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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Effect of Solvent on the Radical Copolymerizability of Styrene with Methyl Vinylsulfoxide

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To cite this Article Ichiasakura, J. L. , Yoshihara, M. , Shindo, T. and Maeshima, T.(1981) 'Effect of Solvent on the Radical Copolymerizability of Styrene with Methyl Vinylsulfoxide', Journal of Macromolecular Science, Part A, 16: 3, 595 — 600
To link to this Article: DOI: 10.1080/00222338108056807
URL: http://dx.doi.org/10.1080/00222338108056807

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J. MACROMOL. SCI.–CHEM., A16(3), pp. 595-600 (1981)

Effect of Solvent on the Radical Copolymerizability of Styrene with Methyl Vinylsulfoxide

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ABSTRACT

Radical copolymerization of styrene (St, M_1) with methyl vinylsulfoxide (MVSO, M_2) has been carried out in various solvents at 80°C. Good linear correlationships were obtained by plotting the values of log r_1 against those of νS–O frequencies of MVSO determined in the solvents and of Ω and E_T values of solvents used.

INTRODUCTION

Recently, we showed that solvent effects were observed in the radical copolymerization of styrene (St) with a few vinyl monomers bearing rather polar group, i.e., methyl methacrylate [1], N,N-dimethyl acrylamide [2] and 2,6-dimethyl-pyridazine-3-one [3]. In all these cases, protic solvents such as phenol and carboxylic acid were found to affect the reactivities specifically, and these results were discussed in terms of the hydrogen bonding solvation to the polar groups both in the ground state and in the transition state.

Furthermore, we extended our experiments to an asymmetric inductive copolymerization of St with maleic anhydride in ℓ-menthol to obtain an optically active copolymer [4].

This manuscript deals with the radical copolymerization of St(M_1) with methyl vinylsulfoxide (MVSO, M_2) in a few protic solvents, and the results are discussed in terms of the solvent effect both in the ground state and in the transition state.

Recently, the radical copolymerizability of ethyl vinylsulfoxide with St was reported to be strongly affected by the reaction media [5]. In this case, however, the results were discussed in terms of solvation only at the ground state and no treatment at the transition state was involved.

EXPERIMENTAL

Styrene (St, M_1), methyl vinylsulfoxide (MVSO, M_2), and azobisisobutyronitrile (AIBN) were purified by the conventional methods.

Solvents were purified by the ordinary methods.

Radical copolymerization of St with MVSO was carried out with AIBN as an initiator in several solvents at 80°C in a degassed ampule.

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

The compositions of the copolymers were determined by elemental analysis.

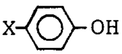
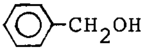
RESULTS AND DISCUSSION

The radical copolymerization of St (M_1) with MVSO has been carried out in several solvents at 80°C.

Table 1 summarizes the values of monomer reactivity ratios (r_1) which varied greatly with the solvents. These observations seem to imply that some different degree of solvation to monomer will occur to affect the reactivity.

Therefore, the stretching frequencies νS→O and νC=C of MVSO were determined in the solvents and are included in Table 1. The stretching frequency of νS→O was found to be considerably affected by the solvents but that of νC=C was slightly affected. These results appear to indicate that the solvents interact with the S=O group of MVSO rather than with the C=C group. On the other hand, no shift was observed in the infrared spectra of St with the solvents. Thus

TABLE 1. Monomer Reactivity Ratios (r_1) for Copolymerization of St (M_1) with MVSO at 80° C and IR Spectra of MVSO in Several Solvents

Solvent 	$[M]^a$ (mol/L)	r_1	$\nu S \to O$ (cm^{-1})	$\nu C{=}C$ (cm^{-1})
X: Cl	1.0	1.81	1039	1604
H	1.0	1.37	1039	1604
CH_3	1.0	1.79	1039	1604
OCH_3	1.0	3.03	1056	1605
AcOH	1.0	3.20	1047	1606
EtOH	1.0	5.34	1047	1605
	1.0	5.11	1047	1605
DMSO	1.0	6.76	1060	1603
DMF	1.0	7.63	1062	1605
CH_3CN	1.0	8.17	1063	1606

$^a[M] = [M_1] + [M_2]$, $[AIBN] = 1 \times 10^{-2}$ (mol/L).

the reactivity is deduced to be exclusively affected by the solvation to MVSO.

It is interesting to note that nearly linear correlationships were observed by plotting the values of log r_1 against those of $\nu S \to O$ (Fig. 1); namely, the stronger the interaction between MVSO and the solvent, especially a protic solvent, the more the reactivity increased.

These observations suggest that a protic solvent interacts with the semipolar sulfoxide group via a hydrogen bonding to decrease the charge density of the double bond of MVSO, thus increasing the reactivity of MVSO with the rather negative polystyryl radical. In other words, the reactivity can be ascribed in part to be due to the different degree of solvation in the ground state. This may be partly supported by the fact that in the phenol system (Fig. 2) a negative γ value (-2.18) was obtained by plotting log $1/r_1$ values against σ values with the modified Hammett's equation demonstrated by Otsu et al., where a positive ρ value was observed.

In a series of works on the solvent effect in radical copolymerization, however, the authors have emphasized that the solvent effect should be discussed in terms of the stabilization not only in the ground state but also in the transition state. In the present study the authors obtained information supporting such an hypothesis. Namely, good

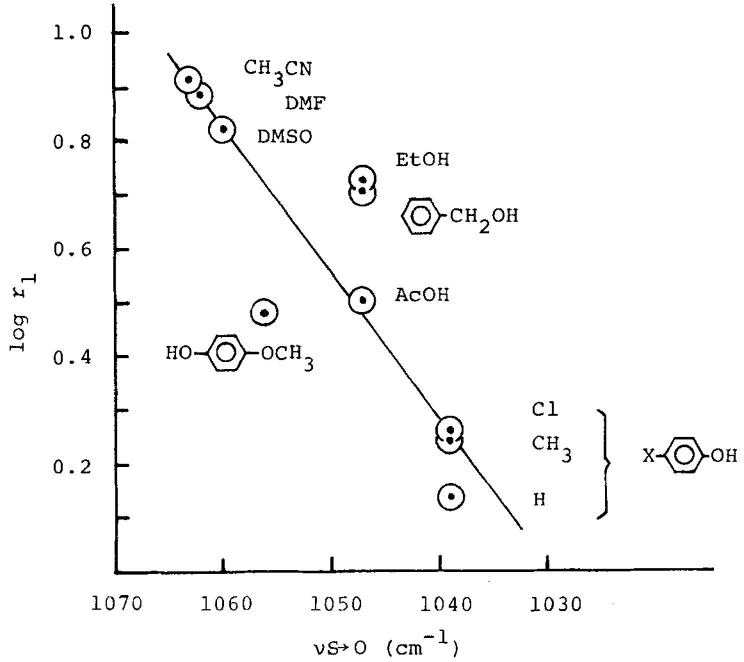


FIG. 1. Relationship between log r_1 and νS→O of MVSO in solvents.

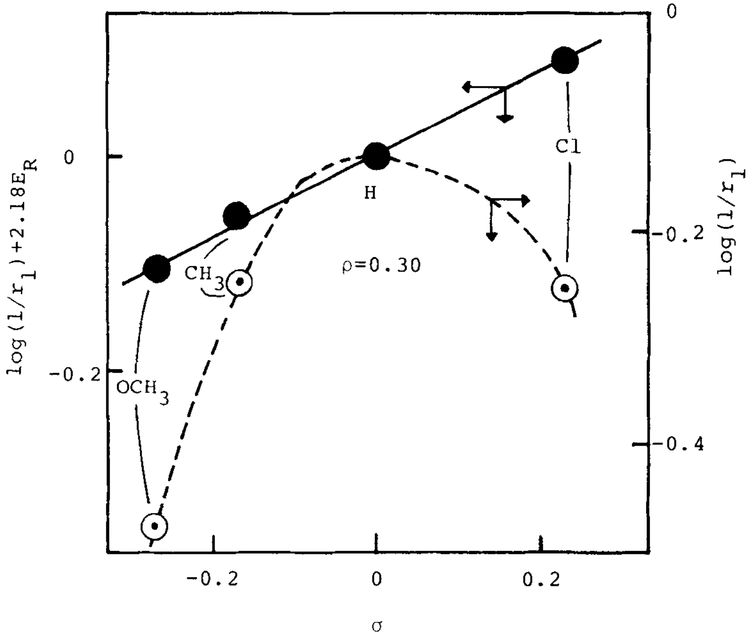


FIG. 2. Correlationships of log $1/r_1$ with Hammett's σ constant for the copolymerization of St(M_1) with MVSO in p-substituted phenols.

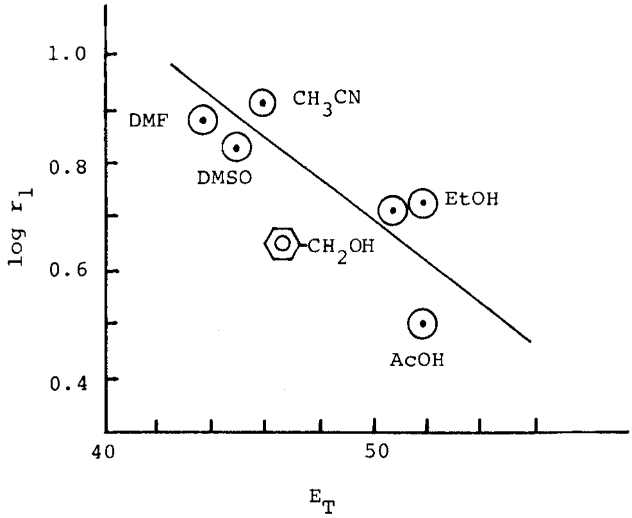


FIG. 3. Dependence of log r_1 on the E_T values of solvents.

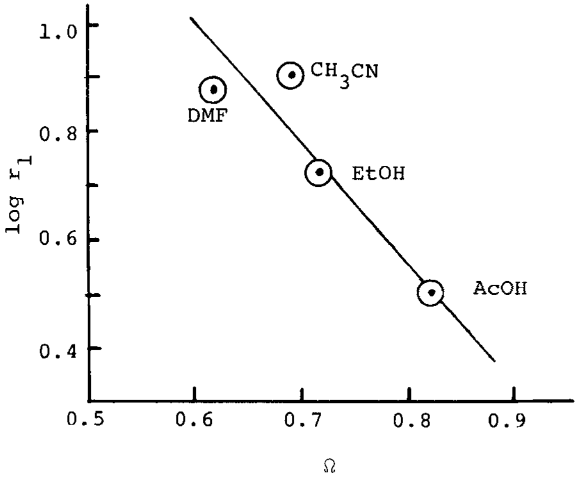


FIG. 4. Dependence of log r_1 on the Ω values of solvents.

linear relationships were observed in the plots of log r_1 values with the E_T and Ω values of the solvents used (Figs. 3 and 4). These values are regarded as a measure of the solvation ability to a polar structure at the ground state and at the transition state. Thus the linear correlationships observed in Figs. 3 and 4 suggest that the polarized structure of the MVSO or the poly-MVSO radical became important in the transition state. In the radical copolymerization of p-substituted styrene with MVSO, a ρ value in acetic acid with Hammett's equation was observed to be larger than that in benzene [6], and this was also ascribed to a stabilization of the transition state due to the electron-accepting hydrogen bonding solvation to the sulfoxide group.

In summary, the copolymerizability of St with MVSO is affected by the different degree of solvation of the S=O group of MVSO in the ground state and in the transition state.

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Accepted by editor April 20, 1980
Received for publication April 22, 1980