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Radical Copolymerization of Methyl Methacrylate with Styrene in Several Solvents

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ABSTRACT

Radical copolymerization of styrene (M_1) with methyl methacrylate has been carried out in several solvents. The monomer reactivity ratio (r) was affected by the solvent. The values of log 1/r, Q_2, and e_2 were found to increase with the decreases of the $\nu_{C=O}$ and $\nu_{C=C}$ stretching frequencies determined in the corresponding solvents.

INTRODUCTION

Previously, the authors showed that solvent caused the monomer reactivity ratios (r) for the copolymerization of 3(2-methyl)-6-methylpyridazinone with styrene (St) to vary [1]. We have already postulated a hypothesis that the transition state might be stabilized by specific solvation onto the polar carbonyl group of the pyridazinone unit [2]. A similar phenomenon was observed for the copolymerization of St with N,N-dimethylacrylamide [3]. On the other hand, the reactivity of acrylamide [4] or N-methylacrylamide [5] was discussed by the different degree of the solvation on the amide-enol equilibrium at the ground state. This suggests that the effect of solvent in the reactivity of vinyl monomer bearing the polar group has to be discussed not only at the ground state but also at the transition state.

The present work shows the experimental finding that in the radical copolymerization of St with methyl methacrylate (MMA) the reactivity ratio was considerably influenced by the solvent medium. This system was already studied by Otsu et al. [6] but it seems to remain to be resolved satisfactorily and/why the solvent should affect the reactivity.

EXPERIMENTAL

Material

Styrene (St) and methyl methacrylate (MMA) were purified by distillation in steam of nitrogen before use.

Benzene, dioxane, acetonitrile (CH_3CN), N,N-dimethylformamide (DMF), dichloromethane (CH_2Cl_2), ethanol, and phenol were purified according to the usual method.

Polymerization Procedure

All polymerizations were carried out in degassed ampules into which the required amounts of monomers, solvent, and initiator were placed. The reaction mixture was poured into an excess of methanol to precipitate the polymer, which was purified by repeated reprecipitation from benzene and methanol. The compositions of the copolymers were determined by elementary analysis of carbon.

RESULTS AND DISCUSSION

The radical copolymerization of St(M_1) with MMA was carried out in several solvents at 60°C and 80°C. The monomer reactivity ratios r obtained are summarized in Table 1. The r values were found to vary with the solvents, implying some solvent effect in the reaction. The reaction temperature slightly altered the r values enough to permit the activation energy and enthalpy to be calculated [2].

Figures 1 and 2 show the relationships between the values of

TABLE 1. Copolymerization Parameters of St (M_1) with MMA

Solvent	T (°C)	r_1	r_2	Q_2	e_2
Benzene	80	0.62	0.59	0.72	0.20
Dioxane	60	0.48	0.54	0.83	0.36
	80	0.52	0.60	0.79	0.28
CH_2Cl_2	80	0.50	0.63	0.85	0.28
DMF	80	0.55	0.58	0.78	0.27
CH_3CN	60	0.52	0.54	0.78	0.33
	80	0.55	0.64	0.81	0.22
EtOH	60	0.40	0.45	0.88	0.51
	80	0.41	0.41	0.83	0.54
Phenol	80	0.29	0.38	1.05	0.69

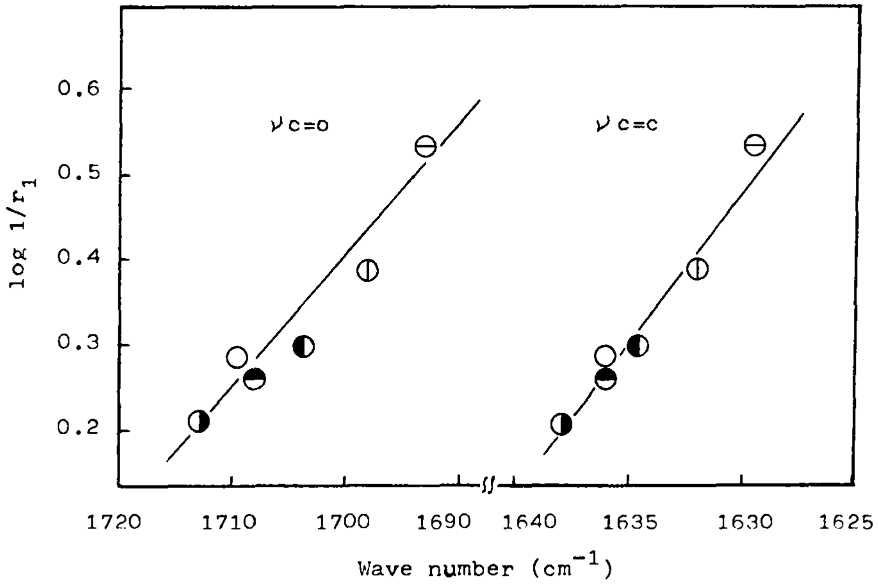


FIG. 1. Relationships between log 1/r_1 and $\nu_{C=O}$ or $\nu_{C=C}$: (◑) benzene; (○) dioxane; (◐) CH_2Cl_2; (◓) CH_3CN; (⦶) EtOH; (⊖) phenol.

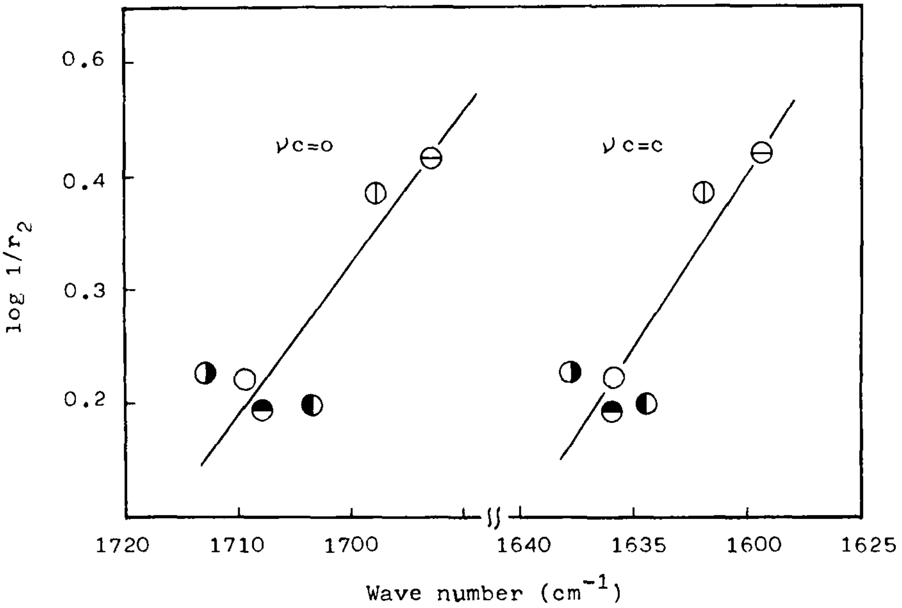


FIG. 2. Relationships between log $1/r_2$ and $\nu_{C=O}$ or $\nu_{C=C}$; symbols are as in Fig. 1.

log $1/r_1$ or log $1/r_2$ and those of the $\nu_{C=O}$ or $\nu_{C=C}$ stretching frequencies determined in the corresponding solvents; good corelationships were observed. The $\nu_{C=C}$ value of St was found to be unchanged with the solvents. These observations suggest that the reactivity is essentially influenced by some solvation to MMA unit and that the possibility of the solvation to St unit may be excluded. On the other hand, the kinetics of St [7] and MMA [8] suggested that the growing radical forms a complex with the solvent and that this complex determines the stability and reactivity of the reaction. Our observations, however, couldn't be explained by this type of solvation.

Price Q_2 and e_2 values were determined and are also included in Table 1. Both values were also found to vary with the solvents. It is interesting to note that straight lines were obtained by plots of the e_2 values against both the $\nu_{C=O}$ and $\nu_{C=C}$ values (Fig. 3), in which the stronger the interaction of MMA with the solvent the more the e_2 value increased. This seems to suggest that the solvent alters the

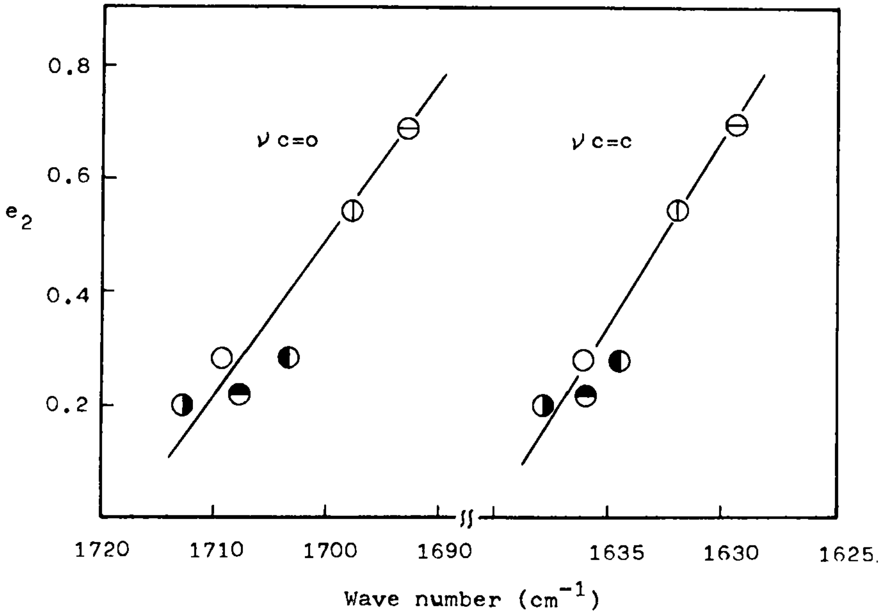
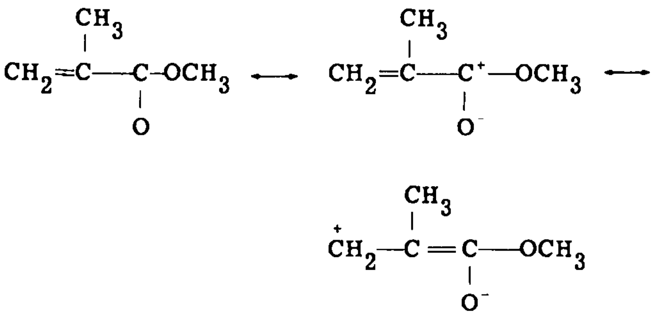


FIG. 3. Relationships between e_2 and $\nu_{C=O}$ or $\nu_{C=C}$; symbols are as in Fig. 1.

charge density of the reaction center of MMA in the ground state, maybe via the resonant forms I.



$$CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}\underset{\underset{O}{|}}{C}{-}OCH_3 \longleftrightarrow CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}\underset{\underset{O^-}{|}}{C^+}{-}OCH_3 \longleftrightarrow \overset{+}{C}H_2{-}\overset{\overset{CH_3}{|}}{C}{=}\underset{\underset{O^-}{|}}{C}{-}OCH_3$$

I

Protic solvent would increase a drift of a charge electron to carbonyl group via a specific solvation on the carbonyl-O atom and this will result in an increase of e_2 value.

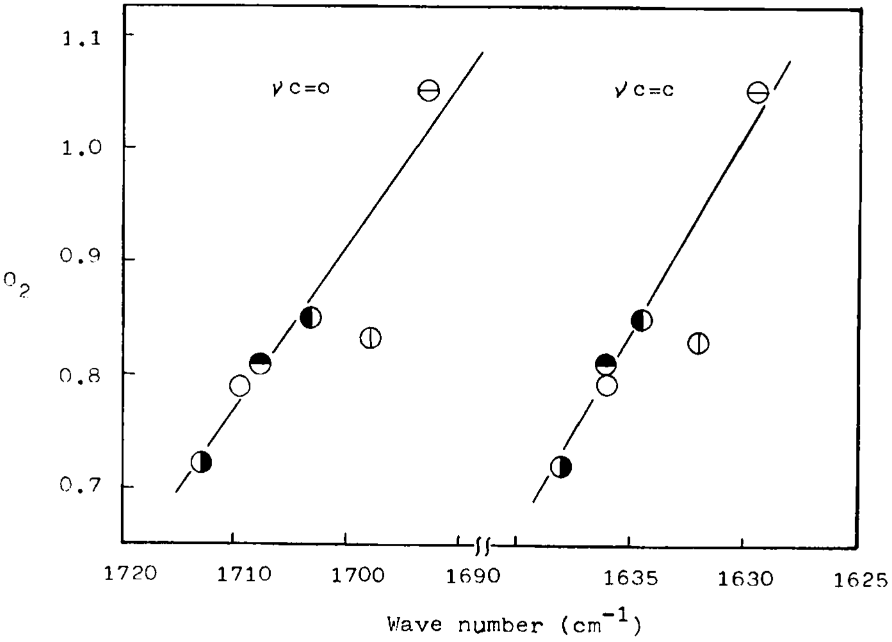


FIG. 4. Relationships between Q_2 and $\nu_{C=O}$ or $\nu_{C=C}$; symbols are as in Fig. 1.

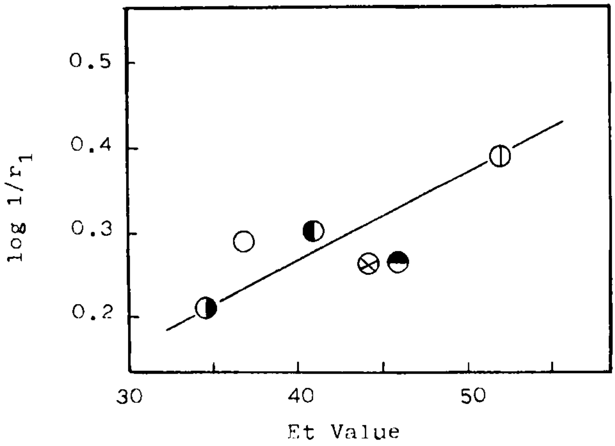


FIG. 5. Relationship between log $1/r_1$ and Et value: (◑) benzene; (○) dioxane; (◐) CH_2Cl_2; (⊕) DMF; (◓) CH_3CN; (⦶) EtOH.

Figure 4 shows the correlationships between the Q_2 values and $\nu_{C=O}$ and/or $\nu_{C=C}$ values. Here again, linear correlationships were observed, and thus the increase of the interaction of MMA with the solvent increased the Q_2 value. This seems to imply that the stability of a growing MMA radical will increase with the increase of such interaction. We wish to suggest that this may be caused by the solvent-stabilization effect of the transition state, which may be rather easily explained by taking account of the solvation effect on K_{12} step in r_1. In the transition state of the K_{12} step, the MMA unit will acquire some negative charge while the polystyryl unit will get some positive charge because a negative ρ value was obtained for the copolymerization of MMA with several substituted styrene [9, 10]. Such a drift of electrons to the MMA unit will increase with an increase of the interaction of MMA with the solvent, especially protic solvent, as described above. In other words, the stronger such solvation, the more the transition state will be stabilized and this will result in an increase of the Q_2 value. This suggestion may be partly supported by the fact that the values of log $1/r_1$ increased with the increase of the E_t values of the solvents used (Fig. 5): the E_t values are empirical values of proton-donating ability of the solvent. The same relationship was already described by Otsu et al. [6].

All these observations suggest that the reactivity is influenced by solvation to the MMA unit both in the ground state and in the transition state.

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