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Radical Copolymerization of 3(2-Methyl)-6-methylpyridazinone with Styrene in Several Substituted Acetic Acids

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ABSTRACT

The radical copolymerization of 3(2-methyl)-6-methylpyridazinone (I) with styrene (St) (M_1) was carried out in several substituted acetic acids at 60 and 80°C. The monomer reactivity ratios were found to vary with the reaction conditions. The values of both $\Delta\Delta E^{\ddagger}$ (= $\Delta E_{11}^{\ddagger}$ - $\Delta E_{12}^{\ddagger}$) and $\Delta\Delta S^{\ddagger}$ (= $\Delta S_{11}^{\ddagger}$ - $\Delta S_{12}^{\ddagger}$) increased with the increase of the interaction of I with the solvents.

INTRODUCTION

Saini et al. [1] reported that monomer reactivity ratio r for the copolymerization of acrylamide with styrene (St) was strongly affected by solvents used. Similar trends in the r values were also observed for the copolymerizations of St with vinyl monomers having rather polar groups, such as methacrylonitrile [2], ethyl vinylsulfoxide [3], and acrylamide derivatives [4]. In these cases, the results were discussed mainly on the basis of the modification of the association of monomer and/or polymer radical with solvents at the ground state. In a previous paper [5], we also showed that the copolymerizability of 3(2-methyl)-6-methylpyridazinone (I) with St (M_1) was considerably affected by the reaction media, and the results were discussed in terms of the solvation to the polar pyridazinone unit. On the other hand, from the kinetics of polymerization of St [6] and methylmethacrylate [7], it was suggested that a growing radical forms a complex with solvent and that the stability and reactivity of this complex determines the velocity of the propagation reaction. This suggestion implies that the solvent alters the values of both k_{11} and k_{12} in r_1 values. In these connections, therefore, the polymerization of St (M_1) with I was reinvestigated in several substituted acetic acids to estimate which is more important, the solvation to a radical or the monomer I, and the results were discussed in terms of the solvation not only in the ground state but also at the transition state.

EXPERIMENTAL

Material

3(2-Methyl)-6-methylpyridazinone (I) was prepared by the method previously described [5]; bp 123°C/23 Torr; mp 37°C.

Styrene (St) was purified by distillation under reduced pressure in a stream of nitrogen.

The solvents used in this work were purified by the usual methods.

Polymerization Procedure

All polymerizations were carried out in degassed ampoules at 60 and 80°C in which the required amounts of monomers, initiator, and solvents were placed. The reaction mixture was poured into an excess of methanol to precipitate the copolymer, which was purified by repeated reprecipitation from benzene and methanol. No other impurities in the copolymers were determined by infrared and NMR analysis. The compositions of the copolymers were determined by elementary analysis of nitrogen.

RESULTS AND DISCUSSION

Table 1 includes r_1 values obtained at 60 and 80°C. The r_1 values varied with both the solvents and the temperature, implying an

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

Solvent	Concn (mole/liter)	r_1		$\Delta\Delta E^{\ddagger}$	$\Delta\Delta H^{\ddagger}$[b]	$\Delta\Delta S^{\ddagger}$[b]	$\Delta\Delta F^{\ddagger}$[b]
		60°C	80°C				
$ClCH_2COOH$	2	9.32	12.77	3.68	3.02	15.49	-2.14
$Cl(CH_2)_2COOH$	2	11.38	14.17	2.57	1.91	12.54	-2.27
CH_3COOH	2	12.24	14.70	2.14	1.48	11.40	-2.32
C_2H_5COOH	2	12.67	14.39	1.49	0.83	9.52	-2.34
$(CH_3)_2CHCOOH$	2	11.63	13.43	1.68	1.02	9.93	-2.29
Benzene	1.77	9.28	9.65	1.71	1.05	9.56	-2.14
DMF	1.77	8.98	9.76	1.74	1.08	9.58	-2.11
Bulk		6.65	7.52	1.82	1.16	8.78	-1.77

[a] Dimension of activation parameters: $\Delta\Delta E^{\ddagger}$ (kcal/mole), $\Delta\Delta H^{\ddagger}$ (kcal/mole), $\Delta\Delta S^{\ddagger}$ (e. u.), $\Delta\Delta F^{\ddagger}$ (kcal/mole).

[b] At 60°C.

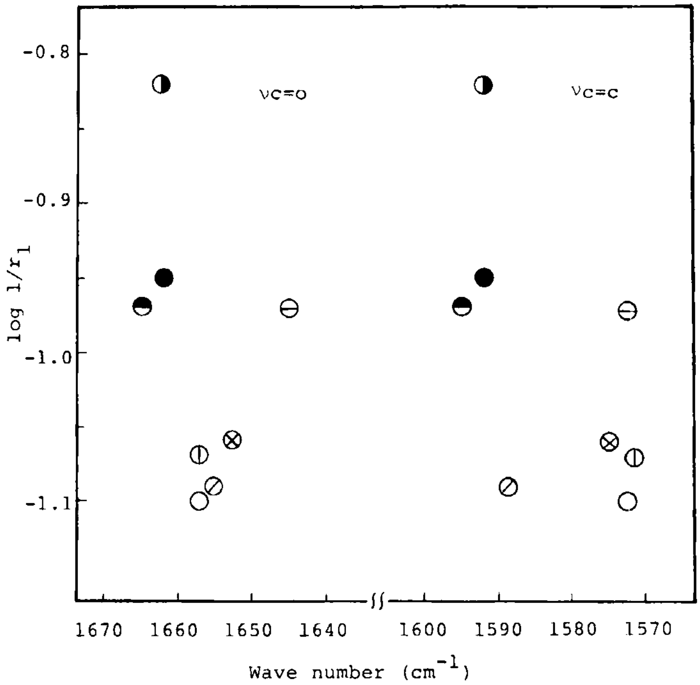

FIG. 1. Relationships between log $1/r_1$ and $\nu_{C=O}$ or $\nu_{C=C}$:
(◑) bulk; (◓) benzene; (●) DMF; (⊖) $ClCH_2COOH$;
(⊗) $Cl(CH_2)_2COOH$; (⊘) CH_3COOH; (⦶) $Me_2CHCOOH$; (○) EtCOOH.

occurrence of solvation effect in the reaction. It was postulated that this might be due to some difference in solvation onto the pyridazinone ring in the ground state, because plots of log $1/r_1$ against the values of both $\nu_{C=O}$ and $\nu_{C=C}$ stretching frequencies of I showed a linear relation [8]. However, plots of log $1/r_1$ values in Table 1 with these IR values determined in various solvents did not give such clear relationships and seem to divide into two different kinds of lines (Fig. 1). There seems to be two plausible possibilities for these results. One is due to a different degree of solvation to a styryl radical causing a variation in the values of both k_{11} and k_{12}. The other is the possibility of the different degree solvation to I unit at the transition state.

The differences of the activation free energy $\Delta\Delta F^{\ddagger}$, the activation

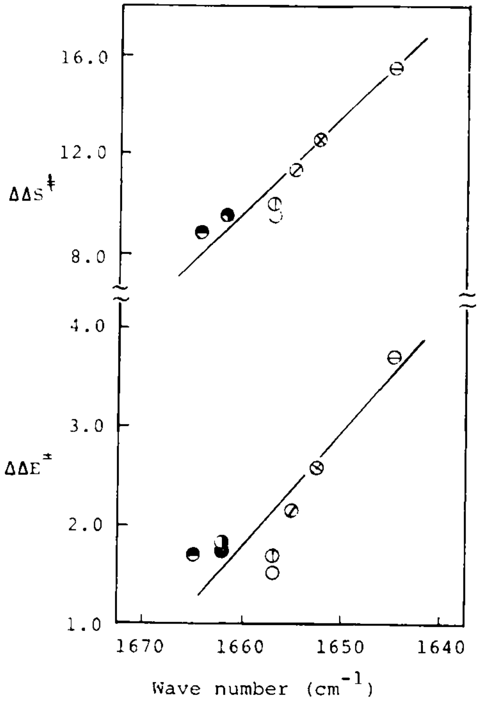

FIG. 2. Relationships between $\Delta\Delta E^{\ddagger}$ or $\Delta\Delta S^{\ddagger}$ and $\nu_{C=O}$. Symbols as in Fig. 1.

enthalpy $\Delta\Delta H^{\ddagger}$ and energy $\Delta\Delta E^{\ddagger}$, and the activation entropy $\Delta\Delta S^{\ddagger}$ for the r_1 values were determined from the equation:

$$\begin{aligned}\log r_1 &= \log(k_{11}/k_{12}) \\ &= -\exp\{\Delta\Delta F^{\ddagger}/RT\} \\ &= -\exp\{(\Delta\Delta H^{\ddagger} - T\,\Delta\Delta S^{\ddagger})/RT\}\end{aligned}$$

where $\Delta\Delta F^{\ddagger} = \Delta F_{11}{}^{\ddagger} - \Delta F_{12}{}^{\ddagger}$, $\Delta\Delta H^{\ddagger} = \Delta H_{11}{}^{\ddagger} - \Delta H_{12}{}^{\ddagger}$, $\Delta\Delta S^{\ddagger} = \Delta S_{11}{}^{\ddagger} - \Delta S_{12}{}^{\ddagger}$, and $\Delta\Delta E^{\ddagger} = \Delta\Delta H^{\ddagger} + RT$ (Table 1). As can be seen in Table 1, the values of $\Delta\Delta F^{\ddagger}$ varied little with the solvents but those

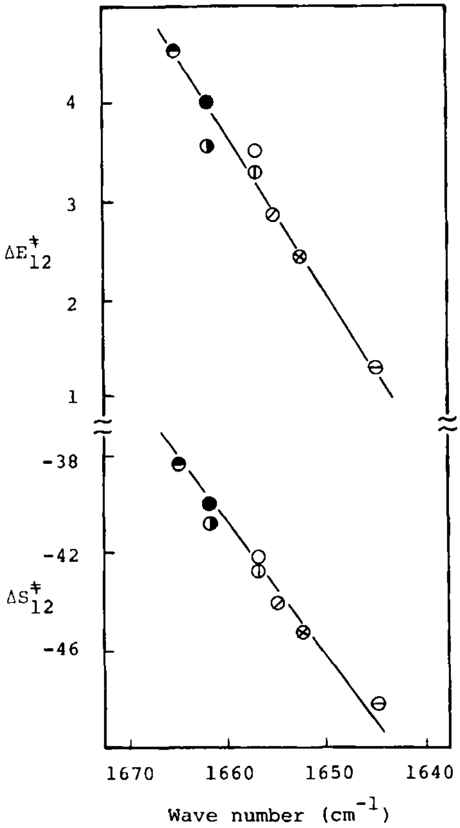

FIG. 3. Relationships between $\Delta E_{12}^{\ddagger}$ or $\Delta S_{12}^{\ddagger}$ and $\nu_{C=O}$. Symbols as in Fig. 1.

of both $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ varied considerably. Here, it is quite interesting to note that linear relationships were observed when the values of $\Delta\Delta E^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ were plotted against the values of the frequencies $\nu_{C=O}$ (Fig. 2). Although unfortunately we could not estimate the degree of the solvation to the styryl radical, these results seem to imply that the reactivity will not be affected by the solvation to a styryl radical but vary primarily with some differences in solvation to the I unit between at the ground state and at the transition state. Thus, the possibility of solvation to the St unit would be expected to be slight compared with solvation to I. The solvation to I perhaps takes place on the carbonyl group of I because no linear relationships

TABLE 2. Activation Parameters for Copolymerization of I with St

Solvent	k_{12}[a]	k_{12}[b]	$\Delta E_{12}^{\ddagger}$ (kcal/mole)[a]	$\Delta S_{12}^{\ddagger}$ (e. u.)[a]
$ClCH_2COOH$	29.40	32.89	1.31	-48.1
$Cl(CH_2)_2COOH$	24.08	29.64	2.43	-45.2
CH_3COOH	22.39	28.57	2.85	-44.0
C_2H_5COOH	21.63	29.19	3.51	-42.1
$(CH_3)_2CHCOOH$	23.56	31.27	3.31	-42.6
Benzene	29.56	43.52	4.54	-38.4
DMF	30.51	43.03	4.02	-39.9
Bulk	41.20	55.85	3.56	-40.7

[a] At 60°C.
[b] At 80°C.

were observed on plotting the $\Delta\Delta E^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ values with the values of $\nu_{C=C}$ frequencies. This assumption is partly supported by the fact that a straight line was obtained by the plots of the $\nu_{C=O}$ values with Taft's σ^* values of substituted acetic acids while no linear relationship was observed in the case of $\nu_{C=C}$ values.

We can see another interesting fact in Fig. 2: namely, the stronger the interaction of the I monomer with the solvents the more the values of both $\Delta\Delta E^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ increased. Although these values are the differences of the corresponding values in k_{11} and k_{12}, each k_{11} value may be regarded to be little changed by the solvents compared with k_{12}, as discussed above. In other words, the k_{11} values are assumed to be almost unchanged with the solvents. From this point of view, we tried to calculate k_{12} values from the equation, $k_{12} = k_{11}/r_1$ on assumption of k_{11} (60°C) as 274 and k_{11} (80°C) as 420 liter/mole-sec, calculated by least-squares method with all the k_{11} values cited in the literature [9], and then to get the values of $\Delta E_{12}^{\ddagger}$ and $\Delta S_{12}^{\ddagger}$ from these k_{12} (Table 2 and Fig. 3). Here again, straight lines were obtained by plotting $\Delta E_{12}^{\ddagger}$ and $\Delta S_{12}^{\ddagger}$ values against the $\nu_{C=O}$ values: both values decreased with an increase of the interaction between I and the solvents.

We wish to postulate a hypothesis that this may arise by the solvent stabilization of the transition state of the k_{12} step. In the transition state the styryl unit will acquire some positive charge while the I unit gets some negative charge because positive ρ values were obtained by plotting the values of log $1/r_1$ against σ values in the copolymerization of substituted pyridazinones with St (M_1) [8]. A drift of charge electrons from polystyryl carbon to the pyridazinone ring may be increased with increasing electron-accepting ability of the solvent, and this is expected to increase an ionic character in the transition state. In other words, the stronger such interaction, the more the transition state will be stabilized; this will result in the decrease of the values of both $\Delta E_{12}^{\ddagger}$ and $\Delta S_{12}^{\ddagger}$.

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