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Polymerizations of N-Vinylpyridazinones in the Presence of Acids

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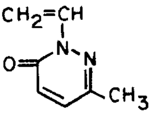
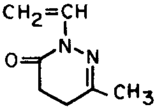
ABSTRACT

Polymerizations of two N-vinylpyridazinones, 3-(2-vinyl)-6-methylpyridazinone (I) and 3-(2-vinyl)-6-methyl-4,5-dihydropyridazinone (II), were carried out in the presence of several acids. The cationic polymerization of II was found to take place in the presence of acids, but not of I. Radical copolymerization of the I-BF_3OEt_2 complex with styrene gave an alternating copolymer.

During the course of our studies on the polymerizations of the pyridazinone derivatives [1-4], we found that the pyridazinone ring should be stabilized by the effective ring conjugation involving the carbonyl group, the degree of which would be varied by the solvent [5, 6]. In connection of these observations, two N-vinylpyridazinones, 3-(2-vinyl)-6-methylpyridazinone (I) and 3-(2-vinyl)-6-methyl-4,5-dihydropyridazinone (II), were polymerized in the presence of several acids.



I



II

The present paper deals with the homo- and copolymerizabilities of these monomers in the presence or in the absence of the acids.

N-Vinylpyridazinones were prepared by the previous methods [3, 4]. The complexes of I-Lewis acids were prepared by mixing I with Lewis acid(BF_3OEt_2, $TiCl_4$, $SnCl_4$) in methylene chloride, and their structures were determined by both IR and NMR spectroscopy. Radical polymerization was carried out with azobisisobutyronitrile (AIBN) as an initiator in methylene chloride at 60°C. Cationic polymerization of II was carried out in methylene chloride under nitrogen at 37, 25, 0, and -78°C.

Table 1 shows the results of cationic polymerizations of I and II under changing reaction conditions. It is interesting to note that no cationic polymer of I was obtained in spite of changing such reaction conditions as temperature, catalyst, and solvent. The polymerization of II was found to take place with $TiCl_4$, $SbCl_5$, H_2SO_4, and BF_3OEt_2, where the value of the polymerization rate (R_p) increased with a rise of the reaction temperature. It is noted that a value of 1000 was determined for the number-average molecular weight of the polymer obtained by BF_3OEt_2 catalyst. The positions of the NMR spectral bands of the polymer obtained by BF_3OEt_2 coincided with those of the AIBN-initiated polymer, indicating that only terminal vinyl propagation took place. The differences in reactivity of I vs II might be due to differences in both the resonance stabilities of the pyridazinone rings and the electron densities on the terminal vinyl groups, as is described later.

Both IR and NMR spectroscopy were found to reveal the formation of the 1:1 complex between I and Lewis acids. In the IR spectra of I in the presence of various amount of BF_3OEt_2 in methylene chloride, the increase in the concentration of the acid decreased the intensity of the peak at 1673 cm^{-1} due to the C=O group in the pyridazinone ring and increased that at 1647 cm^{-1} due to the C—O group. The continuous variation of results of I with BF_3OEt_2 by NMR spectroscopy indicates the formation of an oxygen atom in I. Similar results were obtained for both the I-$TiCl_4$ and I-$SbCl_5$ systems.

Although no polymer was obtained from these complexes at 60°C for 10 hr, AIBN was found to initiate polymerization. Figure 1 shows the results for the I-BF_3OEt_2 system. A sharp decrease in the R_p value was observed by the addition of a small amount of the acid. This same phenomenon has been reported for the polymerization of acrylonitrile or methyl methacrylate in the presence of several Lewis acids [7].

Radical copolymerization of the I-BF_3OEt_2 complex with styrene (St) was carried out at 60°C in methylene chloride. In the IR spectra of the copolymer obtained in the absence of the acid, peaks were

TABLE 1. Results of Cationic Polymerizations of I and II under Various Conditions

	Monomer (g)	Catalyst (mg)	Solvent (ml)	Temperature (°C)	Time (hr)	Rate (%/hr)	$\overline{M}_n$
I	0.252	BF_3OEt_2 (1.13)	CH_2Cl_2 (1)	0	20	0	-
	0.252	BF_3OEt_2 (11.25)	CH_2Cl_2 (1)	30	2	0	-
	0.252	$TiCl_4$ (1.78)	CH_2Cl_2 (1)	0	20	0	-
II	0.552	H_2SO_4 (3.92)	CH_2Cl_2 (2)	25	6	0.24	-
	0.552	BF_3OEt_2 (11.36)	CH_2Cl_2 (2)	0	20	0.12	1210
	0.276	BF_3OEt_2 (11.36)	CH_2Cl_2 (2)	37	2	3.48	-
	0.276	BF_3OEt_2 (0.29)	CH_2Cl_2 (1)	-78	3	0	-
	0.552	$TiCl_4$ (15.18)	CH_2Cl_2 (2)	0	1	4.78	1420
	0.276	$TiCl_4$ (0.38)	CH_2Cl_2 (1)	-78	3	0.19	-
	0.552	$SbCl_5$ (23.92)	CH_2Cl_2 (2)	0	1	9.82	1360
	0.276	$SbCl_5$ (0.60)	CH_2Cl_2 (1)	-78	3	0.31	-

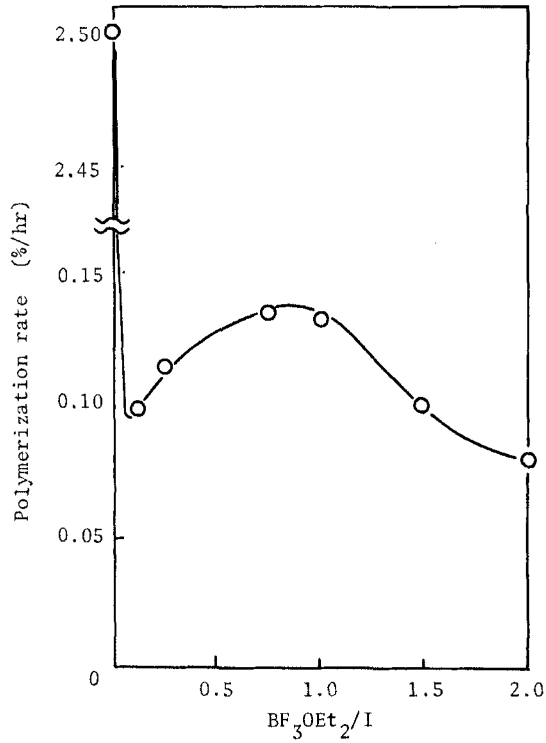


FIG. 1. Effect of BF_3OEt_2 on radical polymerization of N-vinyl pyridazinone I.

TABLE 2. Copolymerization Parameters

M_1	M_2	r_1	r_2	Q_1	e_1
I-BF_3OEt_2	St	0.20	0.15	1.12	1.07
I	St	0.90	0.90	0.74	-0.34
	MMA	0.47	0.71	0.72	-0.63
II	St	0.13	5.20	0.31	-1.34
	MMA	0.11	1.20	0.35	-1.02

observed at 1640, 970, and 895 cm^{-1} due to the terminal vinyl group, suggesting intermolecular polymerization between the vinyl group and the ring olefin. These bands, however, completely faded out for the copolymer obtained in the presence of the acid. This suggests that polymerization in the presence of the acid proceeds via terminal propagation alone.

Monomer reactivity ratios and Q, e values were determined and are tabulated in Table 2. It is observed that I has larger Q and positive e values than II, indicating that the unsaturated pyridazinone ring is more stabilized by the effective ring conjugation than the saturated one. It is interesting to note that the copolymerization system of I in the presence of the acid gave rather smaller monomer reactivity ratio values and larger Q and positive e values than the system in the absence of the acid. One possible explanation would be an effect of increased resonance stabilization by chelation of the acid on the carbonyl oxygen atom in the ring. However, another question is whether the reaction proceeds via some charge transfer propagation between the complex and St, although the present investigation alone could not answer the question.

Further investigation is now underway in our laboratory.

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