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Tsunehito Eda<sup>a</sup>; Yoshio Matsubara<sup>a</sup>; Masakuni Yoshihara<sup>a</sup>; Toshihisa Maeshima<sup>a</sup>

<sup>a</sup> Department of Applied Chemistry Faculty of Science and Engineering, Kinki University Higashi, Osaka, Japan

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## Radical Copolymerization of 6-Methyl-2-phenyl-3-pyridazinone with Styrene in the Presence of Lewis Acid

TSUNEHITO EDA, YOSHIO MATSUBARA, MASAKUNI YOSHIHARA,  
and TOSHIHISA MAESHIMA

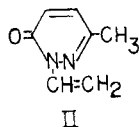
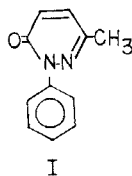
Department of Applied Chemistry  
Faculty of Science and Engineering  
Kinki University  
Higashi Osaka, 577 Japan

### ABSTRACT

Free radical copolymerization of 6-methyl-2-phenyl-3-pyridazinone (I) with styrene ( $M_1$ ) has been carried out in the presence of  $\text{BF}_3\text{OEt}_2$ . Lewis acid was found to decrease the copolymerizability of I, perhaps due to the increased resonance stabilization of the pyridazinone ring by chelation of acid on the carbonyl-oxygen atom of the ring.

### INTRODUCTION

In a series on the polymerization of pyridazinone derivatives [1-7], we showed that the pyridazinone has a radical copolymerizability which might be influenced by the ring conjugation between a carbonyl group and a pair of electrons on a nitrogen atom. In the present paper we want to report the results of the copolymerization of 6-methyl-2-phenyl-3-pyridazinone (I) with styrene (St) in the presence of  $\text{BF}_3\text{OEt}_2$ .



### EXPERIMENTAL

6-Methyl-2-phenyl-3-pyridazinone (I) was prepared in the following manner. A mixture of phenylhydrazine (0.1 mole), levulinic acid (0.1 mole), and 60 mL of methanol was refluxed for 12 hr with stirring. After cooling, 0.08 mole of selenium dioxide was added, and then the mixture was refluxed for 36 hr with stirring. After both the solvent and the unreacting material were removed at reduced pressure, the residue was recrystallized from ligroin to yield 9.3 g (50%) of I; mp 73.5–75°C; NMR in  $\text{CDCl}_3$  (ppm): 7.08 (d, 1H), 6.87 (d, 1H), 7.08 (s, 5H), 2.23 (s, 3H). Elementary analysis (calculated for  $\text{C}_{11}\text{H}_{11}\text{N}_2\text{O}$ ): C, 70.95% (70.97%); H, 4.81% (4.84%); N, 15.04% (15.05%).

Solvents and monomers were purified by the usual method.

All the radical polymerizations were carried out using azobisisobutyronitrile (AIBN) at 60°C in a sealed tube. The reaction mixture was poured into a large amount of methanol to precipitate the polymer, which was purified by repeated reprecipitation from DMF and methanol. The composition of copolymer was determined by elemental analysis.

TABLE 1. Effect of  $\text{BF}_3\text{OEt}_2$  on the Copolymerization Rate of 6-Methyl-2-phenyl-3-pyridazinone (I) with St in DMF at 60°C<sup>a</sup>

| $[\text{BF}_3\text{OEt}_2] \times 10$<br>(mole/L) | Conversion<br>(hr) | $R_p$<br>(%/hr) |
|---|--------------------|-----------------|
| 0   | 30.14              | 1.44            |
| 1   | 18.14              | 0.86            |
| 2   | 15.10              | 0.72            |
| 4   | 13.31              | 0.63            |
| 5   | 12.83              | 0.61            |
| 6   | 12.69              | 0.60            |
| 8   | 11.86              | 0.56            |
| 10  | 7.79               | 0.37            |

<sup>a</sup>Copolymerization time: 21 hr.  $[\text{I}] + [\text{St}] = 2$  mole/L;  $[\text{I}]/([\text{I}] + [\text{St}]) = 0.5$ ;  $[\text{AIBN}] = 1 \times 10^{-2}$  mole/L.

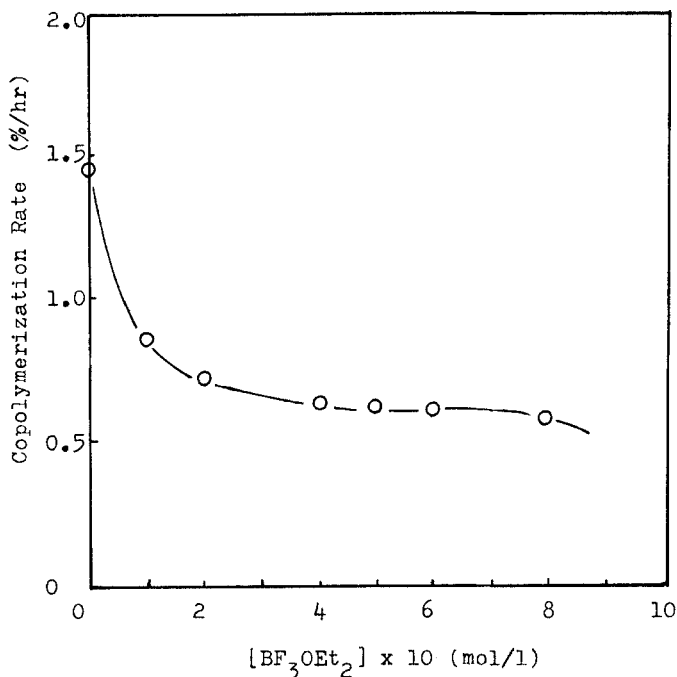


FIG. 1. Effects of the concentration of  $\text{BF}_3\text{OEt}_2$  on the copolymerization rate of (I) with St.

## RESULTS AND DISCUSSION

Homopolymerizability of I was investigated using a few initiators, i.e., AIBN,  $\text{BF}_3\text{OEt}_2$ , and  $n\text{-BuLi}$ : no polymer was obtained.  $\text{BF}_3\text{OEt}_2$  was not found to cause the cationic copolymerization of I with St. Similar phenomenon was observed in the polymerization of 6-methyl-2-vinyl-3-pyridazinone (II) with St in the presence of a few Lewis acids and was ascribed to the 1:1 complex formation between II and the acid [6]. In this connection, therefore, the IR spectra of I was taken. In the IR spectra of I in the presence of various amount of  $\text{SnCl}_4$  in methylene chloride, the increase in the concentration of the acid decreased the intensities of both peaks at  $1672\text{ cm}^{-1}$  due to  $\text{C}=\text{O}$  and at  $1608\text{ cm}^{-1}$  due to  $\text{C}=\text{C}$  groups of I and increased those at  $1631$  and  $1510\text{ cm}^{-1}$  due to the chelated  $\text{C}=\text{O}$  and  $\text{C}=\text{C}$  groups, respectively. The continuous variation by NMR spectroscopy revealed the formation of the 1:1 complex between I and  $\text{SnCl}_4$ . Similar results were obtained for the I- $\text{SnCl}_4$  and I- $\text{BF}_3\text{OEt}_2$  systems. AIBN was found to initiate the copolymerization of I- $\text{BF}_3\text{OEt}_2$  complex with St. Table 1

TABLE 2. Copolymerization of 6-Methyl-2-phenyl-3-pyridazinone (I) with St ( $M_1$ ) in the Presence of  $\text{BF}_3\text{OEt}_2$  in DMF at  $60^\circ\text{C}^a$

| Monomer composition<br>$M_1$ (mole %) | Time (hr) | Conversion (%) | $R_p \times 10^6$ <sup>b</sup><br>(mole/L sec) | N (%) | Copolymer composition<br>$m_1$ (mole %) |
|---------------------------------------|-----------|----------------|--|-------|---|
| 80                                    | 10        | 9.43           | 5.92   | 1.34  | 94.81                                   |
| 60                                    | 15        | 11.85          | 5.64   | 2.10  | 91.68                                   |
| 50                                    | 18        | 9.66           | 4.06   | 2.98  | 87.93                                   |
| 40                                    | 33        | 10.48          | 2.54   | 3.20  | 86.70                                   |
| 20                                    | 144       | 6.44           | 0.39   | 4.36  | 81.52                                   |

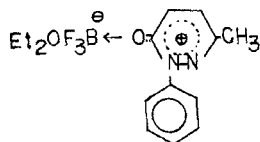
<sup>a</sup> $[M_1] + [M_2] = 2$  mole/L;  $[AIBN] = 1 \times 10^{-2}$  mole/L;  $[\text{BF}_3\text{OEt}_2] = 0.2$  mole/L.  
<sup>b</sup> $-d[M_1 + M_2]/dt$ .

TABLE 3. Copolymerization Parameters

| $M_2$                       | $M_1$ | $r_1$ | $r_2$ | $Q_2$  | $e_2$ | Ref.      |
|-----------------------------|-------|-------|-------|--------|-------|-----------|
| I                           | St    | 4.70  | 0.01  | 0.052  | 0.95  | 7         |
| I- $\text{BF}_3\text{OEt}$  | St    | 7.10  | 0.01  | 0.0393 | 0.80  | This work |
| II                          | St    | 0.90  | 0.90  | 0.74   | -0.34 | 6         |
| II- $\text{BF}_3\text{OEt}$ | St    | 0.15  | 0.20  | 1.12   | 1.07  | 6         |

and Fig. 1 show the effect of the concentration of  $\text{BF}_3\text{OEt}_2$  on the copolymerization rates ( $R_p$ ) at  $60^\circ\text{C}$ , clearly indicating that the  $R_p$  value decreases with an increase of the concentration of the acid. Table 2 shows the results of the radical copolymerization of I with St ( $M_1$ ) in the presence of  $\text{BF}_3\text{OEt}_2$ .

Monomer reactivity ratios and  $Q_2, e_2$  values were determined and tabulated in Table 3, together with previous results. It is interesting to note that copolymerization in the presence of the acid gave a rather larger monomer reactivity ratio ( $r_1$ ) value than that in the absence of



the acid. On the other hand, the copolymerization of II with St in the presence of the acid had previously given rather smaller monomer reactivity ratio ( $r_1$ ) and larger  $Q_2$  and positive  $e_2$  values than in the absence of the acid.

These results may be explained by taking account of an increased resonance stabilization of I by chelation of the Lewis acid on the carbonyl oxygen atom as described above and thus decreasing the reactivity of the ring olefin.

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