Solvent Effects on the Radical Copolymerizabilities of Styrene with p-Substituted N,N-Diethylcinnamamides and of p-Substituted Styrenes with Methyl Vinyl Sulfoxide

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ABSTRACT

Radical copolymerizations of styrene (St) with p-substituted-N,N-diethylcinnamamides (I) and also of p-substituted styrenes (II) with methyl vinyl sulfoxide (MVSO) have been carried out in benzene, acetic acid or acetonitrile. The monomer reactivity ratios (r_1) were found to be affected by the solvents. ρ values obtained by using the modified Hammett equation, i. e., $\log(1/r_1) = \rho\sigma + \gamma E_R$, were also found to be altered by the solvents. The results are discussed in terms of the solvent effect in the transition state of the propagation reaction.

INTRODUCTION

Previously we reported that the radical copolymerizability of styrene with vinyl monomers bearing polar groups, i. e., 2,6-dimethylpyridazine-3-one [1], methyl methacrylate [2], and N,N-dimethyl-

acrylamide [3], were considerably influenced by such protic solvents
as phenol and carboxylic acid, due apparently to the hydrogen-bonding
solvation to the polar groups of vinyl monomers, which would stabil-
ize the growing radicals both in the ground state and in the transition
state to affect the reactivities of these monomers.

In this work, the authors have re-investigated the effects of solvents
on the copolymerizabilities of styrene (St) with p-substituted-N,N-
diethylcinnamamides (I) and also of p-substituted styrenes (II) with
methyl vinyl sulfoxide (MVSO).

EXPERIMENTAL

Materials

Styrene (St) was purified by distillation in a stream of nitrogen
before use.

Syntheses of p-substituted-N,N-diethylcinnamamides (I) were de-
scribed previously [4, 5]; p-$CH_3C_6H_4CH$=$CHCON(C_2H_5)_2$ had bp
160°C/3 Torr; p-ClC_6H_4CH=$CHCON(C_2H_5)_2$ had mp 44-45°C;
C_6H_5CH=$CHCON(C_2H_5)_2$ had mp 68-69°C.

p-Substituted styrenes (II) were prepared by the method described
elsewhere [6-8]; p-$CH_3C_6H_4CH$=CH_2 had bp 55°C/12 Torr;
p-ClC_6H_4CH=CH_2 had bp 72°C/12 Torr.

Methyl vinyl sulfoxide (MVSO) was prepared by the method of
Price et al. [9]; CH_2=$CHSOCH_3$ had bp 70-71°C/11 Torr.

The compounds were purified according to the usual method and
were characterized by means of infrared (IR) and NMR spectra and
elementary analysis.

Benzene, acetonitrile (CH_3CN), and acetic acid (AcOH) were puri-
fied according to the usual method.

Polymerization

All polymerizations were carried out at 80°C in degassed ampules,
into which the required amounts of monomer, solvent, and initiator
were placed. The reaction mixture was poured into a large amount
of methanol to precipitate the polymer, which was purified by repeated
reprecipitation from benzene and methanol. No other impurities in
the copolymers were determined by infrared (IR) and NMR spectral
analysis and by TLC. The compositions of copolymers for the St-I
system were determined by elementary analysis of nitrogen while
the copolymer compositions for the II-MVSO system were determined
by elementary analysis of carbon.

TABLE 1. Monomer Reactivity Ratios for the Copolymerization of St (M_1) with I at 80°C

	r_1	
X	In benzene	In AcOH
CH_3	4.95	6.08
H	4.17	4.92
Cl	2.99	3.56

   $r_2 = 0.01$.

TABLE 2. Monomer Reactivity Ratios for the Copolymerization of II(M_1) with MVSO at 80°C

	r_1		
X	In benzene	In AcOH	In CH_3CN
CH_3	2.73	2.28	6.90
H	3.57	3.20	8.17
Cl	6.46	6.54	10.85

   $r_2 = 0.01$.

RESULTS AND DISCUSSION

Tables 1 and 2 show the results of the radical copolymerizations of styrene with I and II with MVSO in a few solvents. Monomer reactivity ratios (r_1) obtained in both systems were found to vary with the solvents, implying some solvent effect in the copolymerizations.

The r_1 values were plotted against Hammett σ values by using Otsu's equation [10], i. e., $\log(1/r_1) = \rho\sigma + \gamma E_R$, to give linear relationships as shown in Figs. 1 and 2. The values of ρ and γ are given in Table 3. It is quite interesting to note that the ρ values obtained in both systems were altered by the reaction solvents, indicating that the ionic character in the transition state of the K_{12} step might be influenced by the solvents used. In the case of the St-I system, the ρ value in benzene was found to be smaller than that in acetic acid. This fact may be explained in the following manner. In the transition state of K_{12} the drift of an electron to the I unit is accelerated by acetic acid compared with benzene, perhaps due to a hydrogen-bonding
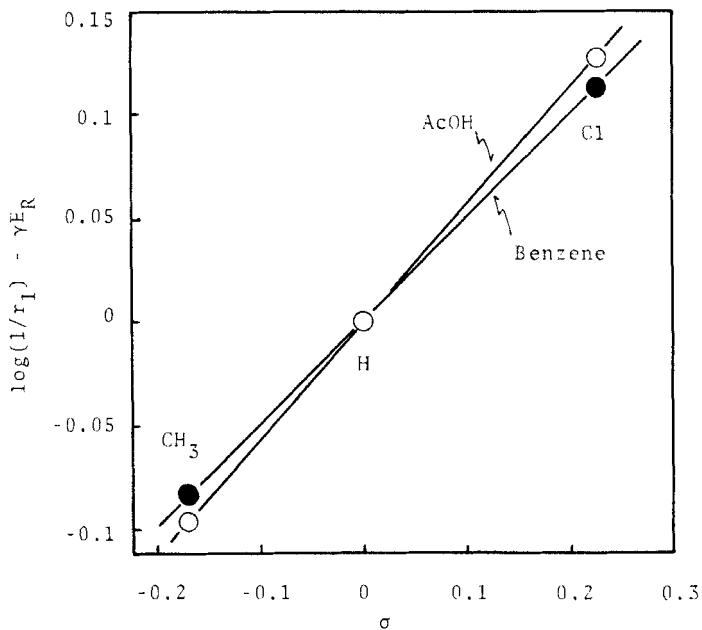
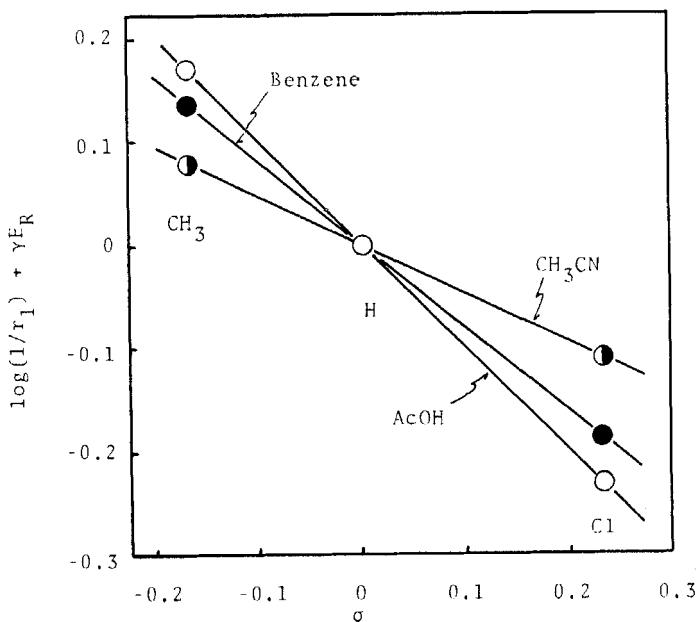**FIG. 1.** Hammett plots for the copolymerization of St (M_1) with I in benzene and in acetic acid at 80°C.

FIG. 2. Hammett plots for the copolymerization of II (M_1) with MVSO in benzene, acetonitrile, and acetic acid at 80°C.

TABLE 3. ρ and γ Values Obtained by Plotting the Values of $\log(1/r_1)$ against σ Values

M_1	M_2	Solvent	ρ	γ
St	I	Benzene	0.49	0.31
		AcOH	0.56	0.12
II	MVSO	Benzene	-0.81	-0.73
		AcOH	-1.01	-0.81
		CH₃CN	-0.46	-0.18

solvation to the carbonyl group of I as shown in the following scheme.
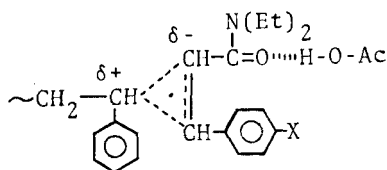

A similar explanation could be applied for the II-MVSO system, in which the largest negative ρ value was obtained in acetic acid. In other words, acetic acid might accelerate the drift of the charge electron to the MVSO unit at the transition state of K_{12}, due to the hydrogen bonding solvation to the sulfoxide group of MVSO and hence
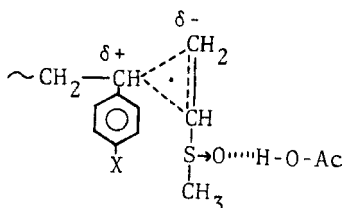
increase the ρ value as compared with benzene. In acetonitrile, the ρ value was found to be quite small. We do not have any evidence to deduce the mechanism. However, this fact means that the drift of the charge electron to the MVSO unit might be decreased by aceto-nitrile. We wish to postulate one possibility that this might be caused by a solvation between the sulfoxide and the cyano groups which affects

the charge distribution of the transition state. Actually, Ritchie et al.
showed that the sulfoxide group forms a specific solvated complex

$$
\begin{array}{cc}
\delta + & \delta - \\
R-C & \equiv N \\
\vdots & \vdots \\
O \leftarrow S & -R' \\
\delta - & \delta +
\end{array}
$$
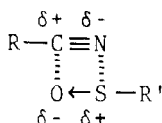
with the cyano group [11].

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