Structure and Reactivities of Alkyl Vinyl Ketones in Their Radical Copolymerizations with Styrene

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Synopsis

To clarify the effect of the alkyl substituents in alkyl vinyl ketones (RVK) on their radical copolymerizations, the copolymerizations of six such alkyl vinyl ketones with styrene were investigated. From the results obtained, the relative reactivities of RVK toward the polystyryl radical were correlated with the Taft equation: $\log (1/r_1) = \rho^* \sigma^* + \delta E_s$, in which σ^* and E_s are polar and steric substituent constants, respectively, and ρ^* and δ are reaction constants. The values of ρ^* and δ obtained were 0.40 ± 0.05 and 0, respectively. It was observed that the Q and e values obtained for RVK increased with increasing of σ^* values, and that both relative reactivities and Q,e values of methyl vinyl ketone also increased with increasing of the E_T values of the solvents used. From the spectral determination of the RVK monomers, it was also found that their n–π interactions were related to the copolymerization reactivities. Furthermore, the radical polymerization of *tert*-butyl vinyl ketone (*t*-BVK) with azobisisobutyronitrile (AIBN) was investigated, and its rate R_p was found to be expressed by the following rate equation: $R_p = k [\text{AIBN}]^{0.5}[t\text{-BVK}]^{1.0}$.

INTRODUCTION

Recently alkyl vinyl ketones (RVK) have received attention as comonomers in obtaining photodegradative polymer.[1,2] However, systematic investigations of their radical copolymerization behavior, especially on the relationship between their structure and reactivity, have not been carried out.

Since 1961, we have been studying the relationship between the reactivities and the structure of various vinyl monomers having a series of substituents in their radical polymerizations and copolymerizations,[3] with special emphasis on the role of the substituent.

In the present paper, a study of various RVK monomers was undertaken as an extension of this series of investigations. The present paper deals with the results of the radical copolymerizations of six RVK monomers with styrene and of the effects of the alkyl substituent in RVK and of solvents. Kinetic studies of radical polymerization of *tert*-butyl vinyl ketone are also described.

EXPERIMENTAL

Preparation of Monomers

The Mannich reaction of pinacolone and paraform in the presence of dimethylamine hydrochloride was used to prepare *tert*-butyl vinyl ketone (*t*-

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BVK).[4] Ethyl and isopropyl vinyl ketones (EVK and IPVK) were also prepared according to the methods described by McMahon et al.[5] and Thomas et al.,[6] respectively.

In a typical run, a mixture of anhydrous aluminum chloride (1.1 mole) and acyl chloride (1 mole) dissolved in dry methylene chloride (400 ml) was cooled to $-30°C$, and ethylene gas was passed through this mixture at such a rate that the temperature did not rise above $0°C$ until its absorption ceased. The reaction mixture was then poured into a mixture of crushed ice and dilute hydrochloric acid. The methylene chloride layer was separated, washed with water, dried and finally distilled to remove solvent. The crude alkyl β-chloroethyl ketone was then distilled under reduced pressure.

The dehydrochlorination was carried out by refluxing in a mixture of triethylamine (1 mole) and diethyl ether (400 ml) for 75 hr. After reaction, ether was distilled, and the product was distilled under reduced pressure. Chloromethyl vinyl ketone (CMVK) was also prepared in the same manner, monochloroacetyl chloride being used as an acyl chloride.[7] Phenyl vinyl ketone (PVK) was prepared by Friedel-Crafts reaction of β-chloropropionyl chloride with benzene.[8]

The resulting RVK monomers were purified by fractional distillation under reduced pressure before use. Infrared, NMR, and gas chromatographic determinations confirmed these monomers to be pure. Methyl vinyl ketone (MVK) (Aldrich Chem. Co.) was distilled under reduced pressure before use. The physical properties of the monomers used in this study are shown in Table I.

TABLE I
Physical Properties of Alkyl Vinyl Ketones (RVK), $CH_2{=}CHCOR$

RVK	R in RVK	Boiling point, °C/mm Hg[a]	n_D^{20}[a]	Reference
MVK	CH_3	32/120 (32/120)	1.4088 (1.4086)	9
EVK	C_2H_5	38–39/65 (38/60)	1.4185 (1.4185)	5
IPVK	$CH(CH_3)_2$	50–51/70 (50/70)	1.4186 (1.4188)	6
t-BVK	tert-C_4H_9	65–66/110 (65–66/105)	1.4220 (1.4222)[b]	4
CMVK	CH_2Cl	56–57/31 (56.5–57/31)	1.4694 (1.4690)	7
PVK	C_6H_5	72–74/3 (70–73/3)	1.5584 (9.5588)	8

[a] Values in parentheses indicate those reported in the references.
[b] Indicates the value of n_D^{15}.

Other Reagents

Styrene used as a comonomer was purified by usual method. 2,2′-Azobisisobutyronitrile (AIBN) was used after recrystallization from ethanol. Benzene, ethanol, and other solvents were also purified by ordinary methods.

Polymerization Procedure

The polymerization of t-BVK and the bulk copolymerization of RVK with styrene were carried out in sealed ampoules with shaking at 60°C in the presence of AIBN. The ampoule which contained the required amounts of re-

agents was degassed by a freezing and thawing technique, and then sealed off under vacuum. After the polymerization for a given time, the contents of the ampoule were poured into a large amount of methanol to isolate the polymer. The copolymer thus obtained was purified by reprecipitating from its benzene solution into methanol. The composition of the copolymers was calculated from carbon contents observed by elementary analysis. The monomer reactivity ratios were determined by the curve-fitting method.

RESULTS AND DISCUSSION

Radical Polymerization of t-BVK

The bulk polymerization of t-BVK was carried out with AIBN at temperatures ranging from 50 to 80°C. The time–conversion curves are shown in Figure 1, from which these polymerizations were found to proceed linearly as a function of reaction time without induction period. Moreover, it is noted that no gelation is observed during the polymerization even if the conversion of polymer became as high as 80%, in contrast to the case of MVK which gels at about 70% conversion.

Figure 2 shows the relationship between the rates of polymerization R_p determined from the slopes of straight lines of Figure 1 and the reciprocal
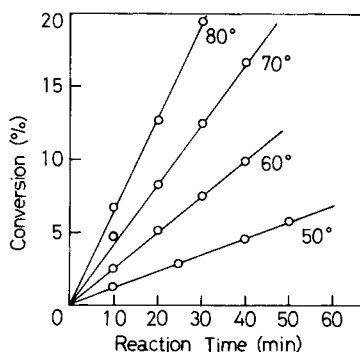

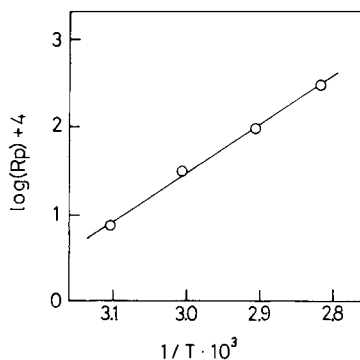Fig. 1. Time–conversion curves for bulk polymerization of t-BVK; [AIBN] = 1.59×10^{-2} mole/l.

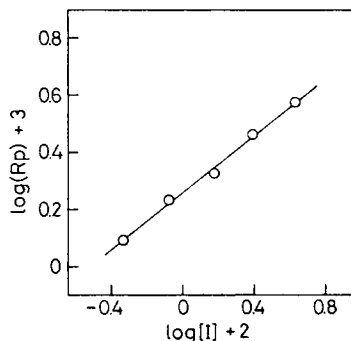Fig. 2. Plot of log R_p with $1/T$ for the bulk polymerization of t-BVK.

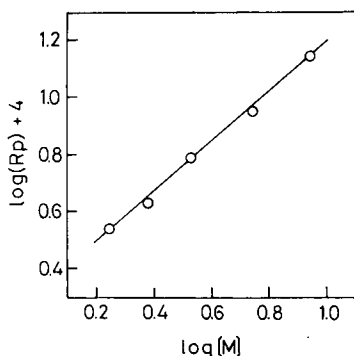Fig. 3. Relationship between $\log R_p$ and logarithm of AIBN initiator concentration [I].

Fig. 4 Relationship between $\log R_p$ and logarithm of the monomer concentration [M].

values of the absolute polymerization temperatures. From the resulting straight line, the apparent activation energy for overall polymerization is calculated to be 21.0 kcal/mole. A similar value (19.7) has been reported for the radical polymerization of PVK.[10]

Figures 3 and 4 show plots of R_p with concentrations of AIBN initiator and the monomer, respectively, in the radical polymerization of t-BVK at 60°C. From the linear relationship obtained, the rate equation of eq. (1) is derived:

$$R_p = k[\text{AIBN}]^{0.5}[t\text{-BVK}]^{1.0} \tag{1}$$

This result strongly suggests that the polymerization is initiated through the reaction of t-BVK with a 2-cyano-2-propyl radical produced by thermal decomposition of AIBN and terminates bimolecularly, as in ordinary radical polymerization.

Copolymerization of RVK with Styrene

The results of bulk copolymerizations of six RVK monomers (M_2) with styrene (M_1) initiated by AIBN at 60°C are shown in Table II. The rates of copolymerization increase with increasing concentration of the RVK monomer in all copolymerization systems studied.

Table III summarizes the monomer reactivity ratios, r_1 and r_2 and the Q_2

TABLE II
Results of Bulk Copolymerizations of RVK (M$_2$) with Styrene (M$_1$)
with AIBN at 60°C[a]

RVK	[M$_1$] in feed, mole-%	Time, min	Conver-sion, %	Copolymer	
				Carbon, %	[M$_1$], mole-%
MVK	83.2	40	2.6	86.36	66.8
	68.0	40	3.7	84.36	56.8
	54.2	40	3.8	82.74	49.9
	41.5	40	4.7	81.31	43.8
	19.1	40	6.0	77.83	30.1
	9.20	40	7.4	74.28	17.9
EVK	88.6	30	2.2	87.60	73.5
	63.9	30	3.2	84.53	57.6
	37.5	30	4.0	82.10	45.8
	22.9	30	4.6	79.93	35.7
	13.8	30	4.7	77.39	24.4
	4.4	30	5.0	73.95	10.0
IPVK	87.1	30	2.0	87.83	75.6
	72.4	30	2.2	85.79	64.7
	60.5	30	2.6	84.34	57.0
	34.3	30	4.1	82.26	46.1
	25.0	40	3.1	80.95	39.3
	12.7	40	5.8	77.80	23.2
t-BVK	87.6	70	6.6	87.95	76.2
	72.7	60	6.6	85.97	65.1
	57.7	60	6.2	84.44	56.4
	42.7	30	5.0	83.33	50.0
	27.7	30	4.6	82.15	43.1
	12.6	30	4.0	78.91	23.9
CMVK	81.9	30	3.3	72.81	58.2
	70.5	30	3.7	69.37	50.7
	62.3	30	4.7	68.92	50.2
	46.8	30	6.0	65.30	41.9
	37.1	20	5.8	62.74	36.4
	21.0	20	7.0	57.68	25.5
PVK	86.6	40	5.2	88.55	69.4
	68.3	40	6.0	86.82	54.1
	53.8	40	6.8	85.93	45.0
	47.4	40	8.8	85.89	44.4
	36.6	20	4.2	85.33	39.1
	13.4	20	5.6	83.89	19.7

[a] Polymerization conditions: M$_1$ + M$_2$ = 4 ml, [AIBN] = 3.5 × 10^{-3} mole/l.

TABLE III
Copolymerization Parameters for the Copolymerizations of
RVK (M$_2$) with Styrene (M$_1$)

RVK	r_1	r_2	Q_2[a]	e_2[a]
MVK	0.27	0.40	1.12	0.69
EVK	0.45	0.31	0.87	0.69
IPVK	0.40	0.30	0.78	0.66
t-BVK	0.40	0.30	0.78	0.66
CMVK	0.13	0.52	2.07	0.84
PVK	0.21	0.48	1.40	0.74

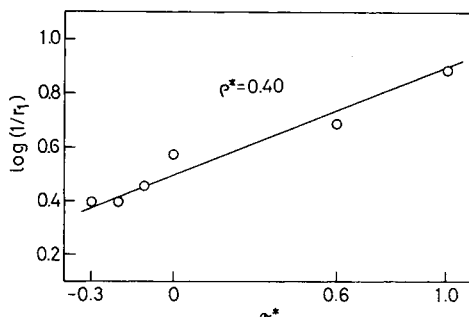[a] Calculated by assuming that Q_1 and e_1 for styrene are 1.0 and −0.8, respectively.

Fig. 5. Relationship between log $1/r_1$ and σ^* constants of alkyl groups in RVK.

and e_2 values for RVK. It is clear that these RVK are electron-accepting conjugative monomers.

To ascertain the effect of alkyl substituents on the copolymerization reactivity, the relative reactivities $(1/r_1)$ of RVK toward the polystyryl radical were plotted with their polar substituent constants, σ^*, in Taft's equation [eq. (2)]:

$$\log (1/r_1) = \rho^*\sigma^* + \delta E_s \qquad (2)$$

where E_s is the steric substituent constant, and ρ^* and δ are reaction constants giving the susceptibility caused by the substituent for a given reaction series.

The plots of log $(1/r_1)$ calculated from Table III with σ^* constants are shown in Figure 5, from which a good straight line relationship with a ρ^* value of 0.40 ± 0.05 is observed. This result indicates that the reactivities of RVK are independent of their E_s constants and controlled only by the polar nature of their alkyl substituents. Similar results were observed for various monomers having a series of alkyl substituents such as alkyl acrylates,[11] alkyl thiolacrylates,[12] alkyl methacrylates[13] and vinyl esters,[14] in which the ρ^* values reported were smaller than 0.56. The ρ^* value obtained for RVK is also close to that obtained for alkyl methacrylates ($\rho^* = 0.33$) and alkyl acrylates ($\rho^* = 0.56$).

Since RVK in which the reacting vinyl group is a cross-conjugated system with the substituents, it is expected that the resonance effect of the substituents influences their reactivities. In fact, Yokota et al.[15] have reported that the copolymerization reactivities of p-substituted PVK were correlated with the generallized Hammett equation [eq. (3)]:[3]

$$\log (1/r_1) = \rho\sigma + \gamma E_R \qquad (3)$$

where σ and E_R are, respectively, polar and resonance substituent constants and ρ and γ are reaction constants showing, respectively, the extent of the polar and resonance effects. From the values ($\rho = 0.34$ and $\gamma = 2.0$) obtained, they concluded that the effects of the substituents in PVK concurrently influenced the reactivity.

Since the values of σ and E_R of the substituents of PVK used in this study are very close to each other, it was impossible to obtain any information with respect to the resonance effect of the substituents by applying eq. (3) to the present RVK.
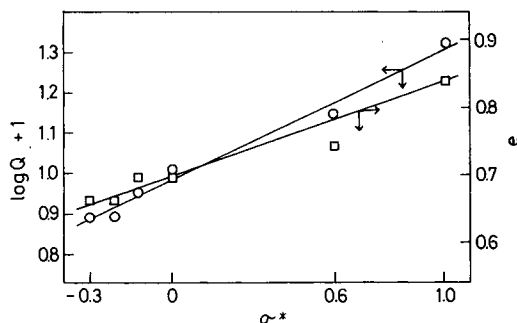
Fig. 6. Relationship between log Q and e values for RVK and σ^* constants of their alkyl groups.
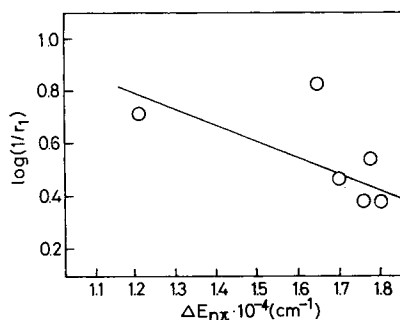

Fig. 7. Plot of log $1/r_1$ against $\Delta E_{n\pi}$ of RVK monomers in n-hexane.

Figure 6 shows the correlation between the Q,e values obtained for RVK and the σ^* constants. Both Q and e values tend to increase with increasing σ^* constant.

In connection with these observations, Kossanyi[16] has shown from the NMR determinations of RVK that the spin coupling constants of their vinyl protons increase with increasing σ^* constants of their alkyl substituents. Although there are some uncertainties as to the spin coupling constants of their *trans* protons, those of their geminal protons were observed to be correlated with their reactivities, as reported for other vinyl monomer series.[17]

TABLE IV
Ultraviolet Absorption Determination of RVK in n-Hexane

RVK	K-band, nm	R-band, nm	$\Delta E_{n\pi}$, cm^{-1}
MVK	208	331	17870
EVK	212	330	16870
IPVK	211	335	17540
t-BVK	211	339	17890
CMVK	216	336	16530
PVK	249[a]	355	11990

[a] PVK shows an additional absorption maximum at 215 nm ($\epsilon = 7900$) besides that ($\epsilon = 11600$) indicated here.

TABLE V
Effects of Solvents on the Radical Copolymerizations of MVK (M_2)
with Styrene (M_1)[a]

Solvent	[M] in feed, mole-%	Time, min	Conversion, %	Copolymer	
				Carbon, %	[M_1], mole-%
Dioxane	83.2	40	1.2	86.95	69.8
	68.0	40	1.5	84.56	58.1
	54.2	40	1.8	82.90	50.6
	41.5	30	1.7	81.38	44.1
	29.8	30	2.4	79.77	37.5
	9.20	30	2.8	74.51	18.4
Acetonitrile	83.2	40	1.4	86.62	68.1
	68.0	40	1.6	84.28	56.8
	54.2	40	1.9	82.59	49.3
	41.5	40	2.3	81.09	42.6
	29.8	40	3.0	79.40	36.3
	19.1	40	3.6	77.25	27.9
Acetonitrile– ethanol[b]	83.2	30	1.1	86.27	66.4
	68.0	30	1.3	84.15	56.2
	54.2	30	1.6	82.46	48.7
	41.5	30	2.1	81.02	42.6
	29.8	30	2.4	79.18	35.2
	19.1	30	2.9	77.21	27.8
Ethanol	83.2	30	1.2	85.79	64.0
	68.0	30	1.3	83.75	54.4
	54.2	30	1.5	82.04	46.9
	41.5	30	2.4	80.61	40.9
	29.8	30	3.0	78.93	34.3
	19.1	30	3.1	76.70	26.0

[a] Copolymerization conditions: $M_1 + M_2 = 5$ ml, solvent = 5 ml, [AIBN] = 2.8 × 10^{-3} mole/l. at 60°C.

[b] Acetonitrile/ethanol = 2:1 (molar ratio).

Similar results were obtained in alkyl methacrylates,[13] and it was suggested from the spectroscopic data that polarization of the carbonyl groups might be increased by electron-donating alkyl groups and that the resonance of the reacting double bond with the carbonyl group might be reduced, resulting in decreased reactivities of the monomers. In the present RVK, the observed results might be explained by a similar manner.

TABLE VI
Copolymerization Parameters for the Copolymerizations of MVK (M_2) with
Styrene (M_1) in Various Solvents and Physical Properties of Solvents Used

Solvent	Parameter				Solvent		
	r_1	r_2	Q_2	e_2	E_T	Dielectric constant	$\Delta E_{n\pi}$, cm^{-1}[a]
Dioxane	0.30	0.40	1.04	0.66	36.0	2.21	17040
Acetonitrile	0.26	0.41	1.15	0.70	46.0	37.5	16210
Acetonitrile– ethanol	0.23	0.41	1.28	0.74	49.0	33.1	16110
Ethanol	0.20	0.46	1.45	0.74	51.9	24.3	15800

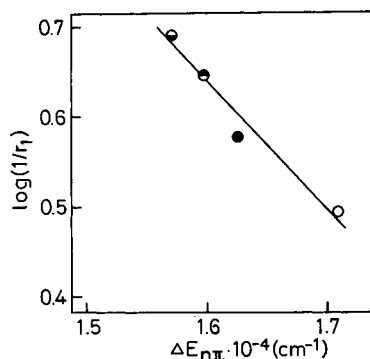[a] Calculated from the UV spectra by using eq. (3).

Fig. 8. Plot of log $1/r_1$ against $\Delta E_{n\pi}$ for the copolymerization of styrene (M_1) and MVK (M_2) in various solvents: (○) dioxane; (●) acetonitrile; (◐) acetonitrile–ethanol; (◖) ethanol.

To obtain further information regarding the interaction between the carbonyl and vinyl groups of the monomer, some spectroscopic determinations of RVK were carried out.[18,19] From the resulting ultraviolet spectra, the energy difference of the $n–\pi$ interaction, $\Delta E_{n\pi}$, is calculated by eq. (4):

$$\Delta E_{n\pi} = \nu_{max}(K\text{-band}) - \nu_{max}(R\text{-band}) \qquad (4)$$

where $\nu_{max}(K\text{-band})$ and $\nu_{max}(R\text{-band})$ are the frequencies of absorption maxima in the K-band and R-band of RVK, respectively.

The results are shown in Table IV, and the plots of relative reactivities of RVK with their $\Delta E_{n\pi}$ obtained are shown in Figure 7. From Figure 7, an approximately linear relationship is observed, indicating that the ease of $n–\pi$ interaction (i.e., decrease in $\Delta E_{n\pi}$) leads to an increase in the reactivities of RVK and also the Q values.

Effect of Solvents in the Copolymerization of MVK with Styrene

To confirm the effect of alkyl substituents of RVK on radical reactivities, the copolymerization of MVK (M_2) with styrene (M_2) was carried out in solvents having different E_T values, which are a measure of solvent polarity. The results are shown in Tables V and VI.

As can be seen from Table VI, relative reactivities of MVK toward the polystyryl radical increase with increasing E_T values of solvents, are independent of dielectric constants, and increase with a decrease in $\Delta E_{n\pi}$ values of MVK in solution (Figure 8). This result is quite similar to that observed in the copolymerization of methyl methacrylate with styrene.[20] It is also noted that Q and e values increase with increasing of E_T values.

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