

Solvent Effect on Radical Polymerization of Vinyl Acetate

Mikiharu KAMACHI, Der Jang LIAW, and Shun-ichi NOZAKURA

*Department of Polymer Science, Faculty of Science, Osaka University,
Toyonaka, Osaka 560, Japan.*

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ABSTRACT: Absolute rate constants of vinyl acetate (VAC) polymerization have been measured by using the intermittent illumination method in various aromatic solvents and ethyl acetate at 30°. It was shown that the solvent effect was mainly ascribed to the variation in propagation rate constants (k_p) with solvents rather than that in termination rate constants (k_t). The k_p increased in the order: benzonitrile < ethyl benzoate < anisole < chlorobenzene < fluorobenzene < benzene < ethyl acetate. This order is almost the same as that for vinyl benzoate (VBZ) previously reported. There was about an eightyfold difference between the largest and the smallest values. This large variation in k_p is explained neither by copolymerization through solvents nor the chain transfer to solvents, but by a reversible complex formation between the propagating radical and aromatic solvents. The k_p was determined in mixed solvents of ethyl benzoate and ethyl acetate, decreasing with increasing content of ethyl benzoate. This result supports the idea of a reversible complex. The stability constants (K_s) of the complex were estimated on the assumption that the complexed radical was in a dormant state and inactive in the polymerization. The correlation between K_s or k_p and the calculated delocalization stabilization energy for the complex was found, and supported the explanation for the solvent effect.

KEY WORDS Vinyl Acetate / Radical Polymerization / Polymerization Rate / Elementary Reaction / Propagation Rate Constant / Termination Rate Constant / Initiation Rate / Solvent Effect / Stability Constant / Delocalization Stabilization /

It is well known that the rate of radical polymerization of vinyl acetate is retarded in benzene without drastically lowering of molecular weight of the polymer.¹ This low rate was once interpreted in terms of copolymerization by aromatic rings,² but evidence for the absence of copolymerization of benzene with vinyl monomers has been confirmed in several papers.³⁻⁸ The reaction behavior has been explained in terms of degradative chain transfer to benzene^{9,10} or complex formation between the propagating radical and benzene.¹¹ Similarly, it has been found that vinyl benzoate is much lower in its bulk polymerization rate than vinyl acetate, in spite of their similar methyl affinities.¹²⁻¹⁷ These results suggest that an aromatic compound participates in the polymerization rate process.⁸ It has been proposed that the slow propagation rate of vinyl benzoate is explained in terms of the reversible complex formation between the growing radical and its own aromatic ring.⁸ The possibility of the complex formation has also proposed in the radical

polymerization of methyl methacrylate and styrene.^{18,20-28} We recently reported that the propagation rate constants (k_p) for vinyl benzoate²⁹ and phenyl methacrylate³⁰ are influenced by aromatic solvents more extensively than those for methyl methacrylate and styrene and explained the solvent effect in terms of the complex formation of the propagating radical with aromatic solvents. Yamamoto *et al.*³¹ and Bengough *et al.*³² have observed that k_p for vinyl acetate in the radical polymerization is retarded in benzene or its derivatives, suggesting that the retardation of the polymerization of vinyl acetate in aromatic solvents may be caused by the complex formation of the propagating radical with aromatic ring.

In order to confirm this view, the rate constants for the radical polymerization of vinyl acetate in various aromatic solvents and ethyl acetate were determined by using intermittent methods, and the solvent effect on the rate constants was compared with that in the polymerization of vinyl benzoate. The solvent effect

similar to that of vinyl benzoate was observed. We discussed the solvent effect on the basis of the participation of the aromatic ring in the polymerization and were led to the view that there is a complex formation between the propagating radical and the aromatic ring of solvents.

EXPERIMENTAL

Materials

Particularly pure vinyl acetate was prepared as follows.³³ Vinyl acetate obtained commercially was washed successively with an aqueous 5% NaHSO₃ solution, an aqueous 5% NH₂OH · HCl solution, and water, dried with CaCl₂, and then distilled through a Widmer column three times. The fraction distilled at 72–73°C was collected. The samples were degassed, polymerized to 10% conversion, and the residual monomer was distilled. The purified monomer was then stored at –78° until required.

Aromatic solvents, 2,2'-azobis(isobutyronitrile) (AIBN), 2,2'-azobis(cyclohexane-1-carbonitrile) (ACN), and *p*-benzoquinone were purified as previously described.^{29,30}

The rate of polymerization (R_p), the rate of initiation (R_i) and radical lifetime (τ) were determined as described in previous papers.^{29,30} All experiments, unless otherwise stated, were performed at the same concentration of initiator (3×10^{-3} mol l⁻¹) and monomer (2 mol l⁻¹). The relationship with $R_p \propto [I]^{0.5}[M]^{1.0}$ was observed only in a narrow

range of monomer and initiator concentrations. Experimental error for the rate constants was estimated in the same method as previously described.³⁰

A Varian A-60 NMR spectrometer was used with tetramethylsilane as an internal reference (5% solution).

RESULTS

Determination of k_p and k_t

The rates of radical polymerization were determined in various solvents, using an initiator or a photosensitizer with steady illumination. These results are shown in Table I, indicating the remarkable solvent effect on the radical polymerization rate irrespective of the methods for initiation.

The rate dependences on initiator and monomer concentrations were investigated in both thermal initiator and photosensitized polymerizations. Typical examples of the results in benzene are shown in Figures 1 and 2. It was found with other solvents that rates of polymerization were proportional to the monomer concentration (1.3–2.5 mol l⁻¹) and to the square root of the initiator concentration (2.0×10^{-3} mol l⁻¹– 4.0×10^{-3} mol l⁻¹). When the monomer or initiator concentration dependence of the polymerization rate were checked over a wider region of concentrations, the polymerization rates deviated from the linear line through the origin. The deviation in vinyl acetate is consistent with that of Deb *et al.*^{34,35} Therefore, all experiments were per-

Table I. Polymerization rates of vinyl acetate in various solvents at 30°C

Solvents	Initiator ^a	Photosensitized ^b ,
	$R_p \times 10^7$	$R_p \times 10^6$
	mol ml ⁻¹ s ⁻¹	mol ml ⁻¹ s ⁻¹
⊙-OCH ₃	5.57 ± 0.51 (2) ^c	6.59 ± 0.20 (2) ^c
⊙	11.90 ± 0.90 (3)	11.30 ± 0.26 (3)
⊙-F	10.21 ± 0.80 (2)	9.44 ± 0.18 (2)
⊙-Cl	7.02 ± 0.24 (2)	7.06 ± 0.17 (2)
⊙-COOC ₂ H ₅	3.45 ± 0.26 (2)	2.76 ± 0.15 (2)
⊙-CN	0.920 ± 0.018(2)	1.05 ± 0.08 (2)
CH ₃ COOC ₂ H ₅	123 ± 12 (2)	79.50 ± 4.70 (2)
C ₆ D ₆	11.30 ± 0.82 (2)	10.05 ± 0.15 (2)

^a [2,2'-Azobis(isobutyronitrile)] = 0.10 M, [Monomer] = 2.0 M.

^b [2,2'-Azobis(cyclohexane-1-carbonitrile)] = 3.00×10^{-3} M, [Monomer] = 2.0 M.

^c The number of repeated runs.

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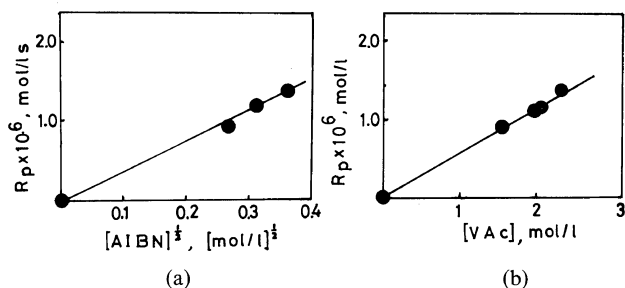


Figure 1. Dependence of the polymerization rate on monomer and initiator concentrations in the initiator polymerization at 30°C in benzene: (a) [Monomer]=2.00 mol/l⁻¹; (b) [AIBN]=0.10 mol/l⁻¹.

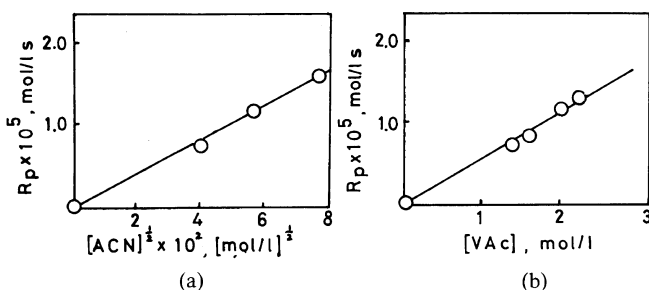


Figure 2. Dependence of the polymerization rate on monomer and initiator concentrations in the photosensitized polymerization at 30°C in benzene: (a) [Monomer]=2.00 mol/l⁻¹; (b) [ACN]=3.00 × 10⁻³ mol/l⁻¹.

formed at a monomer concentration of 2.0 mol/l⁻¹.

In order to evaluate k_p^2/k_t included in the rate of polymerization, initiation rates were determined by the inhibition method using *p*-benzoquinone as an inhibitor. Since rates of polymerization following consumption of *p*-benzoquinone were lower than those without inhibitor in the case of photosensitized polymerizations, initiation rates are considered to be more accurate in the initiator polymerization than in the photosensitized polymerizations. The initiation rates in the former polymerization were thus used for determining k_p^2/k_t . The correlation between the duration of inhibition and the concentration of the inhibitor in benzene is shown in Figure 3. Similar behaviors were observed in the initiator polymerization in other solvents. R_i and k_p^2/k_t are shown in Table II. It can be seen from Table II that the initiation rate was scarcely affected by the solvent, the variation in rate arising from a variation of k_p^2/k_t .

The mean lifetime of the propagating radical was determined in various solvents by the intermittent

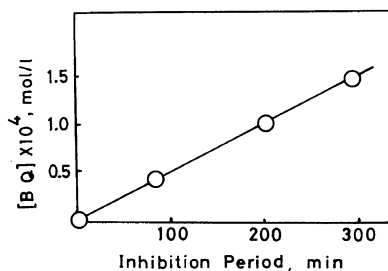


Figure 3. Relation between the inhibitor concentration and induction period: solvent, benzene; polymerization temp, 30°C; [AIBN]=0.10 mol/l⁻¹; [Monomer]=2.0 mol/l⁻¹.

illumination method at 30 ± 0.001°. Figure 4 shows the variation of the rate of polymerization with illumination time in benzene. The mean lifetime of the growing chain was determined by sliding the theoretical curve for a lifetime of one second over the plots of the experimental data until a best fit was achieved. Mean deviation of the lifetime was esti-

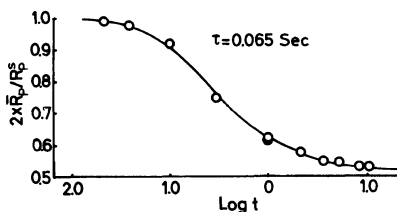
Table II. Initiation rates and k_p^2/k_t values in various solvents at 30°C

Solvents	$R_i \times 10^{9a}$	$k_p^2/k_t \times 10^5$
	1/mol s ⁻¹	1/mol s ⁻¹
-OCH ₃	7.96 ± 0.12 (2) ^b	0.974 ^c
	8.23 ± 0.13 (3)	4.30
-F	8.61 ± 0.15 (2)	3.02
-Cl	8.84 ± 0.12 (2)	1.39
-COOC ₂ H ₅	8.90 ± 0.13 (2)	0.334
-CN	8.99 ± 0.14 (2)	0.0235
CH ₃ COOC ₂ H ₅	8.78 ± 0.10 (2)	430.8
C ₆ D ₆	8.77 ± 0.11 (2)	3.64

^a Thermal initiation rates. [2,2'-Azobis(isobutyronitrile)]=0.10 M [Monomer]=2.00 M, Inhibitor=*p*-benzoquinone.

^b The number of repeated runs.

^c The values calculated from mean values of R_p and R_i .

**Figure 4.** Variation of the polymerization rate with illumination time at 30°C: the ratio of dark to light=3; [ACN]= 3×10^{-3} mol l⁻¹; [Monomer]=2.0 mol l⁻¹.

mated by the deviation of the experimental data of illumination time from 0.1 s to 1 s from the theoretical curve.

In Table III, the lifetime and derived values of k_p/k_t are shown together with k_p and k_t . The limits of accumulated error of k_p and k_t were estimated from the mean deviation of the rate and the lifetime to be around 30% and 40%, respectively.³⁰ The relative errors caused by weighing monomer, initiator, and solvents were less than 0.1% and thus neglected.

The variation of k_p with solvents is far beyond the limit of error, indicating that there is indeed a solvent effect on the propagating process. In order to make clear the participation of aromatic solvent in the propagation process of vinyl acetate, the k_p was determined in mixed solvents of ethyl benzoate and ethyl acetate as shown in Table IV. The k_p decreased

Table IV. The k_p values in mixed solvents of ethyl acetate and ethyl benzoate

Solvents		Observed ^a k_p	Calculated ^b , k_p
EtAc : EtBz	EtAc : EtBz		
Molar ratio	Volume ratio	1/M s ⁻¹	1/M s ⁻¹
8.22 : 0	1 : 0	637	—
5.48 : 1.88	2 : 1	104	100
4.11 : 2.82	1 : 1	78	70
2.74 : 3.76	1 : 2	48	54
0 : 5.64	0 : 1	37	—

^a Polymerization temp. 30°C; [Monomer]=2.0 M; repeated runs 2.

^b $K_s=2.87$ M⁻¹ was used for the calculations.

Table III. Mean lifetime of the propagating radical of vinyl acetate and derived rate constants

Solvents	τ^a	$k_p/k_t \times 10^7$	$k_p \times 10^{-2}$	$k_t \times 10^{-8}$
	s		1/mol s ⁻¹	1/mol s ⁻¹
⊖-OCH ₃	0.061 ± 0.011 (4) ^b	2.01	0.48 ± 0.05	2.39 ± 0.45
⊖	0.065 ± 0.012 (8)	3.67	1.17 ± 0.12	3.19 ± 0.61
⊖-F	0.066 ± 0.012 (4)	3.12	0.97 ± 0.10	3.11 ± 0.59
⊖-Cl	0.065 ± 0.018 (4)	2.29	0.61 ± 0.09	2.66 ± 0.75
⊖-COOC ₂ H ₅	0.065 ± 0.016 (4)	0.897	0.37 ± 0.05	4.12 ± 1.04
⊖-CN	0.059 ± 0.017 (4)	0.310	0.08 ± 0.01	2.58 ± 0.76
CH ₃ COOC ₂ H ₅	0.170 ± 0.042 (2)	67.6	6.37 ± 1.01	0.942 ± 0.237
C ₆ D ₆	0.064 ± 0.011 (2)	3.58	1.13 ± 0.10	3.51 ± 0.54

^a [2,2'-Azobis(cyclohexane-1-carbonitrile)]= 3.00×10^{-3} M, [Monomer]=2.00 M.

^b The number of data for the determination of a lifetime.

while increasing the aromatic component in the mixed solvents.

No correlation of termination rate constants with the reciprocal of the viscosity of the polymerization system could be found (Figure 5). The viscosity of the polymerization system was calculated from the viscosity of the constituents by assuming a linear relation of viscosity to volume composition.

Molecular Orbital Calculation

In order to check the possibility of the complex formation of the propagating radical with solvents, the delocalization stabilization energy (ΔE) for the complex formation of the radical with aromatic solvents was calculated by using the perturbation theory^{36,37} as shown in the previous paper. The

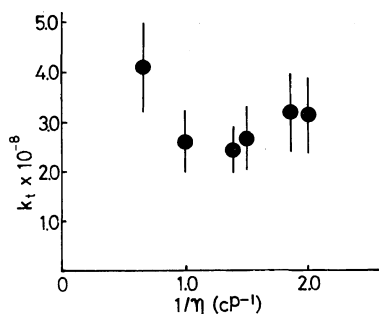


Figure 5. Correlation of k_t values with viscosity of polymerization systems.

parameters for the simple Hückel LCAO MO calculations are shown in Table V. The theory^{36,37} maintains that the charge-transfer interaction takes place according to the way in which the overlap of the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor becomes maximum. The complexed radical was assumed to lie above one of the C=C bonds of aromatic ring as shown in Figure 6. Since the propagating radical of vinyl acetate as well as that of vinyl benzoate is electron-rich and then is considered to become an electron-donor, the complex formation with solvents was assumed to occur at a location such that the absolute value of the sum of the coefficients of adjacent atomic orbitals of the LUMO of the solvent is largest. When the LUMO of the aromatic ring has no adjacent atomic orbitals of the same sign, the second LUMO was assumed to determine the location of the complex. The results of the calculation are shown in Table V and Figure 7. The variation in these values

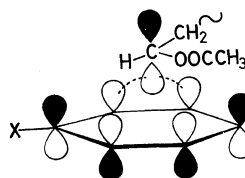


Figure 6. The model of the radical complex.

Table V. Correlation of k_p values of K_s values with delocalization stabilizations for the complex formation

Solvents	$k_p \times 10^{-2}$	ΔE^a	K_s^b
	1/mol s ⁻¹	$-\gamma^2\beta$	1/mol
-OCH ₃	0.48	1.466	1.63
	1.17	1.392	0.48
-F	0.97	1.419	0.64
-Cl	0.61	1.417	1.17
-COOC ₂ H ₄	0.37	1.574	2.87
-CN	0.08	1.723	9.82

^a Anisole⁴⁶ $\alpha_{\text{OCH}_3} = \alpha + 0.5\beta$, $\alpha_{\text{adj,C}} = \alpha$, $\beta_{\text{C-OCH}_3} = 0.6\beta$

Fluorobenzene⁴⁶ $\alpha_{\text{F}} = \alpha + 3.0\beta$, $\alpha_{\text{adj,C}} = \alpha + 0.2\beta$, $\beta_{\text{C-F}} = 0.7\beta$

Chlorobenzene⁴⁶ $\alpha_{\text{Cl}} = \alpha + 2.0\beta$, $\alpha_{\text{adj,C}} = \alpha + 0.18\beta$, $\beta_{\text{C-Cl}} = 0.4\beta$

Ethyl benzoate⁴⁷ $\alpha_{\text{O}} = \alpha + 1.0\beta$, $\alpha_{\text{COO}} = \alpha + 0.20\beta$, $\alpha_{\text{adj,C}} = \alpha$, $\beta_{\text{C-O}} = \beta$, $\beta_{\text{C-O}} = 0.6\beta$

Benzonitrile⁴⁷ $\alpha_{\text{N}} = \alpha + 0.8\beta$, $\alpha_{\text{adj,C}} = \alpha + 0.08\beta$, $\beta_{\text{C-N}} = \beta$

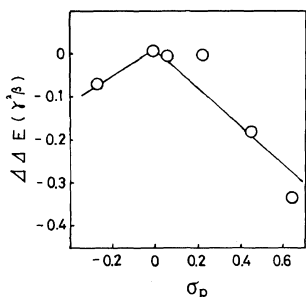


Figure 7. Correlation between delocalization stabilization and Hammett's σ_p of solvent substituents.

with solvents is consistent with that of the k_p in that larger stabilization correlated with smaller k_p .

DISCUSSION

There is an eightyfold difference between the largest and the smallest k_p , as shown in Table III. The variation of k_p with aromatic solvents is the largest ever reported in the radical polymerization of vinyl compounds. The correlation of k_p for vinyl acetate with σ_p of the substituent of solvent is shown in Figure 8 along with that for methyl methacrylate. The solvent effect on k_p for vinyl acetate ($\rho = -0.22^{40}$) is opposite in trend against Hammett σ_p to that observed for methyl methacrylate ($\rho = 0.40^{40}$). Since the propagating radicals of both monomers have been shown to have opposite polarity in the copolymerization with monomers of different polarities,^{41,42} the solvent effect might be due to the inverse polarity of the propagating end.

If these solvent effects result mainly from the polar participation of the solvent in the transition state of the propagation reaction, the variation of the k_p with solvents should be correlated with the polarity or the polarizability of the solvent.⁴³ No correlation could be found between k_p and $1/\epsilon$ or $(\epsilon - 1)/(2\epsilon + 1)$, where ϵ is the dielectric constant of the solvent. Accordingly, the polar participation of solvent in k_p seems to be ruled out. Moreover, a remarkable decrease in k_p in ethyl benzoate compared to that in ethyl acetate in spite of their similar dielectric constants indicates that the rate of propagation is retarded by the presence of the aromatic ring of the solvent rather than its polarity.

This rate variation might be caused by copolymerization through aromatic rings. However, the possi-

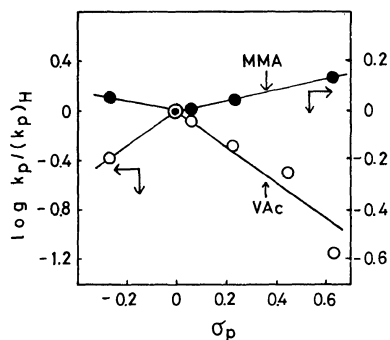


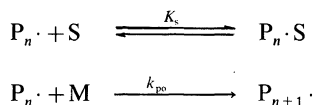
Figure 8. Correlation of k_p values for vinyl acetate and methyl methacrylate with Hammett's σ_p of solvents: —○—, VAc; —●—, MMA. $(k_p)_H$ denotes the propagation rate constant in benzene.

bility of copolymerization is ruled out by the reported evidence that copolymerization of vinyl monomers with simple aromatic compounds does not take place at all.³⁻⁸

Another possible explanation for the solvent effect might be the difference in the chain-transfer rate to solvent and/or difference in the reinitiation rate by the resulting solvent radical. Let us discuss, therefore, the effect of the solvent-transfer reaction on k_p in terms of the following three points: 1, likeliness of chain transfer reaction to solvent; 2, the stability of the obtained solvent radical; 3, the polarity of the radical. The data of chain transfer for vinyl acetate by Stockmayer *et al.*⁴⁴ show that the solvent dependence of k_p does not correlate with the chain transfer constants to solvent. If the stability of the radical, produced from the solvent transfer, is important for the solvent effect, the solvent dependence of k_p should show the same pattern for both vinyl acetate and methyl methacrylate. However, this is not the case as mentioned before (Figure 8). If the polarity of the solvent radical obtained is important, the solvent effect should be correlated with Hammett σ_m or σ_i , which are considered to be the measure of the polarity of the aromatic radical. If both the polarity and stability of the radical influence the propagation-rate constants, the free-energy relationship on the reactivity of the solvent radical should be expected and thus, k_p should be linearly correlated with Hammett σ_p . The expectations too are not consistent with the experimental results. Moreover, if the chain transfer reaction to solvents is an important factor in the solvent effect, a solvent

isotope effect on R_p and k_p might be observed in the radical polymerization. No isotope effect on k_p was observed in deuterated benzene and benzene. (Tables I—III) This fact also suggests that the chain transfer is not important in the solvent effect.

The intermolecular complex formation between the propagating radical and the aromatic solvent must be considered. Bamford *et al.*^{22–25} and Burnett *et al.*^{27,28} have pointed out the possibility of the complex formation of a propagating radical with aromatic solvents in radical polymerization of vinyl compounds. Also, we have recently shown that the complex formation can reasonably explain the solvent effect on k_p for vinyl benzoate.²⁹ The complex formation explains the fact that k_p for vinyl acetate yielding an electron-rich propagating radical is the smallest in benzonitrile which is most likely to accept an electron from among the aromatic solvents used. Since it is quite difficult to estimate the capacity of a free radical to form the complex, the stabilization energy for the complex formation was calculated by the molecular orbital theory.^{36,37} When we calculated the stabilization energy (ΔE) caused by the interaction of the propagating radical with aromatic solvents on the assumption that the radical lies above one of the C=C bonds of the aromatic rings, the variation of these values with solvents explains the experimental result in which k_p in anisole is smaller than that in benzene (Figure 8). Accordingly, these explanations suggest that some of the propagating radicals may be stabilized by the complex formation with aromatic solvents. If the complexed radical is inactive for the propagation, the behavior of the propagating radical can be represented as follows.



where K_s is stability constant for the complex and k_{po} is the true propagation rate constant which is independent of the medium for polymerization. The observed propagation rate constant is given by

$$k_p = \frac{k_{po}}{1 + K_s[S]} \quad (1)$$

Since the polymerization system has no aromatic rings in the polymerization of vinyl acetate in ethyl acetate, the observed k_p in ethyl acetate is reasonably assumed to be k_{po} . The stability constant in aromatic solvents was estimated by using k_{po} and k_p in the

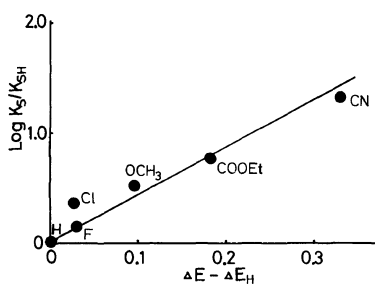


Figure 9. Correlation between delocalization stabilization and the stability constant (K_s) for the complex formation. K_{SH} denotes the stability constant in benzene.

corresponding solvents. The K_s are shown in Table V, being clearly correlated with the delocalization stabilizations for the complex (Figure 9). The k_p in mixed solvents of ethyl acetate and ethyl benzoate was estimated by using k_{po} and K_s in ethyl benzoate. The calculated values are in fair agreement with the observed values. (Table IV). The fact that the polymerization rate deviated from the linear line through the origin at lower monomer concentration than 1.3 mol l^{-1} and higher than 2.5 mol l^{-1} seem to support the eq 1 by the concentration of solvent. Thus, the variation in k_p with aromatic solvents can reasonably be explained in terms of the formation of the reversible radical complex with aromatic solvents.

A solvent effect for vinyl acetate is larger than that for vinyl benzoate. This difference in the solvent effect is due perhaps to the fact that vinyl acetate has no aromatic rings itself, since k_p remarkably decreases with the addition of ethyl benzoate in the polymerization of vinyl acetate in ethyl acetate. (Table V)

Termination rate constants were not correlated with the fluidities (reciprocal viscosities) of the polymerization system, which is different from the results of phenyl methacrylate³⁰ and methyl methacrylate.⁴⁸ Also, no correlation between k_t and the fluidity of solvent has recently been reported by Yamamoto *et al.*³¹ in the polymerization of vinyl acetate, suggesting that the termination reaction is controlled by other factors rather than by diffusion of the polymer chain. When the reversible complex of the propagating radical is taken into account, the correlation of k_t with delocalization stabilization for the complex will also be expected. However, linear correlation could not be found between them. Since

the activation energy for the termination reaction [0—1 kcal mol⁻¹ 49] is smaller than that for the propagation reaction [4—9 kcal mol⁻¹ 49] in the radical polymerization of vinyl acetate, the termination reaction might not be so remarkably influenced by the complex formation as the propagation reaction. The solvent effect on k_t seems to be more complicate than that on k_p in the radical polymerization of vinyl acetate in aromatic solvents.

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