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Conjugative Effect of the Pyridazinone Ring on the Copolymerizabilities of Substituted Pyridazinones

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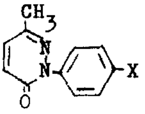
ABSTRACT

The free-radical copolymerizations of 3(2-p-substituted-phenyl)6-methylpyridazinones (I) and 3(2-methyl)6-substituted-pyridazinones (II) with styrene (M_1) or acrylonitrile (M_1) have been carried out in dimethylformamide (DMF) at 60°C. ρ values were determined by plotting the values of log $1/r_1$ against Hammett's σ values to be 0.24 for the I-St system and -0.20 for the I-AN system. In the case of the II-St system, however, the reactivities were found to be nicely correlated with Otsu's equation, i. e., $\log 1/r_1 = 0.06 + 4.8\ E_R$, suggesting that the growing radicals of II are stabilized by the resonance contributions of the substituents of II at their transition states. All these observations are discussed in terms of the conjugative effect of the pyridazinone ring, together with our earlier observations already reported.

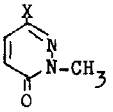
INTRODUCTION

In the course of our studies on the polymerizations of the pyridazinone derivatives [1-4], we have shown that the reactivity of the

TABLE 1. Synthesis of Substituted Pyridazinones



(I)



(II)

	X	Mp or bp (°C or °C/ Torr)	Elemental analysis[a]			NMR spectra	
			C (%)	H (%)	N (%)	δ (ppm)	δ (ppm)
I	CH_3	62-63	72.06	6.08	13.98	6.91	7.03[b]
			(72.01)	(6.01)	(14.02)		
	H	74-75	70.95	4.81	15.04	6.91	7.09[b]
			(70.97)	(4.84)	(15.05)		
	Cl	101.5-102	59.83	4.12	12.74	6.97	7.42[b]
			(59.86)	(4.08)	(12.70)		
	OCH_3	118/15	51.46	5.75	20.03	6.87	6.87[c]
			(51.43)	(5.71)	(20.00)		
II	H	97/14	54.54	5.43	25.41	6.86	7.17[c]
			(54.55)	(5.45)	(25.45)		
	Cl	90-91	41.54	3.43	19.31	6.81	7.15[c]
			(41.52)	(3.46)	(19.38)		
	$COOCH_3$	103-104	49.73	5.35	16.57	6.87	7.77[c]
			(49.70)	(5.32)	(16.56)		

[a] First value calculated; value in parentheses, found.
[b] In $DMSO\text{-}d_6$.
[c] In $CDCl_3$.

double bond of the pyridazinone ring was affected by the conjugative effect of the ring between the carbonyl group and a pair of electrons on the nitrogen atom. However, it remains to be resolved satisfactorily how and/or why the substituent should affect the polymerizability of the pyridazinone ring.

In this point of view, therefore, several 3(2-p-substituted-phenyl)-6-methylpyridazinones and 3(2-methyl)6-substituted-pyridazinones were prepared and copolymerized with styrene and acrylonitrile (M_1) in DMF, and the results, together with those previously obtained, are discussed in terms of the conjugative effect of pyridazinone ring.

TABLE 2. Radical Copolymerization of 3(2-p-Substituted-phenyl)6-methylpyridazinones (M_2) with St (M_1)[a]

	M_2	Monomer composition (M_1)(mole %)	Time (hr)	Conversion (%)	R_p (mole/liter-sec) 10^6	N content (%)	Copolymer composition (m_1)(mole %)
X=	CH_3	20	90	6.94	0.6	6.22	70.60
		40	20	6.90	2.5	4.27	81.41
		50	15	9.47	4.5	3.26	86.37
		60	8	7.04	6.1	2.69	89.00
		80	4	5.05	7.9	1.43	94.42
		100	1	1.75	9.7	0	100
X=	H	20	100	8.89	0.6	6.62	69.50
		40	20	7.60	2.7	4.58	80.36
		50	15	8.32	3.8	3.57	84.90
		60	8	6.40	5.3	2.86	88.40
		80	4	5.29	8.1	1.34	94.80
X=	Cl	20	100	8.95	0.7	6.25	68.61
		40	20	8.47	3.1	4.63	78.69
		50	15	10.76	5.2	3.69	83.81
		60	8	6.73	5.9	2.95	87.40
		80	4	5.61	8.9	1.44	94.29

[a] $[M_1] + [M_2] = 2$ mole/liter; $[AIBN] = 1 \times 10^{-2}$ mole/liter in DMF at 60°C.

TABLE 3. Copolymerization Parameters

	M_2	M_1	r_1	r_2	Q_2	e_2
I	CH_3	St	5.4	0	0.040	1.12
		AN	10	0		
I	H	St	4.7	0	0.042	1.23
		AN	11	0		
I	Cl	St	4.3	0	0.042	1.32
		AN	12	0		
II	OCH_3	St	5.4	0.01	0.011	0.91
II	CH_3	St	10.7	0.01	0.048	0.69
II	H	St	18.0	0.01	0.028	0.50
II	$COOCH_3$	St	3.2	0.01	0.070	1.05

EXPERIMENTAL

The 3(2-p-substituted-phenyl)6-methylpyridazinones (I) were prepared in the following manner. A mixture of p-substituted phenylhydrazine (0.1 mole), levulinic acid (0.1 mole), and 60 ml of methanol was refluxed for 3 hr with stirring. After cooling, 0.8 mole of selenium dioxide was added, and then the mixture was refluxed for 12 hr with stirring. After both the solvent and the unreacting material were removed at reduced pressure, the residue was recrystallized from ligroin to yield 50-60% of I.

3(2-Methyl)6-substituted-pyridazinones (II) were prepared from the reactions of 0.1 mole of methyl iodide with 0.1 mole of the sodium salts of 3(2H)6-substituted-pyridazinones in 100 ml of anhydrous methanol at 20°C for 3 hr. After the solvent was removed at reduced pressure, the residue was distillated or recrystallized from n-hexane to yield 70-90% of II. The results are summarized in Table 1.

All the radical polymerizations were carried out by use of 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.

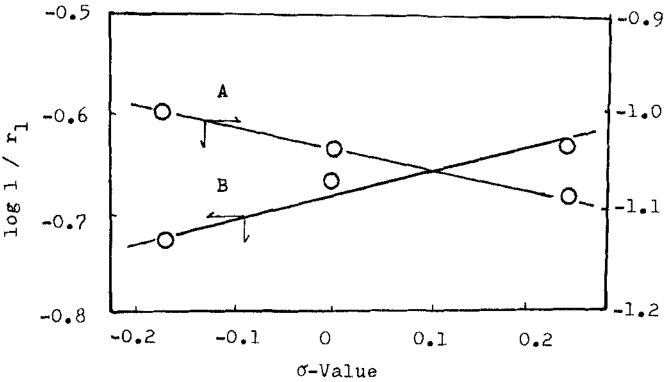


FIG. 1. Plots of log $1/r_1$ vs σ values for the I system: (A) St system; (B) AN system.

RESULTS AND DISCUSSION

Homopolymerizations of both I and II did not take place with a few radical initiators and thermal and photoactivations. Table 2 summarizes the results of copolymerizations of 3(2-p-substituted-phenyl)6-methylpyridazinones with styrene (M_1) in DMF. The increase of the pyridazinone concentration in the monomer feed was found to decrease both the copolymerization rate R_p and the number-average molecular weight ($\overline{M}_w$ = 8000-2000) of the copolymer, suggesting that the pyridazine ring has a rather weak reactivity.

Monomer reactivity ratios and Q, e values were determined as already described [1, 2], and results tabulated in Table 3 indicate that the pyridazinones have only weak copolymerizability with St and AN. It is noted that the values of the monomer reactivity ratios varied markedly with substituents, and a straight line was obtained by plotting against σ values. Figure 1 shows the relationships between the values of log $1/r_1$ and σ values for the systems with I; straight lines were observed. It should be noted, however, that Otsu's equation, i. e., $\log 1/r_1 = \rho\sigma + \gamma E_R$, was effectively applied for the II system (Fig. 2) which will be discussed later. All the values of ρ and γ, together with those of a few related compounds previously obtained, are tabulated in Table 4.

In all the St systems, positive ρ values were found to be obtained, while the ρ-values in the AN systems were negative. These observations seem to be explained in the following manner. Namely, at the transition states of the St systems, the polystyryl unit acquires a positive charge, and the pyridazinone unit gets a negative charge due to the electron-accepting effects of both two nitrogen atoms and the

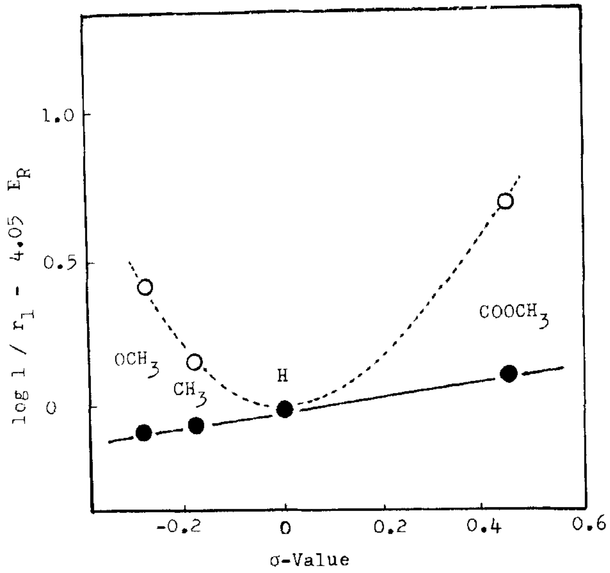
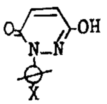
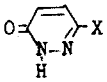


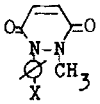
FIG. 2. Plots of log 1/r vs. σ values for the St-II system.

TABLE 4. Hammett ρ and γ Values of Pyridazinone Derivatives

M_1	M_2	ρ	γ
St	I	0.24	-
	III	0.50	-
AN	I	-0.20	-
	III	-0.23	-
St	II	0.06	4.80
	IV	1.49	-
	V	0.20	-







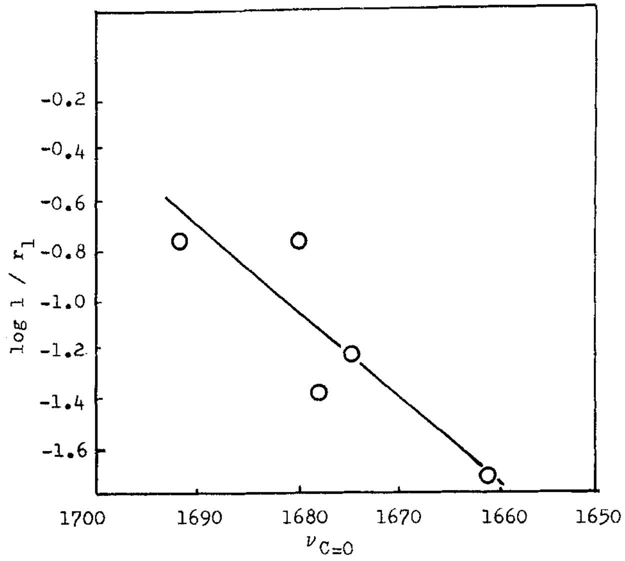
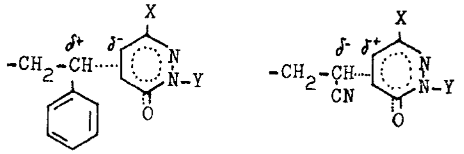


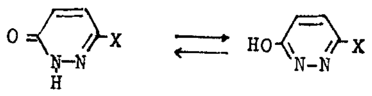
FIG. 3. Relationship between the value of log $1/r_1$ and $\nu_{C=O}$.

carbonyl group of the pyridazinone ring. On the other hand, in the cases of AN systems the polyacrylonitrile unit acquires a negative charge while the pyridazinone unit gets a positive charge, perhaps due to a rather strong electron-withdrawing ability of the cyano group in the polyacrylonitrile radical.



(1)

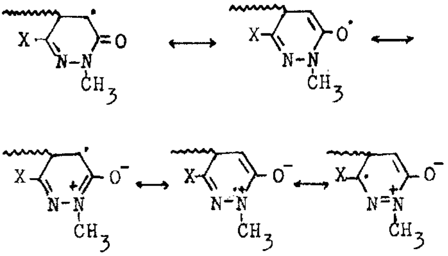
Meanwhile, in the IV-St system, the ρ value was positive and quite large compared with those of the others. One possible explanation is a hypothesis that the amide-enol equilibrium also takes place to form the stable pyridazine ring [Ea. (2)]



(2)

the degree of which may be influenced by the substituent. This is considered to be partly supported by the facts that in the IR data of IV two absorption bands of $\nu_{C=O}$ were observed and these values were almost nicely correlated with those of log $1/r_1$ as shown in Fig. 3. The importance of the amide-enol equilibrium was already emphasized by Saini et al. in the polymerization of acrylamide [6].

In the case of the II-St system, however, a rather large γ value, i. e., 4.80, was obtained. This fact indicates that the growing radicals of II are highly stabilized by resonating directly with the substituents at their transition states. Such a few resonance structures may be involved in the scheme (3).



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