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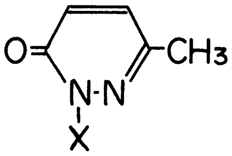
CONJUGATIVE EFFECT OF PYRIDAZINONE RING ON THE COPOLYMERIZABILITIES OF 3(2-SUBSTITUTED)6-METHYLPYRIDAZINONES WITH STYRENE

Yoshio MATSUBARA, Munenori NOGUCHI, Masakuni YOSHIHARA,
and Toshihisa MAESHIMA
Department of Applied Chemistry, Kinki University, Kowakae
Higashi-Osaka City

Radical copolymerizations of several pyridazinones (I - VI) with styrene (M_1) have been carried out. It has been found that plots of log 1 / r_1 against both νc=o and νc=c in the pyridazinone ring gave straight lines, indicating that the reactivity of the double bond in the ring might be affected by the ring conjugation which involves the carbonyl group.

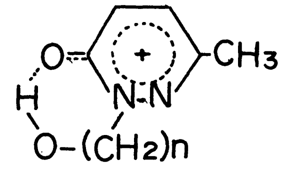
During the course of our studies on polymerizations of pyridazinone derivatives,[1-3] the radical polymerizations of both N-vinylpyridazinone and 6-acryloxypyridazinone have been found to proceed heterogeneously in benzene as a solvent via three-dimensional propagation between terminal vinyl group and ring olefin, while the homogeneous polymerization took place in dimethylformamide (DMF) via usual terminal vinyl propagation alone. We have postulated the idea that a polar solvent like DMF might solvate with carbonyl group in pyridazinone ring to yield the effective conjugation between carbonyl group and a pair of electrons on a nitrogen atom and thus reduce the radical polymerizability of double bond in the ring.[4-5] Such a solvent effect has not been reported, especially in view of the relation between conjugation stability and polymerizability. If this mechanism is true, an existence of some interaction on carbonyl group in the ring, such as hydrogen bonding, would be expected to diminish the reactivity of the ring olefin. In order to investigate these effects, therefore, several pyridazinones (I - VI) were synthesized and copolymerized with styrene (M_1) using AIBN in DMF at 60°C.



I, X = H
II, X = C_6H_5
III, X = CH_2OH
IV, X = CH_2Cl
V, X = C_2H_4OH
VI, X = C_2H_4Cl

The increase of the pyridazinone concentration in the monomer feed was found to decrease both the copolymerization rate (Rp) and the number average molecular weight ($\bar{M}n$). The copolymerization parameters are tabulated in Table 1. All of the pyridazinones were found to have only weak reactivity to copolymerize with styrene. It is quite interesting to note that the monomer reactivity ratios (r_1) obtained for both III- and V-styrene systems were extremely smaller than those for IV - and VI - styrene systems, respectively: perhaps due to an intramolecular hydrogen bonding between the carbonyl group and the hydroxy group.

Furthermore, it should be noted that plots of log 1 / r_1 against both νc=o and νc=c in the pyridazinone ring gave straight lines, as shown in Fig. 1.



All these observations clearly suggest that the reactivity of the double bond in the pyridazinone ring might be affected in the ground state by the ring conjugation which involves the carbonyl group.

Table 1 Monomer reactivity ratios and Q, e values for radical copolymerizations of 3(2-substituted)6-methylpyridazinones with styrene (M_1).[a)]

M_2	r_1	r_2	Q_2	e_2
I	25	0.01	0.016	0.38
II	4.9	0.01	0.051	0.94
III	37	0.01	0.010	0.19
IV	6.8	0.01	0.040	0.84
V	51	0.01	0.010	0.02
VI	14	0.01	0.025	0.50

a) $[M_1] + [M_2] = 1$ mol/l, $[\mathrm{AIBN}] = 1 \times 10^{-2}$ mol/l.

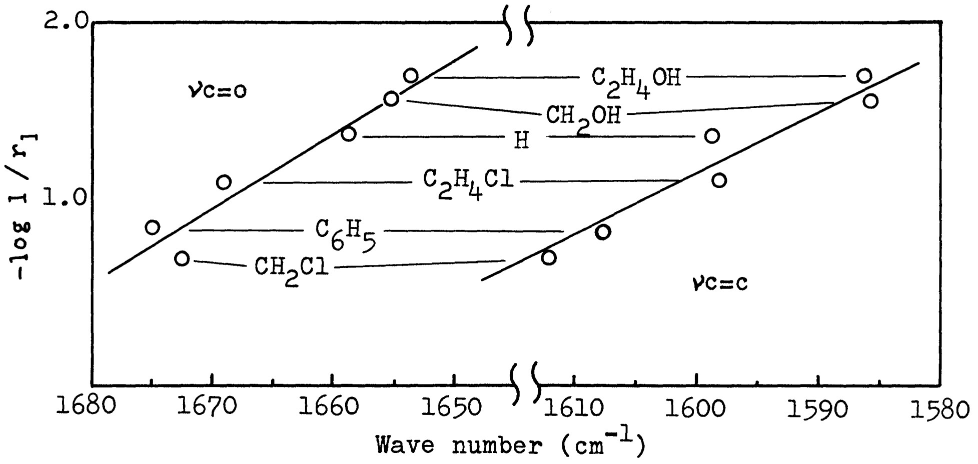


Fig. 1 Correlation between log 1 / r_1 and νc=o or νc=c for copolymerization of 3(2-substituted)6-methylpyridazinones with styrene (M_1).

Reference

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