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## Solvent Effects in Radical Copolymerization of Styrene with N,N-Dimethylacrylamide

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### ABSTRACT

The radical copolymerization of N,N-dimethylacrylamide (I) with styrene (St) ( $M_1$ ) was carried out in several solvents at 60 and 80°C. The monomer reactivity ratios were considerably affected by the reaction conditions. Linear correlations were observed by plots of the values of both  $\nu_{C=O}$  and  $\nu_{C=C}$  stretching frequencies of I obtained in the solvents against those of  $\log r_1$ ,  $\log r_2$ ,  $\Delta\Delta E^\ddagger$  ( $= \Delta E_{11}^\ddagger - \Delta E_{12}^\ddagger$ ), and  $\Delta\Delta S^\ddagger$  ( $= \Delta S_{11}^\ddagger - \Delta S_{12}^\ddagger$ ). The values of both  $\Delta E_{12}^\ddagger$  and  $\Delta S_{12}^\ddagger$  were also determined.

### INTRODUCTION

A number of investigations have been reported for the effect of solvent on the radical copolymerizabilities of vinyl monomers. Saini et al. reported that a strong influence of the solvent on the copolymer compositions was observed for the copolymerizations of styrene (St) or methyl methacrylate (MMA) with acrylamide [1], methacrylamide [2], and N-methylacrylamide [3], and that such

phenomena were due to the influence of the solvent polarities on the amide-enol equilibrium because little solvent effect was observed on the copolymerizability of *N,N*-dimethylacrylamide (I) with vinyl monomers such as St and MMA [4].

Our recent work [5] has shown that the reactivity ratios were considerably influenced by the polymerization media in the copolymerization of St with 3(2-methyl)-6-methylpyridazinone which does not have any group capable of such amide-enol equilibrium. We have already postulated the hypothesis that the transition state might be stabilized by the specific solvation onto the carbonyl group of the pyridazinone ring [6].

In the present work, we give experimental evidence that in the copolymerization of I with St ( $M_1$ ) the reactivity ratios are influenced by a wide variety of solvents.

## EXPERIMENTAL

### Materials

*N,N*-Dimethylacrylamide (I) was purified by distillation before use.

Styrene (St) was also purified by distillation prior to use.

Benzene, dioxane, acetonitrile, ethanol, and acetic acid were dried and purified by distillation according to the usual techniques before use.

### Polymerization Procedure

All polymerizations were performed in degassed glass ampoules which were filled with dry monomers, solvent, and initiator. The polymerizations were stopped by pouring the tube content into an excess of petroleum ether. The yields obtained were invariably lower than 10%. The copolymers were purified by repeated reprecipitation from benzene and petroleum ether. No other impurities in the copolymers were determined by infrared and NMR analysis and by TLC. The compositions of the copolymers were determined by elementary analysis for nitrogen.

## RESULTS AND DISCUSSION

The radical copolymerization of I with St ( $M_1$ ) was carried out in various solvents (benzene, dioxane, acetonitrile, ethanol, and acetic acid) at 60 and 80°C. Table 1 summarizes the values of the monomer reactivity ratios ( $r$ ) obtained on changing the solvent and the reaction conditions, implying some solvent effect in the reaction.

TABLE 1. Copolymerization Parameters of I with St<sup>a</sup>

Solvent	Temp. (°C)	r <sub>1</sub>	r <sub>2</sub>	e <sub>2</sub>	Q <sub>2</sub>
Benzene	60	1.23	0.39	0.06	0.41
	80	1.03	0.42	0.12	0.47
Dioxane	60	1.36	0.34	0.08	0.36
	80	1.11	0.32	0.21	0.40
CH <sub>3</sub> CN	60	1.54	0.18	0.33	0.26
	80	1.25	0.22	0.34	0.32
C <sub>2</sub> H <sub>5</sub> OH	60	1.12	0.18	0.47	0.32
	80	1.00	0.19	0.49	0.36
CH <sub>3</sub> COOH	60	0.76	0.12	0.75	0.38
	80	0.73	0.09	0.83	0.37

$$^a[M_1] + [M_2] = 1 \text{ mole/liter.}$$

It is interesting to note that the values of both  $\log r_1$  and  $\log r_2$  were nearly correlated with those of both  $\nu_{C=O}$  and  $\nu_{C=C}$  stretching frequencies of I determined in the corresponding solvents (Figs. 1 and 2). This seems to imply that the reactivity is essentially affected by the solvation to I. Price  $Q_2$  and  $e_2$  values were determined from these  $r$  values and are also included in Table 1.  $Q_2$  values were almost invariable, but  $e_2$  values were found to much vary with the solvents. Straight lines were obtained by plotting these  $e_2$  values against these  $\nu_{C=O}$  and  $\nu_{C=C}$  values (Fig. 3): the stronger the interaction of I with the solvents, the more the  $e_2$  values increased.

From the kinetics of the polymerizations of St [7] and/or MMA [8], it was suggested that the solvent forms a complex with a growing radical and that this complex determines the stability and the reactivity of the radical. However, our observations seem to suggest that the reactivity is influenced mainly by the solvation onto I unit rather than St.

Table 1 shows another interesting fact: the reaction temperature altered the  $r_1$  values.  $r_2$  values also varied with the temperature, but the degree of variation was very small in comparison with that of  $r_1$  values. Differences of the activation free energy ( $\Delta\Delta F^\ddagger$ ), the activation 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:

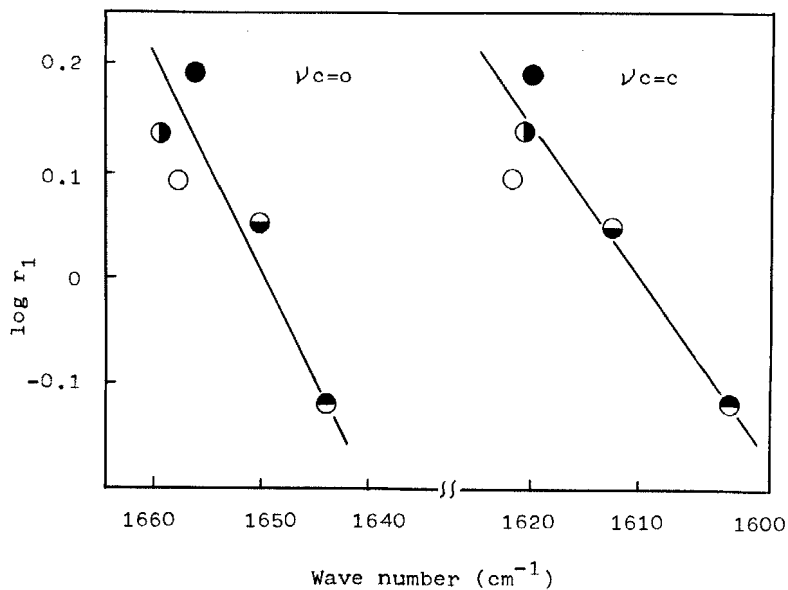


FIG. 1. Relationships between  $\log r_1$  and  $\nu_{C=O}$  or  $\nu_{C=C}$  for copolymerization of I with St at  $60^\circ\text{C}$ : (○) benzene; (●) dioxane; (◐)  $\text{CH}_3\text{CN}$ ; (◑) EtOH; (◒) AcOH.

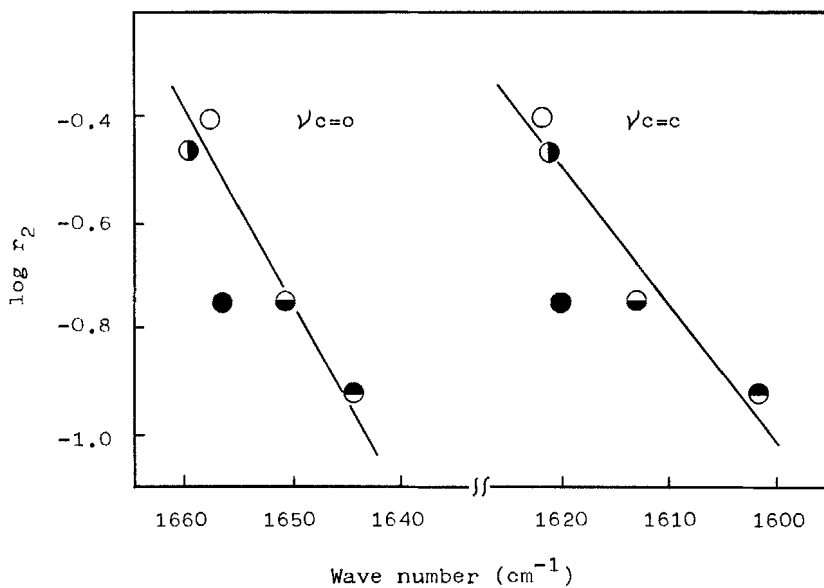


FIG. 2. Relationships between  $\log r_2$  and  $\nu_{C=O}$  or  $\nu_{C=C}$ . Symbols are the same as in Fig. 1.

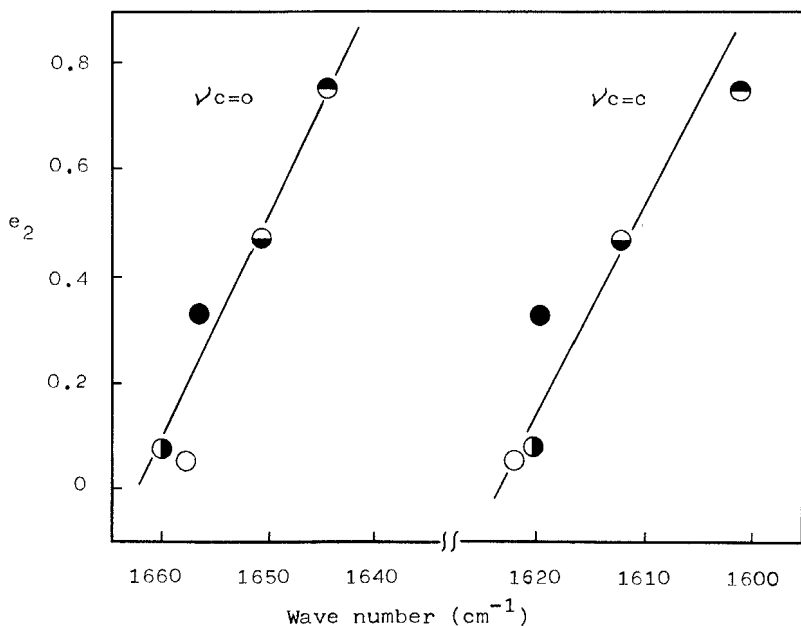


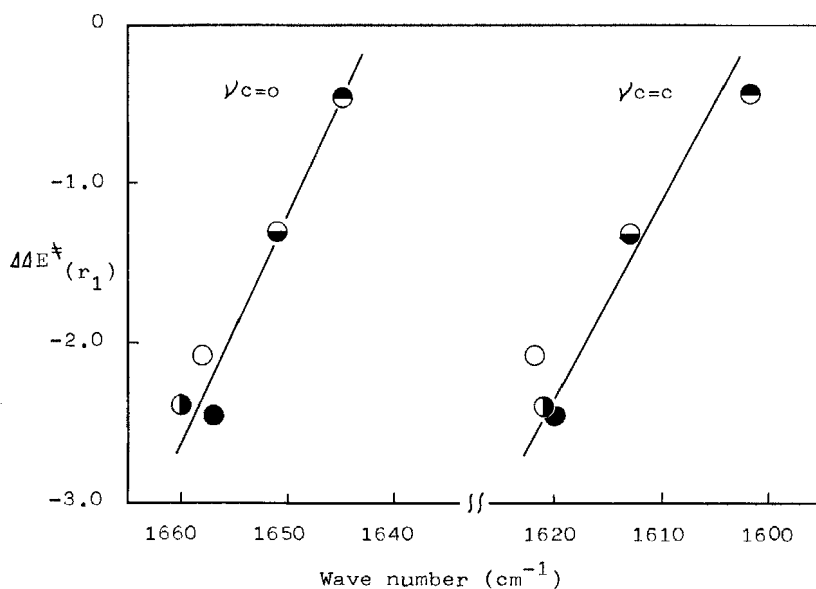
FIG. 3. Relationships between  $e_2$  and  $\nu_{C=O}$  or  $\nu_{C=C}$ . Symbols are the same as in Fig. 1.

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

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 2). All these values were found to vary with the solvents. It is quite interesting to note that linear relationships were observed by plotting  $\Delta\Delta E^\ddagger$  and  $\Delta\Delta S^\ddagger$  values against  $\nu_{C=O}$  and  $\nu_{C=C}$  values (Figs. 4 and 5): namely, the increase of the interaction of I with the solvents increased the values of both  $\Delta\Delta E^\ddagger$  and  $\Delta\Delta S^\ddagger$ . Here, it may be assumed that the values of  $\Delta E_{11}^\ddagger$  and  $\Delta S_{11}^\ddagger$  are almost unchanged with the solvents compared with  $\Delta E_{12}^\ddagger$  and  $\Delta S_{12}^\ddagger$  values because I or poly-I radical would be more strongly solvated than St or polystyryl radical due to the strong polar group in I, as described above. In other words, the variation of the  $K_{11}$  value with the solvents is assumed to be very small compared with that of the  $K_{12}$  value. From this point of view, we tried to get the  $K_{12}$  values from the equation,  $K_{12} = K_{11}/r_1$ , by assuming the  $K_{11}$  values at 60 and

TABLE 2. Activation Parameters for Copolymerization of I with St

Parameter	Solvent	$\Delta\Delta E^\ddagger$ (kcal/ mole)	$\Delta\Delta S^\ddagger$ (e. u.) <sup>a</sup>	$\Delta\Delta H^\ddagger$ (kcal/ mole)	$\Delta\Delta F^\ddagger$ (kcal/ mole) <sup>a</sup>
$r_1$	Benzene	-2.08	-5.81	-2.73	-0.79
	Dioxane	-2.38	-6.52	-3.03	-.086
	CH <sub>3</sub> CN	-2.44	-6.47	-3.10	-0.94
	C <sub>2</sub> H <sub>5</sub> OH	-1.33	-3.75	-1.99	-0.74
	CH <sub>3</sub> COOH	-0.47	-1.96	-1.13	-0.50
$r_2$	Benzene	0.87	0.73	0.21	-0.04
	Dioxane	-0.71	-4.27	-1.37	0.05
	CH <sub>3</sub> CN	2.35	3.64	1.69	0.47
	C <sub>2</sub> H <sub>5</sub> OH	0.63	-1.51	-0.03	0.47
	CH <sub>3</sub> COOH	-0.34	-5.22	-1.00	0.73

<sup>a</sup>At 60°C.FIG. 4. Relationships between  $\Delta\Delta E^\ddagger$  and  $\nu_{C=O}$  or  $\nu_{C=C}$ . Symbols are the same as in Fig. 1.

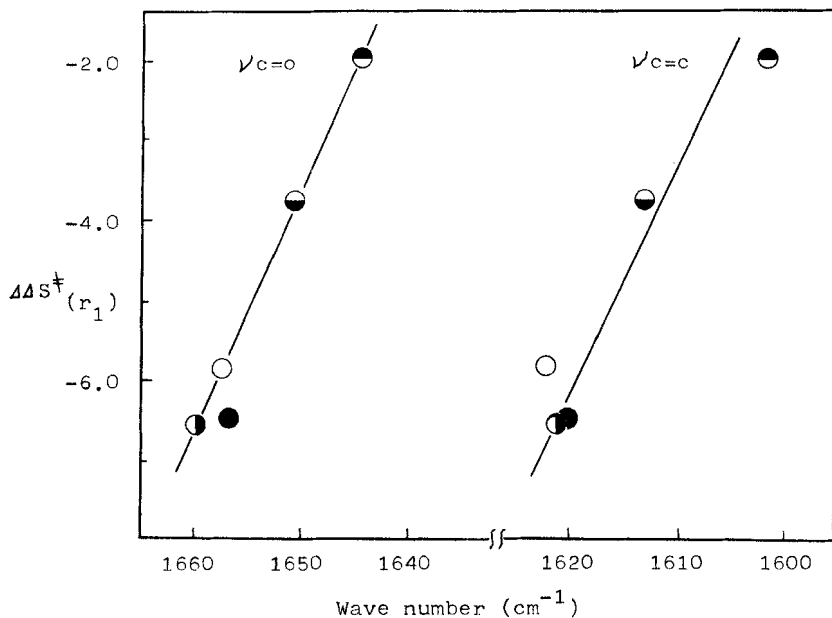
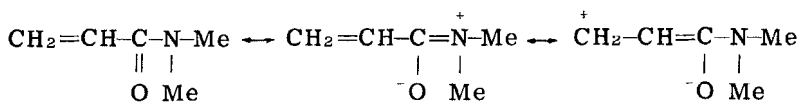


FIG. 5. Relationships between  $\Delta\Delta S^\ddagger$  and  $\nu_{C=O}$  or  $\nu_{C=C}$ . Symbols are the same as in Fig. 1.

80°C to be 274 and 420 liter/mole-sec, respectively, which were calculated by least-squares method with all the  $K_{11}$  values cited in the literature [9];  $\Delta E_{12}^\ddagger$  and  $\Delta S_{12}^\ddagger$  values were obtained from the  $K_{12}$  values thus determined (Table 3). Figures 6 and 7 show the relationships between the values of  $\Delta E_{12}^\ddagger$  and/or  $\Delta S_{12}^\ddagger$  and those of  $\nu_{C=O}$  and/or  $\nu_{C=C}$  stretching frequencies. Here again, good correlation

were observed: namely,  $\Delta E_{12}^\ddagger$  and  $\Delta S_{12}^\ddagger$  values decreased with the increase of the interaction of I with the solvents.

We wish to postulate a hypothesis that all these observations may be explained by taking account of the solvation in the transition state of the  $K_{12}$  step. Acrylamide can be described by several resonant structures:



Solvent will stabilize such structures of both the monomer and the resulting polymer radical. If such solvation is important at the ground state of the  $K_{12}$  step, i. e., some desolvation would occur at



TABLE 3. Activation Parameters

Solvent	$K_{12}^a$	$K_{12}^b$	$\Delta E_{12}^\ddagger$ (kcal/mole) <sup>a</sup>	$\Delta S_{12}^\ddagger$ (e. u.) <sup>a</sup>
Benzene	222.8	407.8	7.07	-26.8
Dioxane	201.5	378.4	7.37	-26.1
CH <sub>3</sub> CN	177.9	336.0	7.43	-26.2
C <sub>2</sub> H <sub>5</sub> OH	244.6	420.0	6.32	-28.9
CH <sub>3</sub> COOH	360.5	575.3	5.46	-30.7

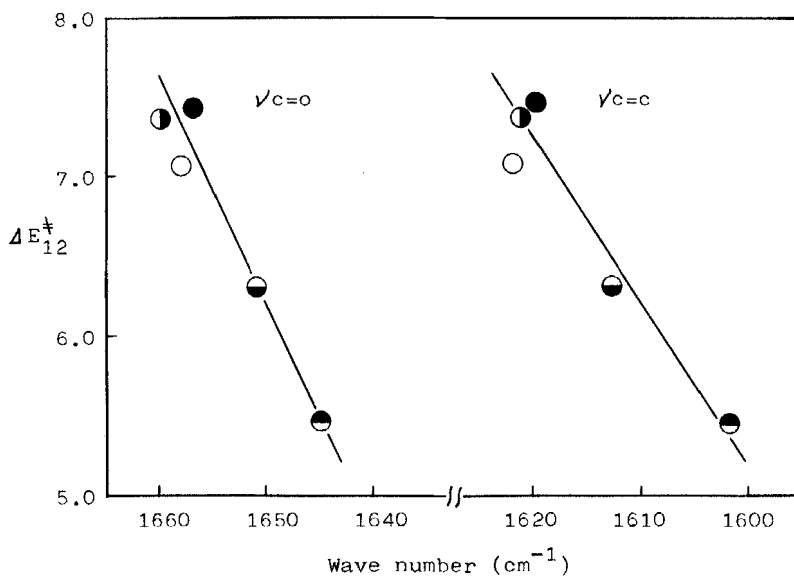
<sup>a</sup>At 60°C.<sup>b</sup>At 80°C.

FIG. 6. Relationships between  $\Delta E_{12}^\ddagger$  and  $\nu_{C=O}$  or  $\nu_{C=C}$ . Symbols are the same as in Fig. 1.

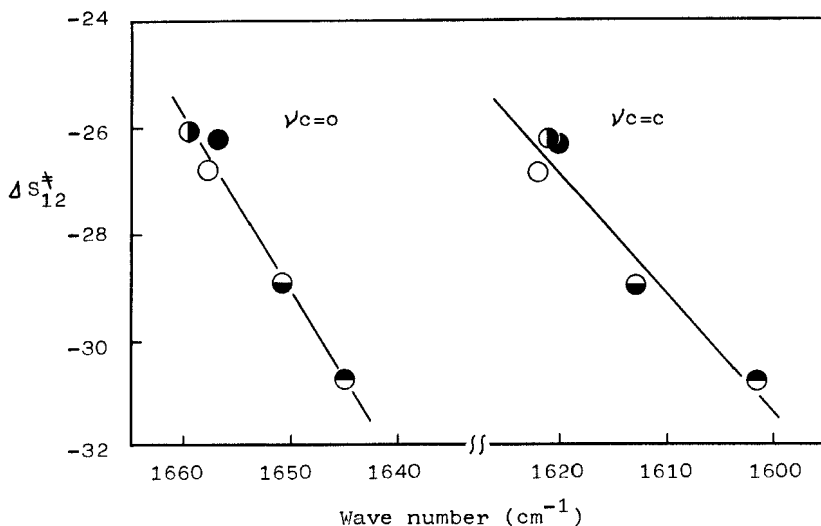


FIG. 7. Relationships between  $\Delta S_{12}^{\ddagger}$  and  $\nu_{C=O}$  or  $\nu_{C=C}$ . Symbols are the same as in Fig. 1.

the transition state,  $\Delta E_{12}^{\ddagger}$  and  $\Delta S_{12}^{\ddagger}$  values might increase with the increase of the interaction of I with the solvent. On the other hand, if the degree of solvation at the transition state is almost equal to that at the ground state, these values, at least  $\Delta E_{12}^{\ddagger}$ , would be almost unchanged with the solvents. The phenomena observed in Figs. 4-7 seem to imply that an additional stabilization of the transition state of the  $K_{12}$  step would occur by the solvents increasing the interaction with a polar amide group. In the transition state, the polystyryl unit will acquire some positive charge while the I unit will get some negative charge. Such a drift of electrons from the polystyryl carbon to the I unit would be increased with increasing electron-accepting ability of the solvent, and this is expected to increase the ionic character of the transition state. Thus, this will result in the decrease of  $\Delta E_{12}^{\ddagger}$  and  $\Delta S_{12}^{\ddagger}$  values.

In the case of  $r_2$ , complicating features are considered to occur because the solvents may influence the values of both  $K_{22}$  and  $K_{21}$ . This is partly suggested by the fact that the data of Table 1 show a fourfold change in  $r_2$ , compared with a twofold change in  $r_1$ . However, unfortunately, the differences of the  $r_2$  values between 60 and 80°C were too small to permit one to get any activation parameters. Nevertheless, linear correlations were observed between the values of  $\log r_2$  and  $\nu_{C=O}$  and/or  $\nu_{C=C}$  values (Figs. 1 and 2), suggesting that the reactivity is essentially influenced by the solvation to the I unit. The relationships between the  $\log r_2$  values and the polarities of the

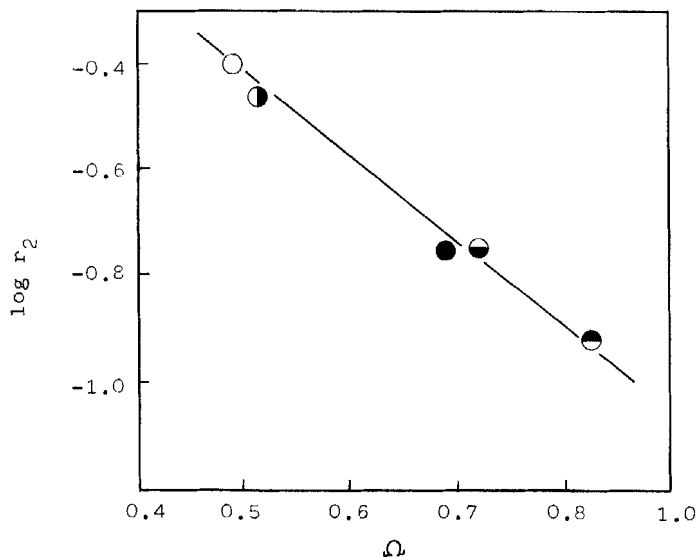


FIG. 8. Relationships between  $\log r_2$  and  $\Omega$  values. Symbols are the same as in Fig. 1.

solvents used are shown in Fig. 8, in which the  $\Omega$  values of the solvents were used as a measure of solvent polarity [10]. The  $\Omega$  values are regarded as a measure of the solvation ability to a polar structure between at the ground state and at the transition state. Linear correlations observed in Fig. 8 might suggest that the polarized structure of I or poly-I radical



became important in the transition state.

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