Solvent Effect on the Radical Copolymerizability of Styrene with p-Substituted Methyl Cinnamates

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ABSTRACT

The radical copolymerization of styrene with p-substituted
methyl cinnamates was carried out in benzene, acetonitrile,
and acetic acid at 60 and 80°C. The ρ values obtained by plotting
the values of log $1/r_1$ against σ values with the modified Hammett's
equation decreased in the order benzene, acetonitrile, and
acetic acid. The activation energy and entropy in copolymeriza-
tion were also estimated. The results are discussed in terms of
the different degrees of solvation between the ground state and
the transition state.

INTRODUCTION

During the course of our investigation on the radical copolymeri-
zation of styrene (St) with vinyl monomers having polar groups in
various solvents, we found that their monomer reactivity ratios were
considerably influenced by the reaction temperature and solvent
[1-6]. We postulated a hypothesis that this might be caused by the
hydrogen bonding solvation to the polar group of the vinyl monomer
both in the ground and transition states of the propagation step.

The present work shows our experimental finding that in the radi-
cal copolymerization of St with p-substituted methyl cinnamate
(MCM) the reactivity ratio was considerably influenced by the solvent.

We also found that the radical copolymerization of maleic anhydride
with St and isobutyl vinyl ether in ℓ-menthol gives optically active
copolymers [8-10].

EXPERIMENTAL

p-Substituted methyl cinnamates (MCM, M_2) were prepared by
reacting p-substituted cinnamoyl chloride with methanol in the pres-
ence of pyridine in benzene. Styrene (St, M_1) and other reagents
were purified by the conventional method.

All copolymerizations were carried out in degassed ampules at
60 and 80°C.

The reaction mixture was poured into a large amount of methanol
to precipitate the copolymer, which was purified by the reprecipita-
tion method from benzene-methanol, and dried in vacuum.

The compositions of copolymers were determined by elemental
analysis.

RESULTS AND DISCUSSION

The radical copolymerization of St (M_1) with p-substituted MCM
(M_2) was carried out in benzene, acetonitrile, and acetic acid at 60
and 80°C.

Table 1 summarizes the monomer reactivity ratios and Hammett's
ρ values obtained in each solvent. The r_1 values were found to vary
with the solvent, implying some solvent effect in the reaction. It is
assumed that the change in r_1 is mainly due to solvation of MCM
rather than of St because MCM or its radical would be more strongly
solvated than St due to the polar group in MCM. Indeed, the stretch-
ing frequency ($\nu C{=}C$) of St did not vary with the solvent, while the
$\nu C{=}O$ of MCM appeared at 1715 cm^{-1} in benzene and shifted to a
longer wavelength (1697 cm^{-1}) in acetic acid. Another interesting
fact in Table 1 is that the ρ values obtained by plotting with the use

TABLE 1. Copolymerization Parameters of St (M_1) with p–Substituted MCM (M_2) in Benzene, CH_3CN, and AcOH[a]

Solvent	Substituent	Temperature (°C)	r_1	r_2	ρ	γ
Benzene	–Cl	80	2.24	0.04		
	–H	80	1.27	0.02		
					1.16	–5.09
	–CH₃	60	2.12	0.20		
		80	2.84	0.00		
CH₃CN	–Cl	80	0.84	0.14		
	–H	80	1.79	0.38		
					0.48	2.19
	–CH₃	60	1.50	0.05		
		80	1.86	0.00		
AcOH	–Cl	80	1.04	0.14		
	–H	80	0.88	0.00		
					0.10	–0.97
	–CH₃	60	1.57	0.16		
		80	0.98	0.08		

[a]$[M_1] + [M_2] = 1$ mol/L, $[AIBN] = 7.0 \times 10^{-3}$ mol/L.

of Otsu's equation [11] decreased in the order benzene, acetonitrile, and acetic acid (Fig. 1). In the copolymerization of St (M_1) with p-substituted cinnamyl diethylamide, the ρ value (0.56) obtained in acetic acid was larger than that (0.49) in benzene, and also in the copolymerization of p-substituted St (M_1) with methyl vinyl sulfoxide ρ values increased in the order benzene, acetonitrile, and acetic acid [4]. These higher ρ values in acetic acid were ascribed to the enhanced ionic character of the transition state via electron-accepting solvation of the polar groups of the M_2 monomers. However, the reversed order of ρ values in the present work does not imply such an electron-accepting stabilization with acetic acid at the transition state rather than at the ground state. For evaluating different degree of solvation between the two states, the values of the differences of activation free energy $\Delta\Delta F\ddagger$, enthalpy $\Delta\Delta H\ddagger$, energy $\Delta\Delta E\ddagger$, and entropy $\Delta\Delta S\ddagger$ for the p-CH₃-MCM system were calculated by the following equation (Table 2),

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

$$= -\exp\left[(\Delta\Delta H\ddagger - T\Delta\Delta S\ddagger + RT)/RT\right]$$

where

$$\Delta\Delta H\ddagger = \Delta H_{11}\ddagger - \Delta H_{12}\ddagger, \qquad \Delta\Delta S\ddagger = \Delta S_{11}\ddagger - \Delta S_{12}\ddagger,$$

$$\Delta\Delta F\ddagger = \Delta F_{11}\ddagger - \Delta F_{12}\ddagger, \qquad \Delta\Delta E\ddagger = \Delta\Delta H\ddagger + RT$$

It is noted that the smallest values of $\Delta\Delta E\ddagger$ and $\Delta\Delta S\ddagger$ were obtained for the acetic acid system. Although these values are the differences of the corresponding values in K_{11} and K_{12}, each K_{11} value is only slightly changed by the solvents as compared with K_{12}, as described above. From this point of view, we tried to calculate K_{12} values from the equation $K_{12} = K_{11}/r_1$ on the assumption of K_{11} (60°C) as 274 and K_{11} (80°C) as 628 L/mol·s. These were calculated by the least-squares method with all the K_{11} values cited in the literature [12], and then the values of $\Delta E_{12}\ddagger$ and $\Delta S_{12}\ddagger$ were obtained from these K_{12} values (Table 2). It should be noted that the values of $\Delta E_{12}\ddagger$
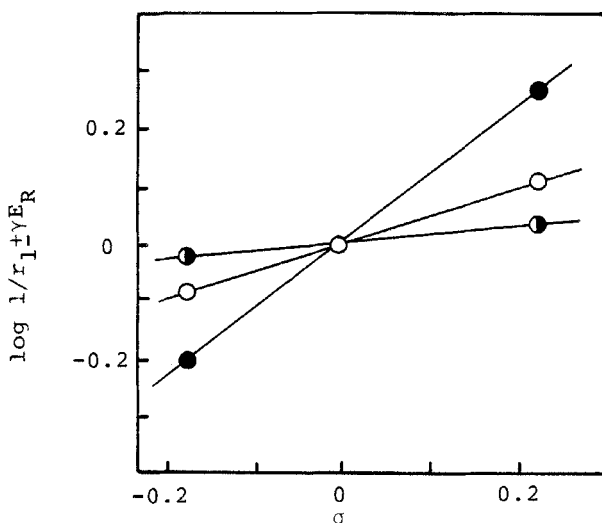

FIG. 1. Hammett plots for the copolymerization of St (M_1) with p-substituted MCM (M_2) in benzene (●), CH_3CN (○), and AcOH (◐) at 80°C.

TABLE 2. Activation Parameters for Copolymerization of St (M_1) with p–CH_3–MCM (M_2) in Several Solvents

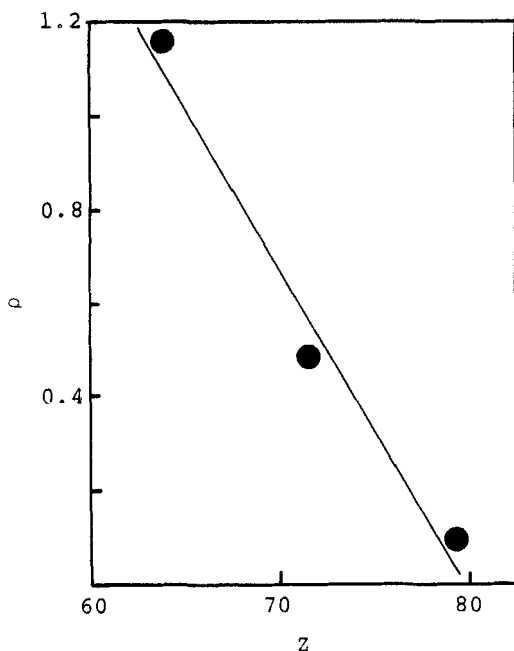| Solvent	r_1		$\Delta\Delta E^{\ddagger}$ (kcal/mol)	$\Delta\Delta H^{\ddagger a}$ (kcal/mol)	$\Delta\Delta S^{\ddagger a}$ (e.u.)	$\Delta\Delta F^{\ddagger a}$ (kcal/mol)	K_{12}		$\Delta E_{12}^{\ddagger}$ (kcal/mol)	$\Delta S_{12}^{\ddagger a}$ (e.u.)
	60°C	80°C					60°C	80°C		
Benzene	2.12	2.84	3.42	2.76	11.76	-1.16	129.24	221.13	6.28	-30.24
CH_3CN	1.50	1.86	2.51	1.85	8.35	-0.93	182.67	337.63	7.18	-26.85
AcOH	1.57	0.98	-5.51	-6.17	-15.64	-0.96	174.52	640.82	15.20	-2.85

[a] At 60°C.

FIG. 2.   Relationship between ρ values and Z values of solvent used.

and $\Delta S_{12}{\ddagger}$ obtained in acetic acid were extremely high compared to the others.   This means that the reaction species may be strongly solvated by acetic acid in the ground state while a considerable desolvation may occur in the transition state.   In other words, solvation in the ground state may be stronger than in the transition state.

It is interesting to note that a linear relationship was observed between the ρ and Z values of the solvents used (Fig. 2).   The Z values are regarded as a measure of the solvation ability of a polar ionic structure in the ground state rather than in the transition state. Therefore, a solvent with a higher Z value, such as acetic acid, is considered to solvate the M_2 monomer strongly in the ground state and thus increase its ionic character, while a decrease of such solvation in the transition state may reduce its ionic character.   Since the magnitude of the ρ value is dependent on a difference in electron density at the reaction center between the ground state and the transition state, the observed discrepancy in ρ values may be explained as due to stronger solvation of a higher ionic structure in the ground state than in the transition state.

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