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Radical Copolymerization of Vinylidene Chloride with 3(2-Methyl)-6-methylpyridazinone in Several Solvents

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ABSTRACT

The radical copolymerization of vinylidene chloride (Vc, M_1) with 3(2-methyl)-6-methylpyridazinone (I, M_2) was carried out in benzene, ethanol, phenol, and acetic acid at 60 and 80°C. The monomer reactivity ratios were found to vary with the reaction conditions. The linear correlationships were obtained by plotting the values of log r_1 against those of $\nu_{C=O}$ and $\nu_{C=C}$ of monomers determined in the solvents.

INTRODUCTION

During the course of our studies on the polymerization of pyridazinone derivatives we found that solvents greatly affected the copolymerizabilities of these derivatives with styrene (St) and this was perhaps due to the different degrees of solvation of the carbonyl groups of the derivatives in both the ground and transition states [1-3]. We recently showed that similar solvent effects were observed in the radical copolymerization of St with a few vinyl monomers bearing such polar groups as ester, amide, and sulfoxide [4-9]. In all these cases the reactivities were considerably influenced by such protic solvent as phenol and carboxylic acid, and these results were discussed in terms of hydrogen bonding solvation of the polar groups in both the ground and transition states.

This article deals with the radical copolymerization of vinylidene chloride (Vc, M_1) with 3(2-methyl)-6-methylpyridazinone (I, M_2) by changing such reaction conditions as solvent, monomer concentration, and reaction temperature. Incidentally, we extended our concept to an asymmetric induction in free radical addition reaction and succeeded in getting optically active copolymers by the radical copolymerization of maleic anhydride with St and isobutyl vinyl ether [10-12] and also optically active addition products by the radical additions of cyclohexanone with 2-octene in ℓ-menthol [13] and of thiols to olefins [14-16].

EXPERIMENTAL

3(2-Methyl)-6-methylpyridazinone (I, M_2) was prepared and purified by the previous method [2].

Vinylidene chloride (Vc, M_1) and azobisisobutyronitrile (AIBN) were purified by the conventional methods.

Other reagents were purified by the ordinary methods.

All copolymerizations were carried out in degassed ampules at 60 and 80° C. The reaction mixture was poured into an excess of methanol to precipitate the copolymer. The copolymers were purified by the reprecipitation method from DMF-methanol. The compositions of the copolymers were determined by elemental analysis for nitrogen.

RESULTS AND DISCUSSION

The radical copolymerization of Vc (M_1) with I (M_2) was carried out in several solvents (benzene, ethanol, phenol, and acetic acid) at 60 and 80°C. Figure 1 shows the relationships between the monomer concentration and the values of the copolymerization rate (R_p)

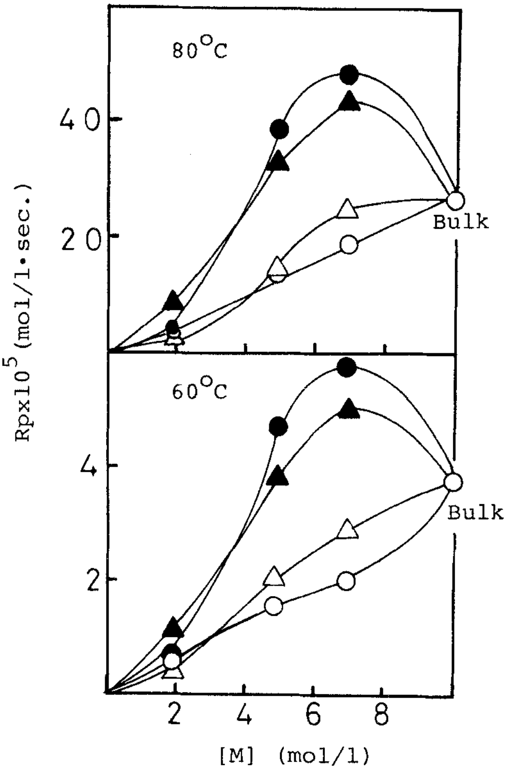

FIG. 1. Relationships between monomer concentration [M] and rate of copolymerization (R_p) for copolymerization of Vc with I. $[M_1]/([M_1] + [M_2]) = 0.5$, [AIBN] = 1×10^{-2} mol/L. (○) Benzene, (△) ethanol, (●) phenol, (▲) acetic acid.

obtained at a molar fraction of 0.5 in various solvents at 60 and 80°C. The R_p values obtained in the protic solvents were not proportional to the monomer concentration for every temperature, and the maximum R_p values were observed for the phenol and acetic acid systems. A similar phenomenon was also detected for the copolymerization of styrene (St) with I in the same solvents and was ascribed to the viscosity effect on the termination reaction because the protic solvents were found to interact with I through hydrogen bonding to form a complex which varied the viscosity of the reaction mixture [2, 3]. In order to check the interaction of the solvents with the monomers, the stretching frequencies $\nu_{C=O}$ and $\nu_{C=C}$ of I and Vc were determined in the solvents and shown in Table 1. These frequencies were

TABLE 1. Infrared Spectra of Vc and I in Several Solvent[a]

	I		Vc,
	$\nu_{C=O}$ (cm^{-1})	$\nu_{C=C}$ (cm^{-1})	$\nu_{C=C}$ (cm^{-1})
Vc-I[b]	1671	1599	1617
Vc-I-benzene	1674	1602	1618
Vc-I-ethanol[c]	1672	1601	1616
Vc-I-phenol[c]	1660	1586	1600
Vc-I-acetic acid[c]	-	1583	1601

[a] [Vc]:[I]:[Solvent] = 1:1:1.
[b] Liquid.
[c] Benzene solution.

TABLE 2. Monomer Reactivity Ratios (r_1) for Copolymerization of Vc (M_1) with I (M_2)[a]

Solvent	[M] (mol/L)	r_1 60° C	80° C
None	10	15.5	14.9
Benzene	7	18.7	17.2
	5	20.3	19.1
Ethanol	7	22.7	19.8
	5	27.5	23.2
Phenol	7	29.6	27.6
	5	39.3	36.5
Acetic acid	7	36.0	30.2
	5	50.1	41.2

[a] [AIBN] = 1×10^{-2} mol/L, $r_2 \approx 0.01$.

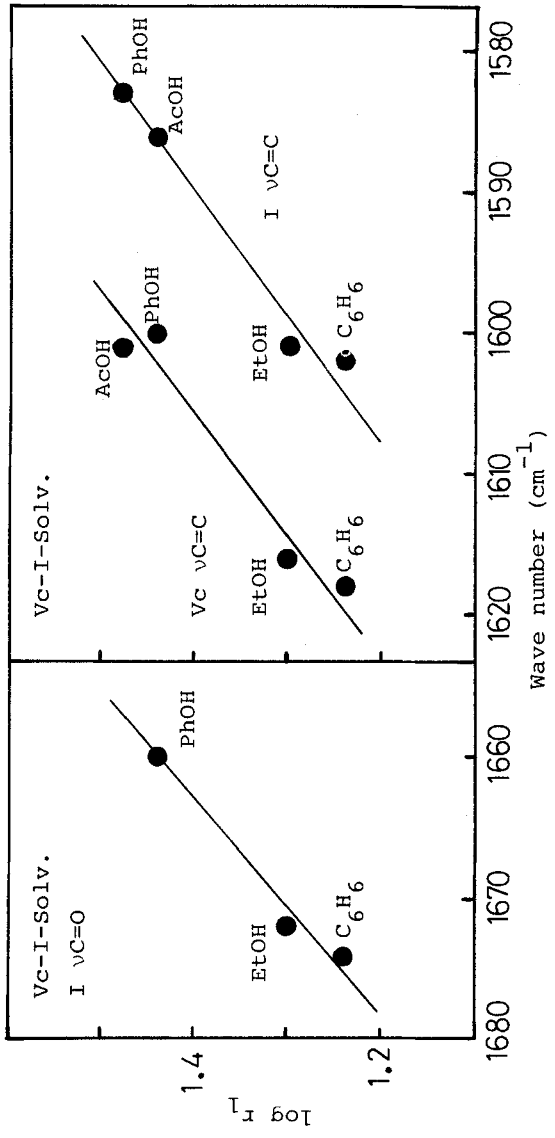

FIG. 2. Relationships between log r_1 and $\nu_{C=O}$ or $\nu_{C=C}$ of I and Vc. [M] = 7 mol/L at 80°C.

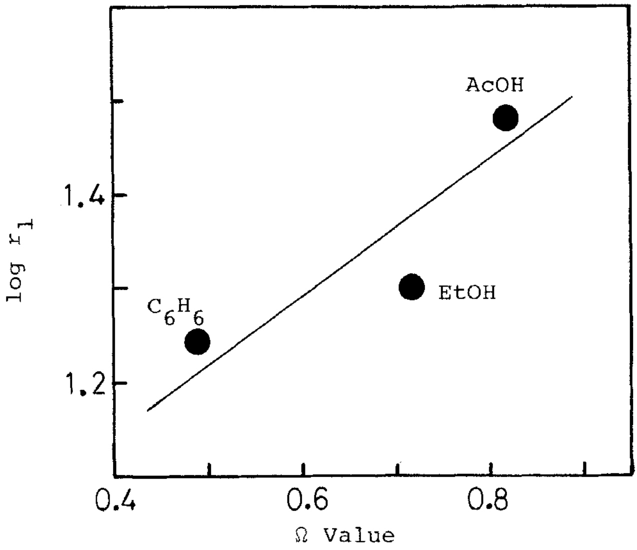

FIG. 3. Relationship between log r_1 and Ω values of solvents. [M] = 7 mol/L at 80°C.

found to be almost constant with benzene and ethanol but were strongly affected with phenol and acetic acid, suggesting that rather stronger protic solvents interact with both the monomers (perhaps through hydrogen bonding) to vary the viscosity of the reaction mixture as described in the previous paper [3]. In other words, the copolymerizability might be affected by the viscosity effect on the termination reaction, the degree of which would be varied by the difference in interaction between the solvent and monomers.

Table 2 summarizes the values of monomer reactivity ratios (r_1) which were varied with the solvents, clearly indicating the occurrence of the solvent effect in the reaction. It was noted that the decrease of the monomer concentration decreased the copolymerizability in every system. Similar results were also observed in the copolymerization of St with I [3]. The reaction temperature also slightly altered the r values. However, these differences do not seem to be significant enough to permit the activation and enthalpy to be calculated [3, 4, 6] because of appreciably larger r values for the copolymerization.

Plots of log r_1 values with the infrared spectra (IR) values determined in the solvents gave linear relationships (Fig. 2); the stronger the interaction, the more the copolymerizability decreased. This result seems to indicate that the copolymerizability might be affected by the different degree of solvation to both I and Vc in the ground state. However, linear corelationships between log r_1 and Ω values of solvent (Fig. 3) suggest that the solvation of a polar structure of the growing radicals became important at the transition state because the Ω values are regarded as a measure of the solvation ability to a polar structure between the ground and transition states.

In any event, the above observation suggest that the copolymerizability of Vc and I is affected by the solvation of the monomers both at the ground and transition states.

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