Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Asakura, Jun-Ichi , Kawabata, Shogi , Fujihara, Hisashi , Matsubara, Yoshio , Yoshihara, Masakuni and Maeshima, Toshihisa(1982) 'Effect of Solvent on the Radical Copolymerizability of Styrene with 3(2-Methyl)-6-methylpyridazinone', Journal of Macromolecular Science, Part A, 18: 7, 1045 — 1054

To link to this Article: DOI: 10.1080/00222338208066478

URL: http://dx.doi.org/10.1080/00222338208066478

J. MACROMOL. SCI.–CHEM., A18(7&8), pp. 1045-1054 (1982-83)

Effect of Solvent on the Radical Copolymerizability of Styrene with 3(2-Methyl)-6-methylpyridazinone

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ABSTRACT

The radical copolymerization of styrene (St, M_1) with 3(2-methyl)-6-methylpyridazinone (I, M_2) has been carried out in several p-substituted phenols at 60 and 70°C. Monomer reactivity ratios (r_1) and activation parameters of copolymerization were found to be affected by phenols. The values of the activation energy ($\Delta\Delta E^{\ddagger}$) and entropy ($\Delta\Delta S^{\ddagger}$) increased with the increase of the interaction of I with the solvents. Linear relationships were observed between the σ-values of p-substituents of phenols and the values of log $1/r_1$ and also of $\Delta\Delta E^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$. The radical copolymerization of St (M_1) with 6-substituted 3(2-methyl)-pyridazinone was also carried out.

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*Deceased.

INTRODUCTION

Recently we showed that solvent effects were observed in the radical copolymerization of styrene (St) with a few vinyl monomers bearing rather polar groups [1-7]. In all these cases their reactivities were influenced considerably by such protic solvents as phenol and carboxylic acid, and these results were discussed in terms of the hydrogen bonding solvation to the polar groups both in the ground and transition states.

In order to obtain accumulated experimental evidence for such a solvent effect, the radical copolymerization of St with 3(2-methyl)-6-methylpyridazinone has been carried out by changing the reaction conditions. The results are discussed in terms of solvent effect both in the ground and transition states.

Incidentally, we have extended our hypothesis to an asymmetric induction in the free radical addition reaction and succeeded in getting optically active copolymers by the radical copolymerization of maleic anhydride with St and isobutyl vinyl ether [8-10] and also optically active addition products by radical additions of cyclohexanone to 2-octene [11] and of thiols to olefins [12-14] in chiral environment.

EXPERIMENTAL

3(2-Methyl)-6-methylpyridazinone (I, M_2) and other 6-substituted 3(2-methyl)-pyridazinones were prepared by the methods described previously [15]. Styrene (St, M_1) was purified by the conventional method. Other reagents were purified by ordinary methods.

Radical copolymerization of St with I was carried out with the use of AIBN as an initiator in p-substituted phenols at 60 and 70°C in a degassed ampule.

The copolymers were purified by the reprecipitation method from benzene-methanol.

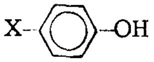
The composition of the copolymers was determined by elementary analysis for nitrogen.

RESULTS AND DISCUSSION

The radical copolymerization of St (M_1) with I (M_2) has been carried out in p-substituted phenols at 60 and 70°C.

Table 1 summarizes the values of monomer reactivity ratios (r_1) and activation parameters of copolymerization. The r_1 values varied with both the solvents and temperature, clearly indicating the effect of phenols in the reaction. Therefore the stretching frequencies of the monomers were determined in the substituted phenols. The value of $\nu C{=}C$ of St did not vary with the phenols while those of $\nu C{=}C$ and

TABLE 1. Monomer Reactivity Ratios (r_1) and Activation Parameters for Copolymerization of St (M_1) with I (M_2)[a]

Solvent 	r_1		$\Delta\Delta E^\ddagger$ (kcal/mol)	$\Delta\Delta H^\ddagger$[b] (kcal/mol)	$\Delta\Delta S^\ddagger$[b] (e.u.)
	60°C	70°C			
X: Br	13.71	18.21	6.27	5.61	24.02
Cl	13.73	18.37	6.42	5.77	24.50
H	14.78	19.38	5.98	5.32	23.32
C_2H_5	15.67	20.40	5.82	5.16	22.96
CH_3	15.69	20.48	5.88	5.22	23.13

[a] $[M_1] + [M_2] = 2$ mol/L, $[\text{AIBN}] = 1 \times 10^{-2}$ mol/L, $r_2 = 0.01$.
[b] At 60°C.

νC=O of I did vary considerably. The plots of these values of I with log $1/r_1$ values gave linear relationships (Fig. 1). Straight lines were also obtained by plotting the log $1/r_1$ values against Hammett's σ-values (Fig. 2). Thus the stronger the hydrogen bonding interaction between I and phenols, the more the copolymerizability increased. These results seem to indicate that the copolymerizability might be affected by the different degree of solvation to carbonyl group of the I unit at the ground state alone. However, it should be noted that the values of the differences of the activation enthalpy ($\Delta\Delta H^\ddagger$), energy ($\Delta\Delta E^\ddagger$), and entropy ($\Delta\Delta S^\ddagger$) in the following equation increased with an increase in the interaction of I monomer with the solvents (Table 1).

$$\log r_1 = \log (K_{11}/K_{12}) = -\exp\left[(\Delta\Delta H^\ddagger - T\Delta\Delta S^\ddagger + RT)/RT\right]$$

where

$$\Delta\Delta H^\ddagger = \Delta H^\ddagger_{11} - \Delta H^\ddagger_{12}, \qquad \Delta\Delta S = \Delta S^\ddagger_{11} - \Delta S^\ddagger_{12},$$

$$\Delta\Delta E^\ddagger = \Delta\Delta H^\ddagger + RT$$

The linear relationships were observed when the value of $\Delta\Delta E^\ddagger$ and $\Delta\Delta S^\ddagger$ were plotted against the values of νC=O frequencies and Hammett's σ-values (Figs. 3 and 4). Although these values are the differences of the corresponding values in K_{11} and K_{12}, the K_{11} values are assumed to be almost unchanged with the solvents as described above. Thus the values of $\Delta E^\ddagger_{12}$ and $\Delta S^\ddagger_{12}$ decreased with an increase of the interaction between I and the solvents. These results may be explained

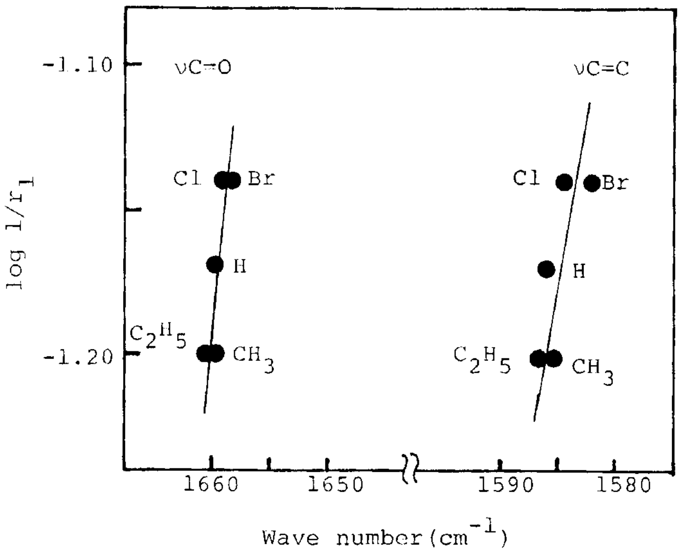


FIG. 1. Relationships between log $1/r_1$ (60°C) and νC=O or νC=C of I in p-substituted phenols.

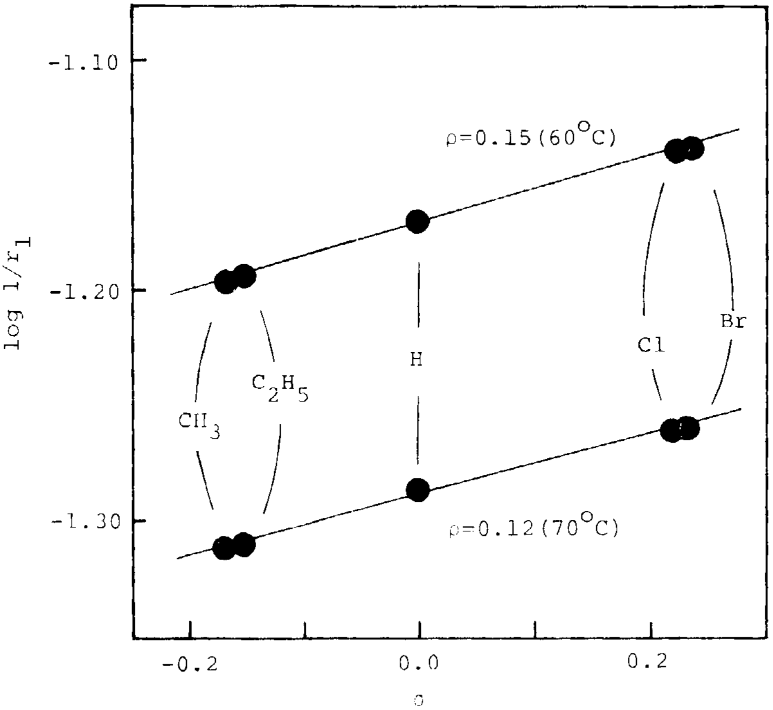


FIG. 2. Hammett plots for the copolymerization of St (M_1) with I in several p-substituted phenols.

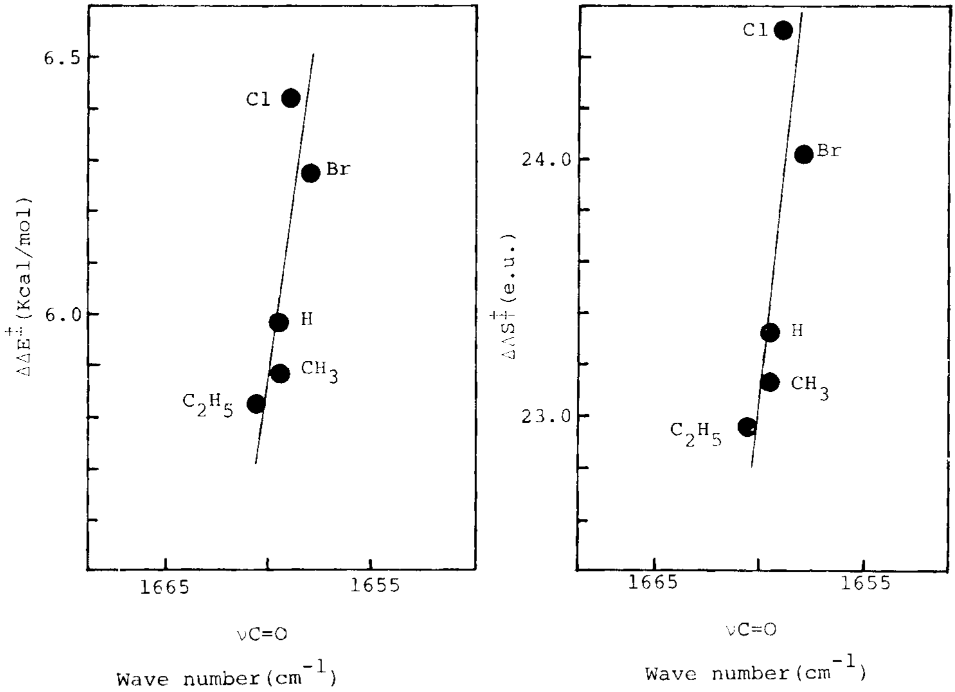


FIG. 3. Relationships between ΔΔE‡ or ΔΔS‡ and $\nu C{=}O$.

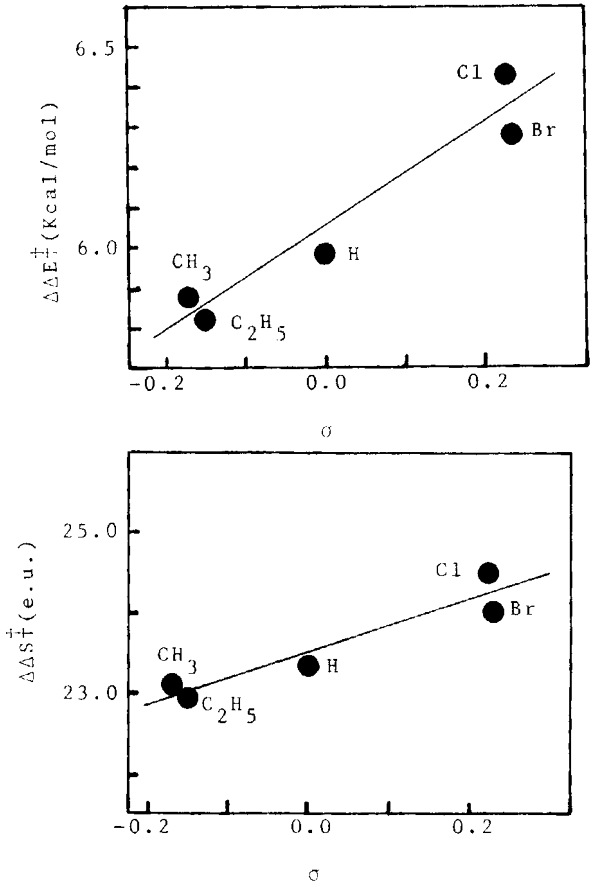


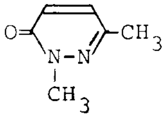
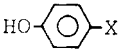
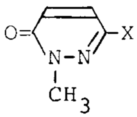
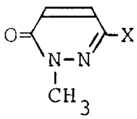
FIG. 4. Relationships between ΔΔE‡ or ΔΔS‡ and σ values of p-substituted phenols.

TABLE 2. Monomer Reactivity Ratios (r_1) for Copolymerization of St (M_1) with 6-Substituted-3(2-methyl)-pyridazinone (M_2) in Acetic Acid[a]

M_2, X	r_1
OCH_3	7.5
CH_3	13.6
H	20.2
$COOCH_3$	4.1

[a] $[M_1] + [M_2] = 2$ mol/L, $[AIBN] = 1 \times 10^{-2}$ mol/L, at 60°C, $r_2 = 0.01$.

TABLE 3. Hammett ρ and γ Values for the Copolymerization of St (M_1) with Pyridazinone Derivatives in Several Solvents[a]

M_1	M_2	Solvent	ρ	γ
St			0.15	-
St		DMF	0.003[b]	4.71[b]
St		Acetic acid	0.11	4.08

[a] At 60°C.

[b] The data obtained previously were incorrectly evaluated to give $\rho = 0.06$ and $\gamma = 4.80$ [15] which should be replaced by the present values.

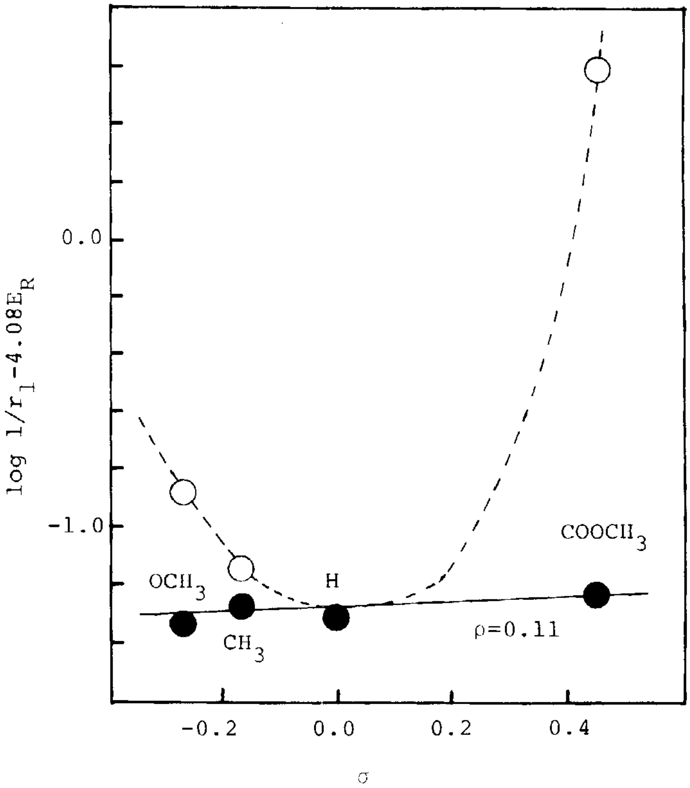


FIG. 5. Plots of log $1/r_1$ vs σ values for the St (M_1)-6-substituted-3(2-methyl)-pyridazinone system in acetic acid.

by taking account of the substituent effect on the solvation in the transition state of K_{12} step. In the transition state the polystyryl unit will acquire some positive charge while the I unit gets some negative charge. The drift of charge electron from polystyryl carbon to the pyridazinone ring may increase with increasing electron-accepting ability of the solvent, and this is expected to increase the ionic character in the transition state. In other words, the stronger the hydrogen bonding interaction, the more the stabilization of the transition state will increase: this will result in decreasing the values of $\Delta E^{\ddagger}_{12}$ and $\Delta S^{\ddagger}_{12}$.

Additional evidence to support such a stabilization of the transition state via electron-accepting solvation can be deduced by the copolymerization of 6-substituted-3(2-methyl)-pyridazinones with St (M_1) ih acetic acid (Table 2) and DMF [15]. Thus, in plotting the log $1/r_1$ values against Hammett's σ-values with Otsu's equation (Fig. 5), the ρ-value obtained in acetic acid was larger than that for the DMF system (Table 3). This also reflects the enhanced ionic character of the transition state for the acid system via an electron-accepting interaction to the carbonyl group of I.

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Accepted by editor December 15, 1981
Received for publication December 29, 1981