

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Radical Polymerizability of 6-Methyl-2-vinyl-3-pyridazinone in Protic Media

Tsunehito Eda^a; Katsuhiro Arai^a; Yoshio Matsubara^a; Masakuni Yoshihara^a; Toshihisa Maeshima^a

^a Faculty of Science and Engineering Kinki University, Osaka, Japan

To cite this Article Eda, Tsunehito , Arai, Katsuhiro , Matsubara, Yoshio , Yoshihara, Masakuni and Maeshima, Toshihisa(1981) 'Radical Polymerizability of 6-Methyl-2-vinyl-3-pyridazinone in Protic Media', *Journal of Macromolecular Science, Part A*, 15: 3, 359 – 365

To link to this Article: DOI: 10.1080/00222338108074376

URL: <http://dx.doi.org/10.1080/00222338108074376>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Radical Polymerizability of 6-Methyl-2-vinyl-3-pyridazinone in Protic Media

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

Faculty of Science and Engineering
Kinki University
Higashi-Osaka, 577 Japan

ABSTRACT

Radical copolymerizability of 6-methyl-2-vinyl-3-pyridazinone (I) has been reinvestigated in acetic acid and also in the presence of polyacrylic acid (PAA). Copolymerization of styrene with I was carried out in a few solvents. A positive e_2 value was obtained in acetic acid while negative e_2 values were obtained in benzene and DMF. I was allowed to copolymerize with a few monomers such as styrene, methyl methacrylate, and acrolein in the presence of PAA to give block-type copolymers. All these observations indicate that polymerizability of I is controlled by the hydrogen bonding interaction between the carbonyl group of I and the hydroxyl group of the additive.

INTRODUCTION

We recently reported that the radical polymerizability of the double bond in the pyridazinone ring was affected by the effective ring conjugation of the ring involving the carbonyl group and a pair of electrons on a nitrogen atom [1-5]. More recently, this reactivity was shown to be considerably influenced by such protic solvents as phenol and

carboxylic acid, perhaps due to hydrogen bonding to the polar pyridazinone ring [6-9]. In connection of these observations, the polymerizability of 6-methyl-2-vinyl-3-pyridazinone (I) has been reinvestigated in protic media as well as in the presence of polyacrylic acid.

EXPERIMENTAL

Acrylic acid (AA), styrene (St), methyl methacrylate (MMA), and acrolein (AL) were purified by distillation under reduced pressure in a stream of nitrogen.

The various solvents used in this paper were purified according to methods described elsewhere.

6-Methyl-2-vinyl-3-pyridazinone (I) and 6-methyl-2-phenyl-3-pyridazinone were prepared by the previous method [4, 8]. Polyacrylic acid (PAA, $\bar{M}_n = 1.6 \times 10^4$) and polystyrene (PSt, $\bar{M}_v = 4 \times 10^4$) were prepared by the radical polymerization of AA and St using 2,2'-azobisisobutyronitrile (AIBN). The average molecular weights were determined by means of osmometry and viscometry methods.

All polymerizations were carried out in degassed ampules (60° C) into which the required amounts of the monomers, the initiator, and the additives were placed. The reaction mixture was poured into a large amount of methanol to precipitate the polymer, which was purified by repeated reprecipitation from the DMF-methanol system or the DMF-water system. By infrared and NMR spectral analysis and elementary analysis, the polymers were found to contain no other impurities, especially compounds such as acetic acid and PAA.

RESULTS AND DISCUSSION

Copolymerization of I with St (M_1) in Acetic Acid

Free-radical copolymerization of St (M_1) with I was carried out in a few solvents and the results, shown in Table 1, clearly indicate that the reactivity was enhanced in acetic acid as compared to benzene and DMF; i.e., the smallest r_1 and r_2 values as well as the largest R_p values were obtained in acetic acid. One of the most interesting facts in Table 1 is that a positive e_2 value was obtained in acetic acid while negative e_2 values were obtained in benzene and DMF. This is reasonably explained by a hydrogen-bonding interaction between I and acetic acid which causes a drift of electrons on a nitrogen atom to the carbonyl-oxygen atom as shown in Fig. 1 and thus increases the copolymerizability with the rather negative St. It should be noted that a larger e_2 value was obtained in the copolymerization of St (M_1) with the I- BF_3OEt_2 complex [6]. This difference in e_2 value is

TABLE 1. Radical Copolymerization of St (M_1) with I in a Few Solvents at 60°C^a

Solvents	r_1	r_2	r_1, r_2	Q_2	e_2	$R_p \times 10^6$ ^b (mol/L·s)
Acetic acid	0.52	0.39	0.20	0.71	0.41	2.12
DMF ^c	0.20	0.15	0.03	1.12	1.07	-
Benzene	0.92	0.96	0.88	0.82	-0.44	1.99
DMF	0.90	0.90	0.81	0.74	-0.34	1.24

^a $[St] + [I] = 1 \text{ mol/L}$.

^b $[St]/[I] = 1$.

^cI-BF₃OEt₂ complex in DMF [6].

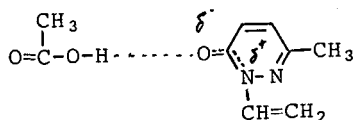


FIGURE 1.

considered to be caused by the different degree of electrophilic interaction between acetic acid and BF₃OEt₂ against the carbonyl oxygen atom of I.

Polymerization of I in the Presence of Polyacrylic Acid (PAA)

When PAA is used in the place of acetic acid, I is considered to be fixed on PAA due to the hydrogen-bonding interaction which will influence the polymerizability of I. In this point of view, I was allowed to polymerize in the presence of PAA and also in other related substances (Fig. 2). It is interesting to note that in the case of PAA the maximum value of the conversion was observed at an I-PAA ratio of 1:1, indicating that there may be some interaction between I and PAA. Similar phenomena have been observed for the polymerization of methacrylic acid and/or p-hydroxystyrene in the presence of poly-N-vinyl-5-methyl-2-oxazolidone and ascribed to the so-called matrix polymerization [10] in which the monomer is considered to be somewhat arranged on the polymer chain.

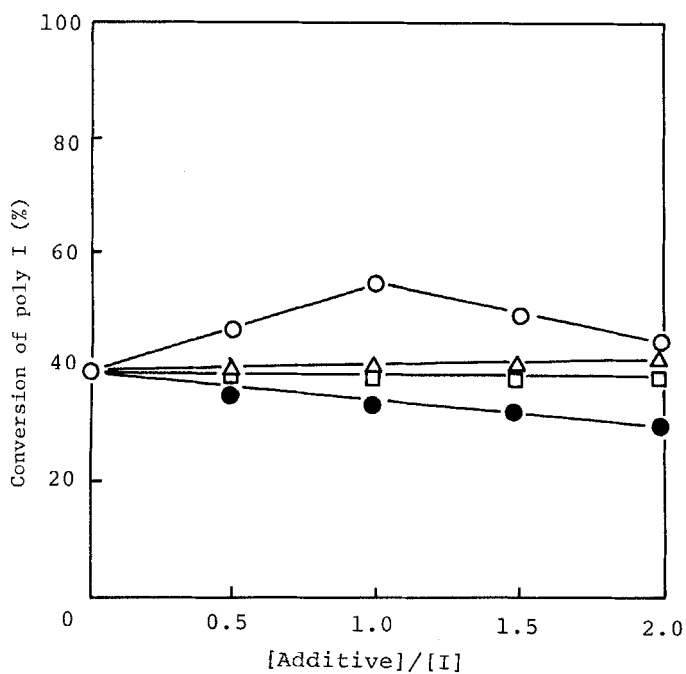


FIG. 2. Polymerization rates of I in the presence of a few additives in DMF at 60°C. Additives: (\circ) PAA, (\bullet) acetic acid, (\square) PST, (\triangle) toluene. Time = 10 h, $[I] = 1$ mol/L, $[AIBN] = 5 \times 10^{-3}$ mol/L.

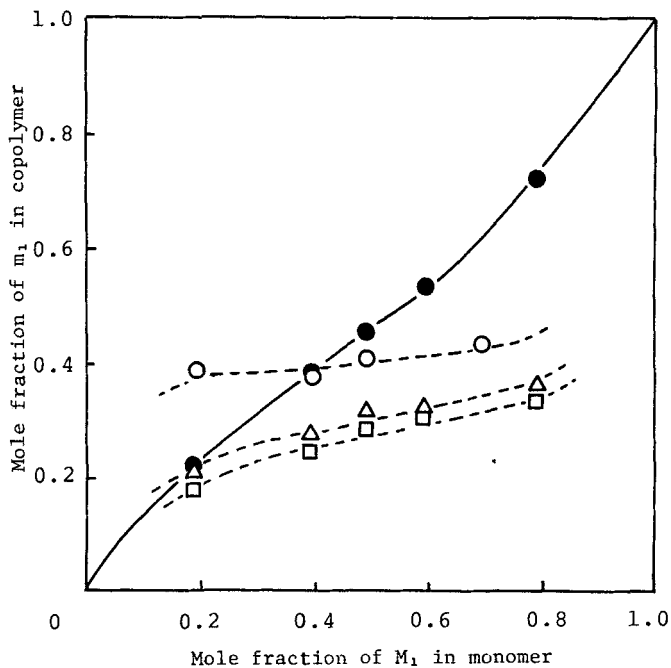


FIG. 3. Copolymerization curves for the copolymerization of I (M_1) with a few monomers in the presence of PAA at 60°C: MMA in DMF in the absence of PAA (●), AL in benzene (○), St in benzene (△), MMA in benzene (□). $[M_1] + [M_2] = 0.5 \text{ mol/L}$, $[AIBN] = 1 \times 10^{-3} \text{ mol/L}$, $[PAA]/[I] = 1$.

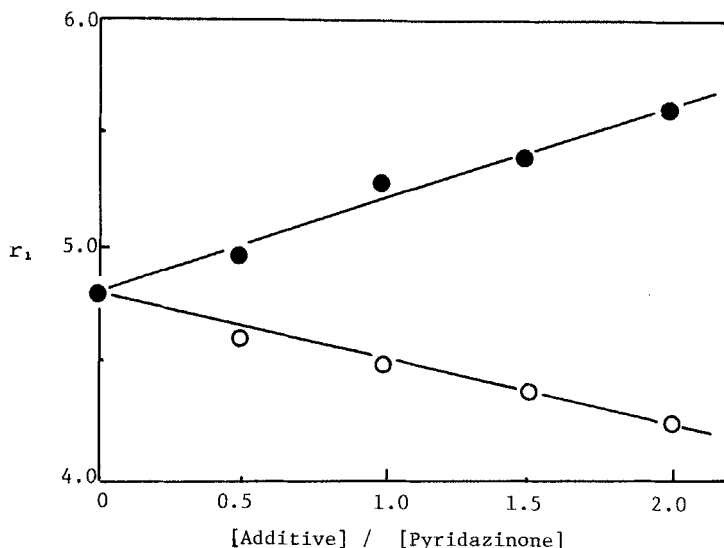


FIG. 4. Relationship between r_1 and additive concentration for copolymerization of II with St (M_1) in the presence of PAA and acetic acid in DMF at 60°C: Acetic acid (●), PAA (○). $[M_1] + [M_2] = 2 \text{ mol/L}$, $[AIBN] = 1 \times 10^{-2} \text{ mol/L}$.

According to this mechanism, I must be concentrated on the polymer chain of PAA due to the hydrogen bonding interaction. In order to investigate this possibility, I has been copolymerized with a few monomers in the presence of PAA (Fig. 3). Unfortunately, all the copolymerizations proceeded heterogeneously; however, it is noteworthy that the copolymer compositions in every case did not vary significantly with a change of I concentration in the monomer feeds. These results seem to imply that block-type copolymer were formed, perhaps by the concentration of I on the polymer chain of PAA due to hydrogen-bonding interaction.

This hypothesis may be partly supported by the following observations (Fig. 4). The r_1 values were found to decrease with an increase of the PAA concentration for the copolymerization of 6-methyl-2-phenyl-3-pyridazinone (II) with St (M_1) in DMF, in which the reaction proceeded homogeneously. This is also considered to be rationalized by the concentration of II on PAA due to hydrogen-bonding interaction.

REFERENCES

- [1] Y. Matsubara, M. Yoshihara, and T. Maeshima, Kogyo Kagaku Zasshi, **74**, 477 (1971).

- [2] Y. Matsubara, M. Yoshihara, and T. Maeshima, Ibid., 74, 2163 (1971).
- [3] Y. Matsubara, M. Noguchi, M. Yoshihara, and T. Maeshima, Chem. Lett., p. 601 (1973).
- [4] Y. Matsubara, K. Kyoji, M. Yoshihara, and T. Maeshima, Nippon Kagaku Kaishi, p. 1992 (1973).
- [5] Y. Matsubara, M. Yoshihara, and T. Maeshima, Ibid., p. 2186 (1974).
- [6] Y. Matsubara, N. Narakino, M. Yoshihara, and T. Maeshima, J. Macromol. Sci.-Chem., A9, 1433 (1974).
- [7] Y. Matsubara, K. Oshiro, M. Yoshihara, and T. Maeshima, Nippon Kagaku Kaishi, p. 188 (1975).
- [8] Y. Matsubara, K. Enyo, M. Yoshihara, and T. Maeshima, J. Polym. Sci., Polym. Chem. Ed., 13, 913 (1975).
- [9] Y. Matsubara, M. Yoshihara, and T. Maeshima, Ibid., 14, 899 (1976).
- [10] T. Endo, R. Numazawa, and M. Okawara, Kobunshi Kagaku, 28, 541 (1971).

Accepted by editor October 16, 1979

Received for publication November 13, 1979