CH}\text{=}\underset{\alpha}{CH}\text{—}CONH_2 \qquad (3)$$

On the other hand, the peak at 6.83τ, which is due to a methylene group existing in vinyl acetamide monomer, could not be observed in the spectra of polymers. Thus it is suggested from the above results that one end of polymer would mainly consist of a 1-propenyl group ($CH_3\text{—}CH\text{=}CH\text{—}$). Assuming that all polymer chains have one 1-propenyl group in its end, the degree of polymerization of polymers are 9–10 by the calculation of the area ratio of the two peaks at 8.75 and 8.10τ. This value is reasonable in comparison with the small inherent viscosity (0.05) of the polymer.

Consequently, it seems reasonable to assume that the polymer obtained by base-catalyzed polymerization of vinyl acetamide would consist of structure (4):



$$CH_3CH\text{=}CH\text{—}CONH\text{—}\left(\underset{}{\overset{CH_3}{\overset{|}{C}}}H\text{—}CH_2CONH\right)_{8-9}\text{—}H \qquad (4)$$

Thus it is concluded that vinyl acetamide was polymerized by a base catalyst through isomerization of an allyl group and proton transfer from an amide group.

Polymerization of Allyl Cyanide

As it was found that vinyl acetamide was polymerized by a base catalyst through isomerization of allyl group into a 1-propenyl group, a similar compound, such as allyl cyanide, was polymerized under similar conditions.

The monomer consumption in the polymerization of allyl cyanide by n-BuLi was followed up by gas-chromatographic methods. A new compound was observed at a shorter retention time than allyl cyanide during the polymerization. The fraction corresponding to this peak was collected by gas chromatography. It is confirmed from IR spectrum that the compound newly formed in the polymerization of allyl cyanide by n-BuLi is crotoncyanide.

The time-conversion curves in the polymerization of allyl cyanide by n-BuLi are shown in Fig. 8. The rate of consumption of allyl cyanide and the formation of crotoncyanide at –78°C was smaller than that at 0°C.

The effects of temperature on the polymer yield are shown in Table 3. Methanol-insoluble product was obtained only at lower temperatures. The methanol-insoluble product was pale yellow powder

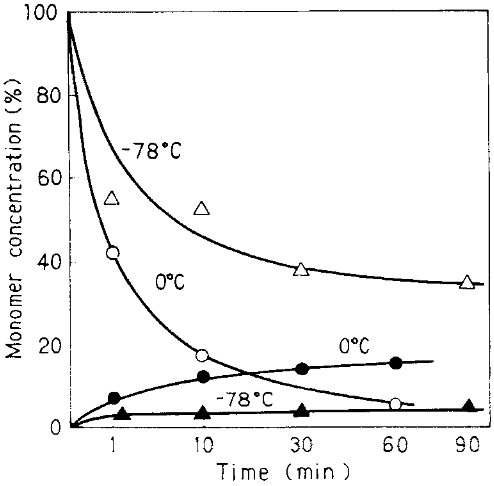


FIG. 8. Rate of monomer consumption in the polymerization of allyl cyanide in toluene: ○△, concentration of allyl cyanide, ●▲, concentration of crotoncyanide in reaction mixture; $[M]_0$, 1.24 moles/liter; [n-BuLi], 96 mmoles/liter.

TABLE 3. Polymerization of Allyl Cyanide in Toluene ($[M]_0$, 1.24 moles/liter; [n-BuLi], 0.10 mole/liter; time, 2 hr)

Temp., °C	Yield of methanol-insoluble product, %	$\overline{M}_n$ of methanol-insoluble product
−78	10	730
0	3	—
40	0	—

(m.p. 80–82°C) and the degree of polymerization of the polymer obtained at −78°C was about 11.

The IR spectrum of the resultant polymer is shown in Fig. 9. It shows characteristic peaks at 2960, 2930, and 1390 cm^{-1}, corresponding to pendant methyl groups, and a sharp peak at 2260 cm^{-1} due to $C{\equiv}N$ stretching. These results suggest that the repeating unit of the polymer is mainly structure (5). However, since peaks at

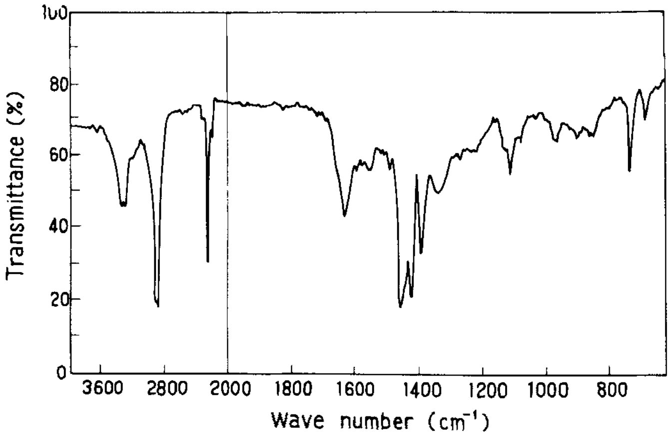
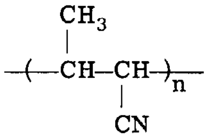


FIG. 9. IR spectrum of poly(allyl cyanide).

3460 and 1640 cm^{-1} were observed, it seems that a part of pendant nitrile might be



$$-\!\left(\overset{\text{CH}_3}{\overset{|}{\text{CH}}}-\underset{\overset{|}{\text{CN}}}{\text{CH}}\right)_{n}\!- \qquad (5)$$

changed to —C=NH by a proton transfer reaction.

On the basis of the above results, one might conclude that allyl cyanide would be polymerized through the isomerization of a allyl group by n-BuLi in a process similar to that with vinyl acetamide, and the reaction of cyanide group would hardly occur.

Acknowledgment

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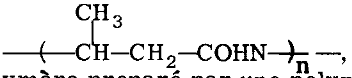
Zusammenfassung

Die basenkatalysierte Polymerisation von Vinylacetamid und Allylcyanid wurde untersucht. Durch chemische und spektroskopische Analyse wurde gefunden, dass das erhaltene Produkt Poly(2-methyl-β-alanin), $-(CH(CH_3)-CH_2-CONH)_n-$ war, welches dieselbe Struktur hatte wie ein durch Basenkatalyse erhaltenes Polymerisat aus Crotonamid. Es wird daher gefolgert, dass sich das Vinylamid über eine Isomerisierung der Allylgruppe und eine Protonenübertragung von der Amidgruppe polymerisiert. Eine gaschromatographische Analyse des Polymerisationssystems ergab, dass Vinylacetamid schneller verbraucht wird als Crotonamid. Diese Tatsache weist darauf hin, dass eine Zwischeprodukt auftritt, das nicht Crotonamid ist. Andrerseits isomerisierte die Allylgruppe in der basenkatalysierten Polymerisation von Allylcyanid, wobei eine Reaktion der Cyanidgruppe kaum auftrat.

Résumé

La polymérisation basocatalysée du vinyl acétamide et du nitrile d'allyle a été etudiée. On a trouvé par les analyses chimiques et spectroscopiques que le polymère obtenu à partir de vinyl acétamide était la poly(méthyl-2-alanine-β),  $-\!\!(\overset{CH_3}{\overset{|}{C}}H-CH_2-COHN)_n-$, possédant la même structure que le polymère preparé par une polymérisation baso-catalysée de l'amide crotonique. On a conclu que le vinyl acétamide a été polymerisé par l'isomérisation du groupe allyle et transfert du proton du groupe amide. L'analyse par chromatographie en phase gazeuse du système de polymérisation a

montré que le vinyl acetamide était consommé plus rapidement que l'amide crotonique. Ce fait suggère la présence probable d'un intermédiaire autre que l'amide crotonique dans le processus d'isomérisation du vinyl acetamide. D'un autre côté, dans la polymérisation baso-catalysée du nitrile d'allyle, le groupe allyle était isomerisé, mais le groupement cyanure a reagit à peine.