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SOLVENT EFFECTS ON THE COPOLYMERIZATION OF 5-HEXENE-2,4-DIONE AND STYRENE

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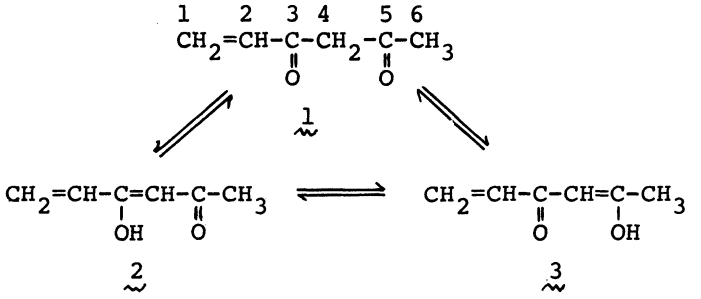
Solvent effects on the copolymerization of 5-hexene-2,4-dione and styrene have been studied. The contributions of polarity and polarizability effects and of monomer-solvent interactions were estimated according to the "Solvatochromic Comparison Method" developed by Taft *et al.*

Many authors have reported about solvent effects on radical polymerization and copolymerization. In the copolymerization, the nature of the solvents governs the relative reactivity of monomers. There is a minor solvent effect which is attributable to the change in the dielectric constant of the solution in the copolymerization of styrene and methacrylonitrile.1) For the acrylamide-styrene copolymerization, the nature of solvents has affected the equilibrium of acrylamide tautomers.2) Minsk *et al.*3) have re-examined the same system in different solvents and presented that both hydrogen bonding and dipole-dipole interaction affect the copolymerization parameters. α,β-Unsaturated carboxylic acids, such as acrylic acid, are in the forms of associated dimer and the free monomer surrounded by the solvent, and their relative reactivity ratio varies with the shift of equilibrium between two forms.

It is obvious fact that the monomer reactivity ratio depends on the nature of solvents. However, the explanation for it is really qualitative. This communication describes the solvent effect on the copolymerization of 5-hexene-2,4-dione (AA) and styrene (St), and the estimation of the contribution of polarity and polarizability effects and of monomer-solvent interactions on the basis of the "Solvatochromic Comparison Method."[4)]

AA was prepared according to the method of Ponticello and Furman.[5)] Bp 65 °C (3333 Pa). UV (hexane) 298 nm; IR (neat) 1720 (C=O), 1645 (C=C), and 1580 (-C(OH)=CH-CO-) cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 2.07$ (3H, s, CH_3), 5.68 (1H, s, -C(OH)=CH-CO-), 5.72 (1H, m, CH_2=CH-), 6.26 (2H, m, CH_2=CH-), and 14.50 (1H, s, OH); ^{13}C NMR ($CDCl_3$) $\delta = 27.07$ (q), 101.12 (d), 125.28 (t), 133.14 (d), 176.28 (s), and 199.55 (s).

Though AA has three theoretically possible tautomers, one ketonic (1) and two enolic (2 and 3) forms, its spectral data revealed that it is only in the enolic form, for the ^{1}H and ^{13}C NMR spectra have no peaks corresponding to the methylene proton and carbon lied between the carbonyl groups, respectively. Using non-decoupled ^{13}C NMR technique, the peak at 199.55 ppm which is corresponding to carbonyl carbon appears as a quintet with the coupling constant of 5.2 Hz. This suggests that the C-5 carbon is the carbonyl one. In order to obtain further information, selective decoupled method was applied. As is shown in Fig. 1, the coupling of the carbonyl carbon is removed by irradiating the methyl proton at its resonance frequency so that the carbonyl carbon appears as a doublet due to spin-spin splitting only by the methyne proton on the adjacent carbon. This finding clearly shows that the carbonyl group is adjacent to the methyl group, and therefore the structure of AA may be represented by Formula (2).



$$\overset{1}{CH_2}=\overset{2}{CH}-\underset{\|}{\overset{3}{C}}\!\!{}_{O}-\overset{4}{CH_2}-\underset{\|}{\overset{5}{C}}\!\!{}_{O}-\overset{6}{CH_3}$$

$$CH_2=CH-\underset{OH}{C}=CH-\underset{O}{C}-CH_3 \rightleftharpoons CH_2=CH-\underset{O}{C}-CH=\underset{OH}{C}-CH_3$$

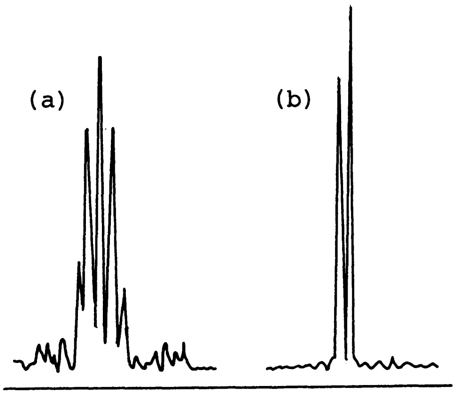


Fig. 1. ^{13}C NMR spectra for carbonyl carbon. (a) Non-decoupled. (b) Single frequency selective decoupled.

The copolymerization of AA (M_1) and St (M_2) was carried out at 60 °C in various solvents. Table 1 shows monomer reactivity ratios obtained. There is a remarkable effect of solvents on both r_1 and r_2. The general trend of variation of them shows that the

r_1-value increases with an increase in the r_2-value. This observation suggests that the solvents interact with both AA monomer and polymer radical having AA unit as the terminal group. If the solvents interact only with AA monomer, the r_1-value increases with a decrease in the r_2-value and *vice versa*. Monomer reactivity ratios appear to be independent of dielectric constants and dipole moment and dependent on E_T-values with a few exceptions.

Table 1. Monomer reactivity ratios for the copolymerization of AA (M_1) and St (M_2)

No	Solvent	r_1	r_2
1	Toluene	1.22	0.031
2	Benzene	1.38	0.049
3	Ethanol	1.52	0.066
4	Tetrahydrofuran	1.91	0.18
5	1,4-Dioxane	2.07	0.17
6	Acetonitrile	2.69	0.24
7	HMPA[a)]	2.93	0.014

a) Hexamethylphosphoramide.

As quantitative description of the solvent effects on chemical processes, linear multiparametric equations have been proposed by many authors. Kamlet and Taft have proposed "Linear Solvation Energy Relationship," and estimated the contribution of polar effect and of solute-solvent interactions.

$$X = X_0 + s(\pi^* + d\delta) + a\alpha + b\beta$$

where π^*, δ, α, and β are referred to as the solvatochromic parameters, and s, d, a, and b as the solvatochromic coefficients, respectively. This equation shows correlation of the solvent effects on many reaction rates, equilibria, and spectroscopic properties.[6)] According to Koppel and Palm,[7)] non-specific

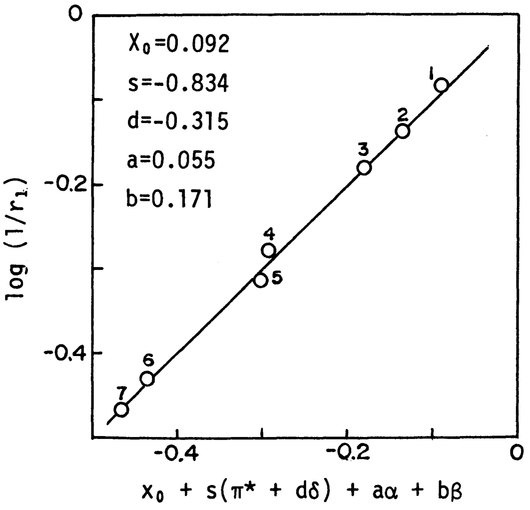


Fig. 2. Regression analysis of r_1 with the solvatochromic parameters. Same symbols as in Table 1.

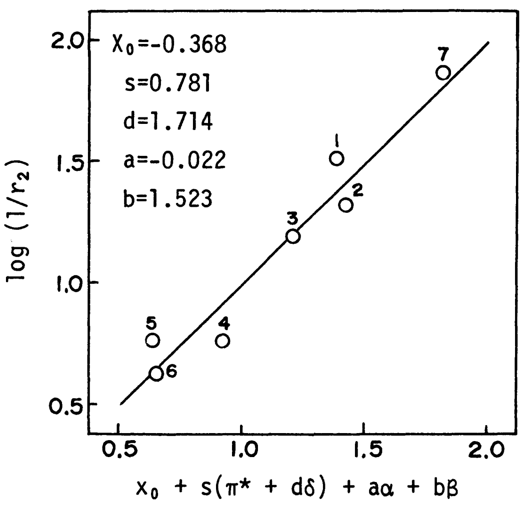


Fig. 3 Regression analysis of r_2 with the solvatochromic parameters. Same symbols as in Table 1.

$$\log(1/r_1) = 0.092 - 0.834(\pi^* - 0.315\delta) + 0.055\alpha + 0.171\beta \qquad R = 0.999$$

$$\log(1/r_2) = -0.368 + 0.781(\pi^* + 1.714\delta) - 0.022\alpha + 1.523\beta \qquad R = 0.966$$

solute-solvent interactions are taken into account by two additive functions, *i.e.*, polarity and polarizability functions. Dimorth's E_T values are known to be correlated quite well with a linear combination of π^* and α parameters.8) In addition, β factor plays an important role when the solute acts as hydrogen-bond acceptor and the solvent as hydrogen-bond donor.9)

AA has a carbonyl and a hydroxyl groups as described above. The former is hydrogen-bond acceptor and the latter hydrogen-bond donor-acceptor. It is accordingly reasonable to correlate the solvent effects on monomer reactivity ratios with π^*, δ, α, and β parameters. As illustrated in Figs. 2 and 3, regression analysis over all the experimental results yields good linear relationship, taking into account, as major factors, solvent polarity-polarizabilities and solvent hydrogen-bond acceptor basicities.

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