Base-Catalyzed Polymerization of *p*-Vinyl Benzamide

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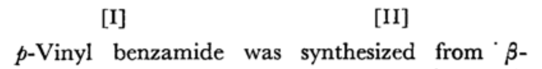
Recently, it has been reported[1,2] that *p*-vinyl benzamide [I] was polymerized by a basic catalyst to give the proton transfer type polymer [II]. In these studies, alkali metals and their alkoxides were used as catalyst. The object of this paper is to elucidate the effect of catalyst and solvent on the polymerization of *p*-vinyl benzamide.



[I] [II]

p-Vinyl benzamide was synthesized from β-phenylethyl alcohol through *p*-carboxy-β-phenylethyl bromide[3] and *p*-vinyl benzoic acid[4]. The crude product was recrystallized from petroleum

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1) K. Kojima, N. Yoda and C. S. Marvel, *J. Polymer Sci.*, A1-**4**, 1121 (1966).

2) S. Negishi and Y. Tamura, International Symposium on Macromolecular Chemistry (Tokyo-Kyoto) Preprints, **II**, 34 (1966).

3) E. L. Foreman and S. M. McElvain, *J. Am. Chem. Soc.*, **62**, 1435 (1940).

4) E. Osawa, K. Wang and O. Kurihara, *Makromol. Chem.*, **83**, 102 (1965).

TABLE 1. POLYMERIZATION OF *p*-VINYL BENZAMIDE

Catalyst mmol/*l*		Solvent	$[M]_0$ mol/*l*	Time hr	Temp. °C	Polymer yield[a] %	*D*-ratio[b]	η_{sp}/c[c]
PhMgBr	32	Toluene	0.27	3	120	23	0	—
PhMgBr	32	Toluene	0.14	10	120	49	0	0.14
PhMgBr	32	Pyridine	0.29	3	120	6	0.07	—
PhMgBr	32	Pyridine	0.14	10	120	12	0.04	—
PhMgBr	32	Pyridine	0.07	5.5	120	31	0	—
n-BuLi	13	Toluene	0.27	10	80	3	0.10	—
n-BuLi	13	Toluene	0.27	10	100	4	0.07	—
n-BuLi	13	Toluene	0.14	10	120	12	0.09	0.34
n-BuLi	13	Pyridine	0.28	10	80	4	—	—
n-BuLi	13	Pyridine	0.26	10	100	4	0.13	—
n-BuLi	13	Pyridine	0.14	20	120	17	0.11	—

a) Acetone-insoluble product b) *D*-ratio; $D_{1500\ \mathrm{cm}^{-1}}/D_{1660\ \mathrm{cm}^{-1}}$

c) Inherent viscosity of a polymer was measured in conc. H_2SO_4 (1w/v%) after heating of the solution at 100°C for 1 hr.

ether/acetone mixture and benzene to give colorless powder, mp 171—172°C (Lit.[5] 168°C).

Catalyst was added to the test tube containing monomer, solvent and inhibitor for radical polymerization (*N*-phenyl-*β*-naphthylamine: 10 mg/10 m*l* solution) and then the test tube was sealed in a nitrogen atmosphere. After polymerization at constant temperature, the mixture was poured into a large amount of acetone. The polymer was removed by filtration, washed with acetone and dried at 40°C for 48 hr in vacuum.

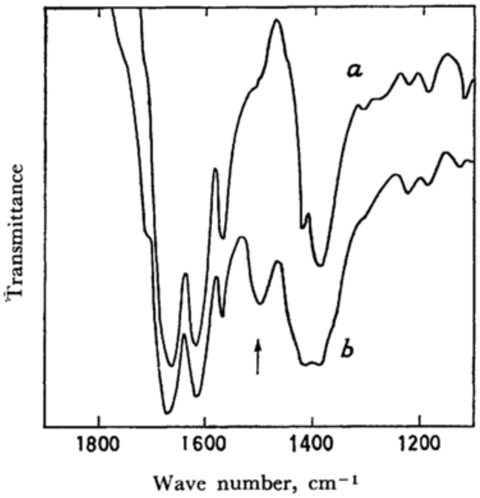
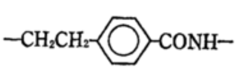


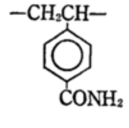
Fig. 1. IR spectra of poly(*p*-vinyl benzamide).
a : Polymer obtained by PhMgBr in toluene at 120°C. (D ratio=0)
b : Polymer obtained by BuLi in pyridine at 100°C. (D ratio=0.13)

The results of polymerization catalyzed by *n*-butyllithium (*n*-BuLi) and phenylmagnesium bromide (PhMgBr) in toluene and pyridine are summarized in Table 1. It is estimated that the product is a polymer as the inherent viscosity of products was larger than 0.1. Moreover, the real values of inherent viscosity might be higher than the observed values since the polymer was to some extent decomposed in conc. H_2SO_4 at 100°C.

IR spectra of polymers obtained by two different polymerization conditions, that is, by *n*-BuLi in pyridine and by PhMgBr in toluene, are different in the absorption at about 1500 cm⁻¹ as shown in Fig. 1. The absorption at 1500 cm⁻¹ corresponds to secondary amide and the existence of this absorption shows that polymers contain the proton transfer unit [III]. On the other hand, the absence of the absorption at 1500 cm⁻¹ indicates that the repeating unit of polymers may be the vinyl unit [IV].



[III]



[IV]

In this paper, the fraction of the proton transfer unit [III] in polymer was not measured quantitatively, but could be compared qualitatively by *D*-ratio[6] which was defined as a ratio of optical densities at 1500 to 1660 cm⁻¹. Hence, *D*-ratio of the polymer which consists of only the vinyl unit [IV] is zero, and *D*-ratio is higher if the polymer contains larger amount of the proton transfer

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[5] D. Faulkner, C. E. Hollis and J. N. Mihe, Brit. Pat., 676376 (1952).

[6] H. Nakayama, T. Higashimura and S. Okamura, *Kobunshi Kagaku (Chem. High Polymers, Japan)*, **23**, 433 (1966).

unit [III]. In fact, *D*-ratio of vinyl polymer obtained by heat polymerization was zero. *D*-Ratio of the polymer[2)] consisting of almost the proton transfer unit [III] was 0.7 according to our calculation.

The *D*-ratios of polymers shown in Table 1 suggest the following facts. In the use of PhMgBr as a catalyst, the polymer was obtained by vinyl polymerization in toluene, but proton transfer polymerization occured to some extent in pyridine. In the case of *n*-BuLi, the proton transfer unit was present in the resultant polymer, and the polymer obtained in pyridine seemed to contain larger amount of the proton transfer unit than that in toluene.

These results are summarized as follows. First, the fraction of the proton transfer unit was very much smaller in the case of *p*-vinyl benzamide than in the case of acrylamide or methacrylamide under the same polymerization condition. Second, in the base-catalyzed polymerization of *p*-vinyl benzamide, there were the polymerization conditions under which proton transfer polymerization did not proceed. These facts may be due to that intramolecular proton transfer might hardly occur in the polymerization of *p*-vinyl benzamide containing *p*-phenylene group between an ethylenic double bond and amide group.