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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Tanaka, Hitoshi and Otsu, Takayuki(1977) 'Cyclodimerizations and Copolymerizations of Vinyl Ketones with Vinyl Monomers', *Journal of Macromolecular Science, Part A*, 11: 2, 231 – 250

To link to this Article: DOI: 10.1080/00222337708061265

URL: <http://dx.doi.org/10.1080/00222337708061265>

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Cyclodimerizations and Copolymerizations of Vinyl Ketones with Vinyl Monomers

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ABSTRACT

Diels-Alder reactions (cyclodimerizations) of chloromethyl vinyl ketone (CMVK) and methyl isopropenyl ketone (MIPK) leading to 2,3-dihydropyran derivatives have been studied kinetically in connection with their radical polymerization. The activation enthalpies and entropies obtained for the cyclodimerizations of CMVK and MIPK were 48.0 and 68.5 kJ/mole and -209 and -177 J/°C-mole, respectively, at 90° C. The rate constants of the cyclodimerizations were almost independent of the solvents used. The reactivities of vinyl ketones as diene or dienophile were also studied for CMVK, MIPK and methyl vinyl ketone in comparison with their structures. The cocyclodimerization and copolymerization of CMVK with various vinyl monomers were also investigated. The results obtained are discussed from the viewpoint of the structures and reactivities of these monomers.

and paraformaldehyde by White's method [11]; bp 38-39° C/90 Torr, $n_D^{20} = 1.4222$ (lit. [11], bp 38° C/85 Torr, $n_D^{20} = 1.4220$). Methyl vinyl ketone (MVK) (Aldrich Chemical Co.) was used after distillation; bp 32° C/120 Torr, $n_D^{20} = 1.4088$ (lit. [12] bp 32° C/120 Torr, $n_D^{20} = 1.4086$). The commercially obtained acrolein and vinyl monomers were used after purification by ordinary method, followed by distillation just before use.

Cyclodimerizations of CMVK and MIPK

The reactions were carried out in refluxing toluene containing a small amount of hydroquinone in a stream of nitrogen without light. After a given time, the unreacted ketone monomer and toluene were removed from the reaction mixture by distillation, and the dimers formed were distilled under reduced pressure. The purity of the resulting dimers was determined by thin-layer and gas-chromatographic analyses, and their structures were confirmed by IR, NMR, and mass spectra.

Determination of Rate Constant of Cyclodimerizations

The concentration of CMVK and MIPK consumed during the reaction was determined from the change in the NMR spectrum of the reaction mixture as a function of time (Figs. 1 and 2) by use of the NMR integral ratio of $-\text{COCH}_2\text{Cl}$ ($\delta = 4.24$ ppm) of CMVK or $-\text{COCH}_3$ ($\delta = 2.29$ ppm) of MIPK against $-\text{CH}_2-$ ($\delta = 3.62$ ppm) of dioxane solvent. When solvents other than dioxane were employed, their characteristic peaks in NMR spectra were taken as $\delta = 6.70-7.40$, $3.50-4.00$, 7.27 and $7.75-8.05$ ppm for *o*-dichlorobenzene, tetrahydrofuran, chloroform, and nitrobenzene, respectively. Then, the second-order rate constants k_D were calculated from the slope of the observed straight lines between the reciprocal of the ketone concentration and the reaction time (see Figs. 3 and 4).

Cocyclodimerizations of CMVK with Vinyl Monomers

The reactions were carried out in a sealed NMR tube under vacuum at 90° C. After a given time, the NMR spectra of the reaction mixtures were recorded, and the yield of the 1:1 cocyclodimers was determined from the ratio of $>\text{CH}-\text{COCH}_2\text{Cl}$ to $-\text{CH}=\text{C}-\text{CH}_2\text{Cl}$ in the pyran ring,

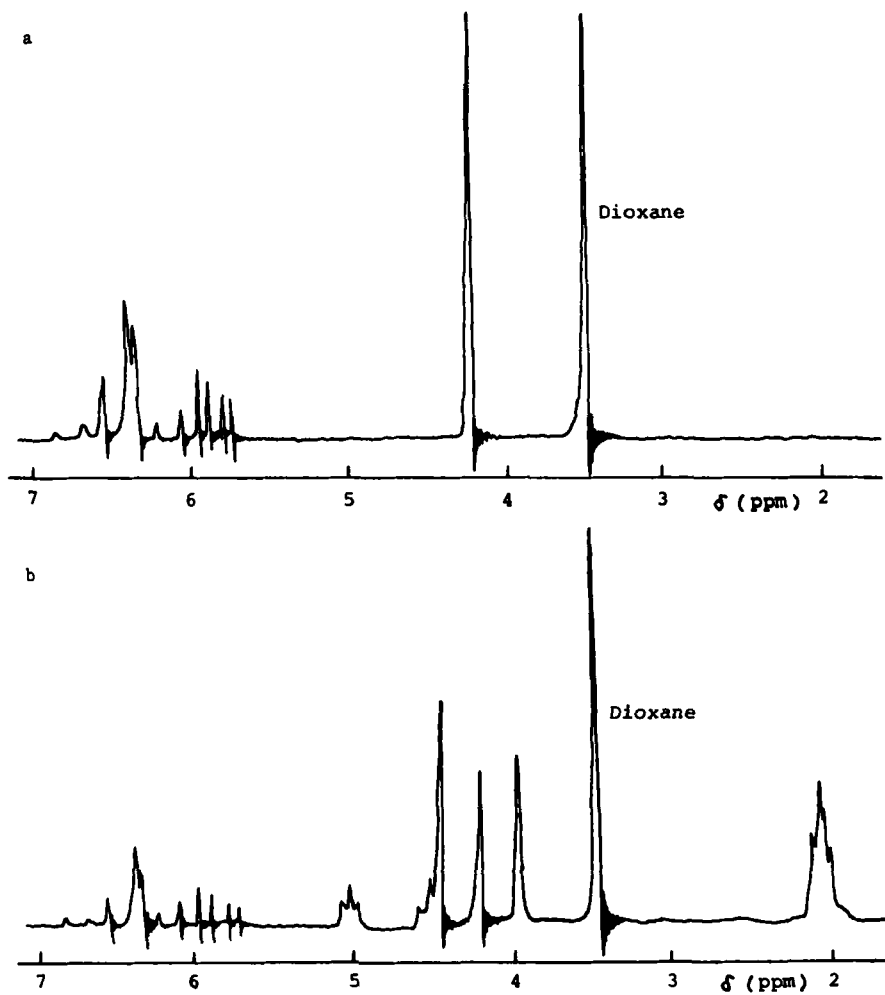


FIG. 1. NMR spectra of the reaction mixture of CMVK (a) before and (b) after heating in dioxane at 90° C for 6 hr.

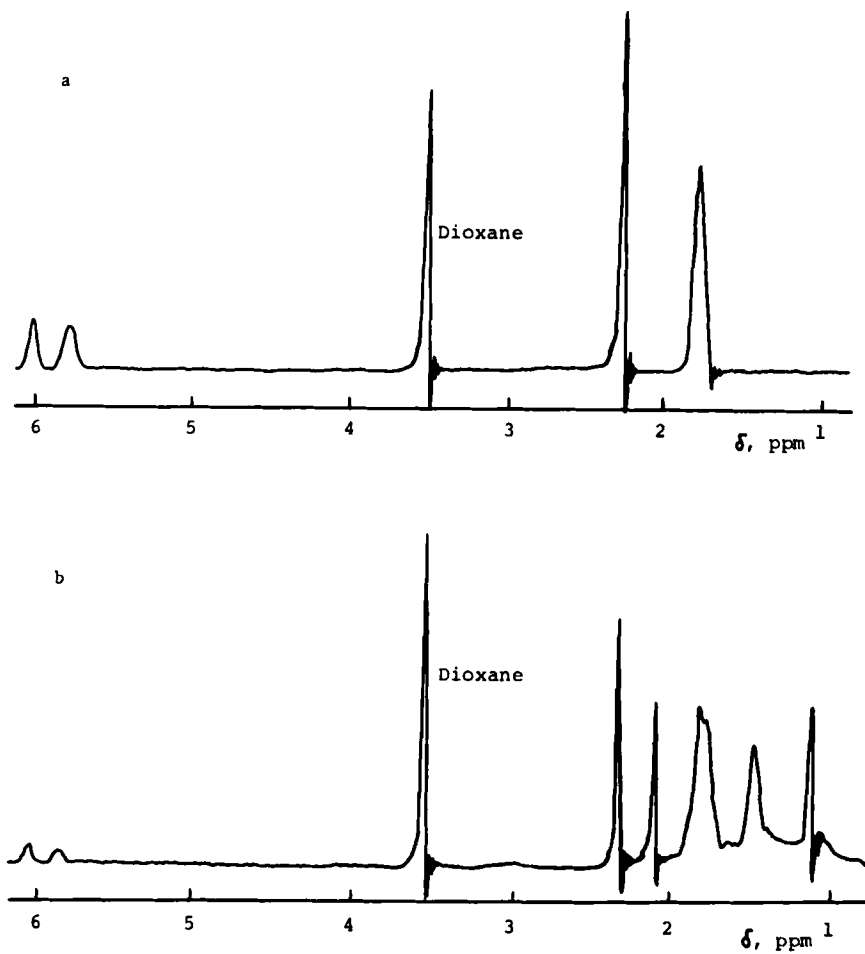


FIG. 2. NMR spectra of the reaction mixture of MIPK (a) before and (b) after heating in dioxane at 90°C for 8 hr.

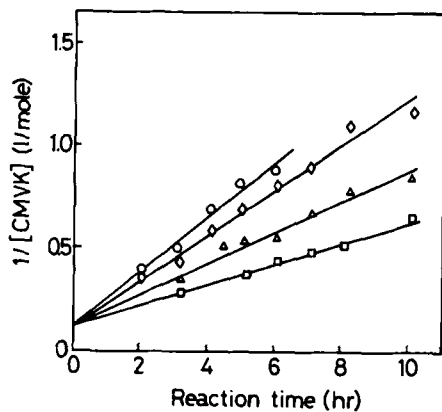


FIG. 3. Second-order plots of $1/[\text{CMVK}]$ with the reaction time for the cyclodimerization of CMVK in dioxane at 60–90°C; (○) 90°C; (◇) 80°C; (△) 70°C; (□) 60°C.

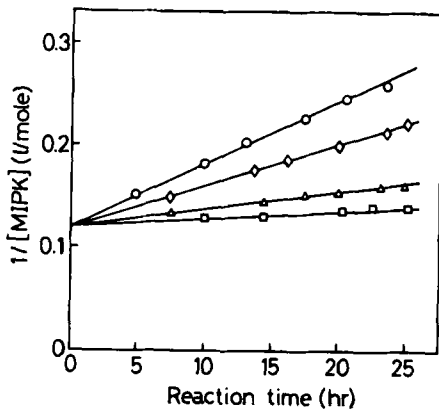


FIG. 4. Second-order plots of $1/[\text{MIPK}]$ with the reaction time for the cyclodimerization of MIPK in dioxane at 60–90°C; (○) 90°C; (◇) 80°C; (△) 70°C; (□) 60°C.

and from the amount of added vinyl monomer consumed. The absence of 3-substituted 2,3-dihydropyran was confirmed from the absence of the peak in the 2.3-3.8 ppm region corresponding to the methylene proton at the 2-position in the pyran ring.

To confirm the structure of the cocyclodimer, the 1:1 cocyclodimer of CMVK and MIPK was isolated, and the structure was confirmed by means of IR, NMR, and mass spectra.

Copolymerizations of CMVK with Vinyl Monomers

The radical copolymerizations were carried out in sealed glass ampoules with α,α' -azobisisobutyronitrile (AIBN) at 60° C. After a given time, the contents of the ampoule were poured into a large amount of methanol to isolate the copolymers. In the case of CMVK-vinyl acetate (VAc) copolymerization, diethyl ether was used as a precipitant. The copolymers obtained were then purified by reprecipitation from the systems dioxane and diethyl ether (for CMVK-VAc), dimethylformamide and diethyl ether (for CMVK-acrylonitrile) and dioxane and methanol (for CMVK-other monomers). The composition of the copolymers was calculated from the carbon contents by elementary analyses. The monomer reactivity ratios were determined by the curve-fitting method.

RESULTS AND DISCUSSION

Cyclodimerizations of CMVK and MIPK

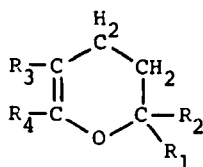
When CMVK was refluxed in toluene (50 vol %) containing 0.5% of hydroquinone for about 3 hr, only a cyclic dimer, 2-chloroacethyl-6-chloromethyl-2,3-dihydropyran (III) was isolated in 86% yield, bp 110-101° C/1.5 Torr, $n_D^{20} = 1.5182$, m/e (M^+) 208 and 210.

Analysis. Found: C, 46.03%, H, 4.80%. Calcd for III: C, 45.95%; H, 4.82%.

In the case of MIPK, a cyclodimer, 2-acetyl-2,5,6-trimethyl-2,3-dihydropyran (IV) was similarly obtained in high yield by refluxing in bulk; bp 60-61° C/6 Torr, $n_D^{20} = 1.4592$, m/e (M^+) 168.

Analysis. Found: C, 71.50%; H, 9.57%. Calcd for IV: C, 71.39%; H, 9.54%.

In this case, to verify the structure of IV, the NMR shift reagent of tris (1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate)



III, IV

III: $R_1 = \text{COCH}_2\text{Cl}$, $R_2 = R_3 = \text{H}$, $R_4 = \text{CH}_2\text{Cl}$

IV: $R_1 = \text{COCH}_3$, $R_2 = R_3 = R_4 = \text{CH}_3$

europium was used in its NMR measurement. In both above reactions, cyclodimers other than III or IV were absent in these reaction mixtures.

Figures 3 and 4 show the plots of the reciprocals of the ketone concentrations with the reaction time in the cyclodimerizations of CMVK and MIPK, respectively, in dioxane containing 0.5% hydroquinone at 60–90°C. From these figures, the reactions were found to proceed by a second-order reaction kinetics.

The values of k_D obtained are shown in Table 1. As is evident, CMVK and MIPK exhibit a much larger k_D value than MVK, i.e., these dimerize about 230 and 13 times, respectively, faster than MVK at 90°C. This result coincides with the fact that the cyclodimerization of MVK is usually carried out at higher temperature than 90°C in an autoclave [13].

From the values of k_D shown in Table 1, the activation enthalpies (ΔH^\ddagger) and entropies (ΔS^\ddagger) for the cyclodimerizations of CMVK and

TABLE 1. Second-Order Rate Constants k_D for Cyclodimerizations of CMVK and MIPK

Ketone	$k_D \times 10^7$ (liter/mole-sec)			
	60°C	70°C	80°C	90°C
CMVK	86.3	120	191	295
MIPK	2.20	4.23	9.72	17.2
MVK	—	—	—	1.3

TABLE 2. Effects of Solvents on Cyclodimerizations of CMVK and MIPK^a

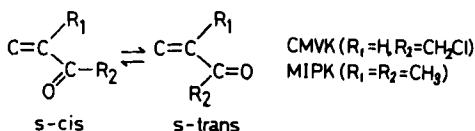
Solvent	$k_D \times 10^6$ (liter/mole-sec)	
	CMVK	MIPK
Dioxane	41.8	2.57
o-Dichlorobenzene	40.4	2.51
Tetrahydrofuran	30.6	3.08
Chloroform	29.8	2.89
Nitrobenzene	21.4	3.20

^aReaction conditions: $[CMVK]_0 = 2.74$ mole/liter, $[MIPK]_0 = 3.37$ mole/liter, at 95°C.

MIPK are obtained as 48.0 and 68.5 kJ/mole, and -209 and -177 J/°K-mole at 90°C, respectively. The ΔH^\ddagger values for both ketones are rather small as compared with a normal multicenter reaction (15-40 kJ/mole [14]), but they are almost same order with those of the Diels-Alder reactions of conjugate dienes with α, β -unsaturated carbonyl compounds (10-20 kJ/mole [14]). This seems to suggest that large negative activation entropies in both reactions show a strong interaction between diene and dienophile, in accord with the hypothesis recently proposed by Alston and Shillady [6], who showed that cyclodimerizations involving three terminal carbon atoms and one terminal oxygen atom proceeded via a "tighter" transition state or a preferential bond formation in the transition state.

Table 2 shows the effect of solvents on the values of k_D at 95°C. The k_D values for both reactions do not change so much with solvent used, judging from the considerations of Alder et al. [15] and Bartlett [16]. Therefore, an unconcerted zwitterion mechanism seems to be unfavorable for these reactions. In this case, the ratio of *s-cis* to *s-trans* conformers does not change markedly with the solvents, from IR spectra of CMVK in dioxane and nitrobenzene; this is similar to the finding, pointed out by Alain [17], for MIPK. Accordingly, it seems that the small effect of solvents on k_D values does not arise from such a conformational contribution.

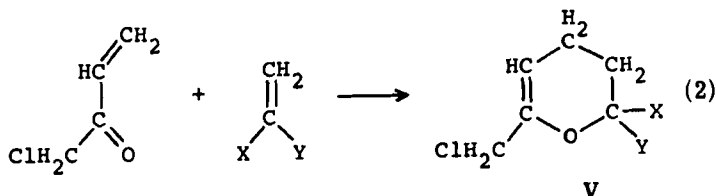
The production of such cyclodimers is also of interest in connection



with elucidating the initiation mechanism of spontaneous thermal polymerizations of vinyl ketones, since these cyclodimers correspond to the Diels-Alder adduct in the molecular assisted homolysis mechanism which is predominantly accepted by many authors in many polymerization systems [18-20]. However, this mechanism seems to be inadequate for the case of vinyl ketones for the following reasons: (1) the addition of their cyclodimers did not accelerate the rates of polymerization of the corresponding vinyl ketones; (2) it was reported [21] that the rate of initiation in the polymerization of vinyl ketone such as MIPK was proportional to the second order of the concentration of MIPK; (3) there is no hydrogen atom in the cyclodimers which can be abstracted easily by the attack of the corresponding vinyl ketones.

Cocyclodimerizations of CMVK with Vinyl Monomers

Table 3 shows the yield of the 1:1 cocyclodimers of CMVK with vinyl monomers [Eq. (2)]. In these reactions, although a considerable



amount of the cyclodimer of CMVK (III) was competitively produced, the 1:1 cocyclodimers were confirmed to consist of only one isomer, i.e., the 2,3-dihydropyran derivative (V).

For example, the cocyclodimerization of CMVK with MIPK (No. 2 in Table 3) gave two cyclodimers, III and V (X = CH₃, Y = COCH₃), the latter in 82% yield. It is noted that there is also a high regioselectivity in these cocyclodimerizations.

TABLE 3. Cocyclodimerizations of CMVK with Vinyl Monomers at 90°C^a

No.	Vinyl monomer	Yield of V (%) ^b	Structure ^c	
			X	Y
1	α -Methylstyrene	90	CH ₃	C ₆ H ₅
2	MIPK	82	CH ₃	COCH ₃
3	Styrene	40	H	C ₆ H ₅
4	Methyl methacrylate	38	CH ₃	COOCH ₃
5	MVK	7	H	COCH ₃
6	Acrolein	<3	H	CHO
7	Methyl acrylate	<3	H	COOCH ₃
8	Acrylonitrile	<3	H	CN
9	Vinyl acetate	<3	H	OCOCH ₃

^aReaction conditions: hydroquinone, 0.5%; [CMVK]/[vinyl acetate] = 1/2 molar ratio.

^bIn all cases, the cyclodimer (III) of CMVK was produced simultaneously.

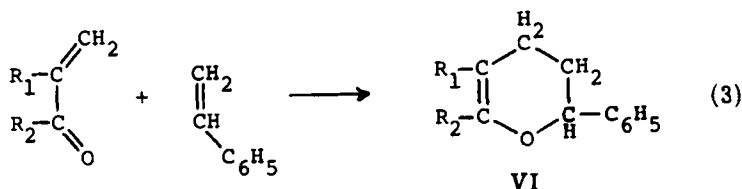
^cX and Y show the substituents in V of Eq. (3).

α -Methylstyrene with a conjugated electron-rich double bond gives the 1:1 cocyclodimer with CMVK in the highest yield (Table 3), while monomers with an unconjugated electron-poor double bond give dimers in low yield. Such an effect of vinyl monomers as dienophiles is well known in the Diels-Alder reactions with acrolein [7] and with butadienes [22], which are inversely related. In Table 3, it is noted that the vinyl monomers with a methyl group in the α -position give the 1:1 cocyclodimers in high yield in all cases. Such effect of the α -methyl group is probably due to an electron-donating [23, 24] or hyperconjugation [25, 26] effect.

In addition, it is also found that CMVK and MIPK are more reactive than MVK as a dienophile (No. 2 and 5 in Table 3). Although their dienophilicities are not correlated with the structure, Alder's rule [27] of maximum accumulation of unsaturated centers (*s-cis* conformer satisfies this rule more than *s-trans* conformer) and the

acceleration effect by the α -methyl group may support the higher reactivities of CMVK and MIPK than MVK as dienophile.

To compare the reactivities of vinyl ketones as dienes, the cocyclo-dimerizations with styrene as a dienophile [Eq. (3)] were attempted;



the results are shown in Table 4. The yield of the 1:1 cocyclodimer (VI) increases in the order: MIPK < MVK < CMVK (Table 4). This order agrees with increasing order of the ratios of *s-cis* to *s-trans* conformers determined by IR spectra, as is shown in Fig. 5. Such a stereochemical requirement is well known in the Diels-Alder reactions of substituted butadienes [28, 29], and it may be also supported by the findings that phenyl vinyl ketone is known to exist predominantly as *s-cis* conformer [30] and to undergo cyclodimerization easily, even at low temperature [31].

TABLE 4. Cocyclodimerizations of Styrene with Vinyl Ketones^a

No.	Vinyl ketone	Yield of VI (%) ^b	Structure of VI	
			R ₁	R ₂
1	CMVK	86	H	CH ₂ Cl
2	MVK	8	H	CH ₃
3	MIPK	<3	CH ₃	CH ₃

^aEvery reaction was carried out for 25 hr at 90° C in the presence of 0.5% hydroquinone.

^bIndicates the yield of VI shown in Eq. (3).

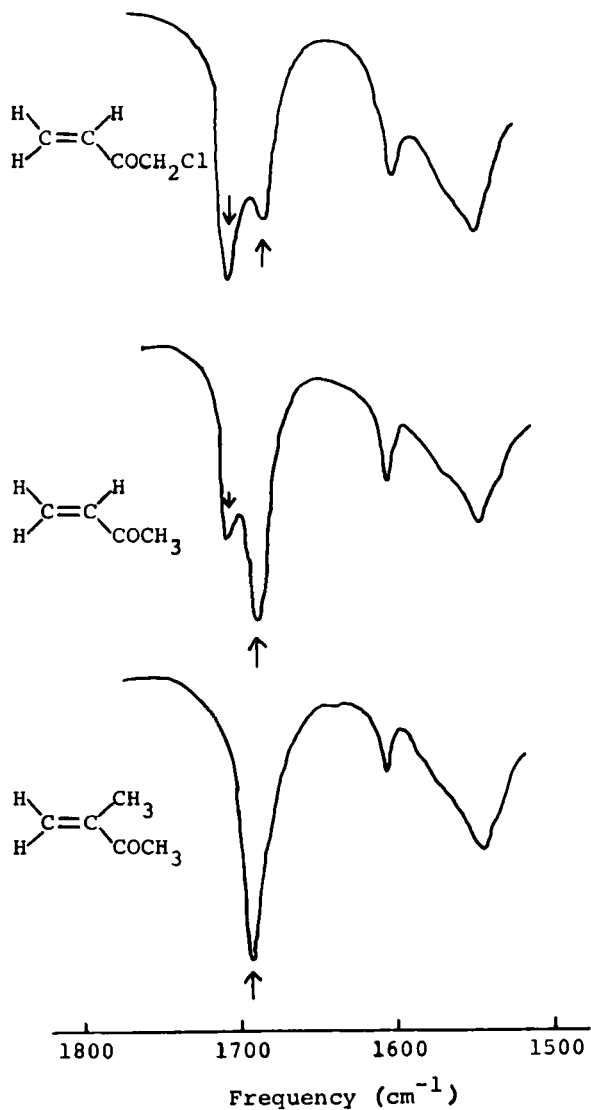


FIG. 5. Infrared spectra of vinyl ketones: (↕) and (↑) indicate the absorption peaks due to the stretching of *s*-trans and *s*-cis C=O groups, respectively. [Ketone] = 1.5 mole/liter in carbon tetrachloride.

TABLE 5. Results of Copolymerizations of CMVK (M_1) with Vinyl Monomers (M_2) at 60' C^a

Comonomer (M_2) ^b	[M_1] in feed (mole %)	Time (min)	Yield (%)	Copolymer	
				Carbon (%)	[M_1] (mole %)
MMA	14.2	35	2.06	54.28	39.6
	27.9	30	2.71	53.04	48.4
	41.1	30	2.59	52.42	52.9
	53.7	25	2.83	51.31	60.7
	65.9	20	1.94	50.57	66.1
	77.7	20	2.14	49.20	76.0
AN	9.35	40	2.81	55.43	39.8
	19.4	40	2.42	53.72	47.9
	30.2	30	1.06	52.19	55.9
	46.9	30	2.11	51.18	61.7
	74.3	25	1.77	48.90	76.4
	89.9	20	1.80	47.05	90.4
VAc	7.57	50	1.45	49.05	63.9
	12.6	50	1.73	46.82	89.2
	17.6	35	1.15	46.68	90.9
	35.2	35	1.80	46.23	96.4
	50.3	30	1.16	46.25	96.1
	65.2	25	1.53	46.02	98.9
VdC	8.84	65	1.92	37.32	57.5
	15.2	55	2.03	39.05	65.9
	29.6	45	1.54	41.58	78.2
	49.1	40	2.06	43.61	88.3
	72.4	40	2.18	44.61	93.3
	85.2	30	2.67	45.44	97.5

TABLE 5 (continued)

Comonomer (M ₂) ^b	[M ₁] in feed (mole %)	Time (min)	Yield (%)	Copolymer	
				Carbon (%)	[M ₁] (mole %)
α-MSt	20.0	65	1.18	70.37	50.5
	32.1	65	1.32	68.38	53.8
	43.3	50	1.50	67.32	56.1
	51.1	50	1.54	66.04	58.9
	61.0	40	1.96	64.21	61.7
	80.9	40	2.03	59.91	71.9

^aPolymerization conditions: [AIBN] = 4×10^{-3} mole/liter, in bulk.

^bMMA, methyl methacrylate; AN, acrylonitrile; VAc, vinyl acetate; VdC, vinylidene chloride; α-MSt, α-methylstyrene.

TABLE 6. Monomer Reactivity Ratios for the Copolymerizations of CMVK (M₁) with Vinyl Monomers (M₂)

Comonomer (M ₂)	Q ₂ ^a	e ₂ ^a	r ₁	r ₂	1/r ₁
α-MSt	0.98	-1.27	0.45	0.02	2.22
MMA	0.74	0.40	0.60	0.10	1.67
AN	0.60	1.2	0.83	0.06	1.20
VdC	0.22	0.36	6.30	0.02	0.16
VAc	0.026	-0.22	50.0	0.01	0.02
St ^b	1.00	-0.80	0.13	0.52	7.69

^aData of Young [32]. These values were calculated from the results of radical copolymerizations of these monomers with styrene.

^bData of the previous paper [9].

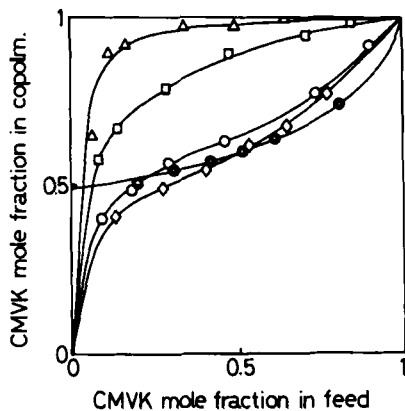


FIG. 6. Copolymer composition curves for the copolymerizations of CMVK (M_1) with various vinyl monomers (M_2) at 60°C : (Δ) vinyl acetate; (\square) vinylidene chloride; (\circ) acrylonitrile; (\diamond) methyl methacrylate; (\bullet) α -methylstyrene. $[\text{AIBN}] = 4 \times 10^{-3}$ mole/liter in bulk.

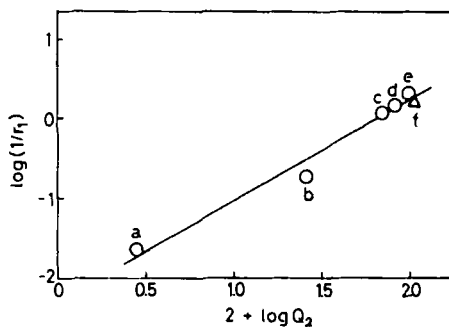


FIG. 7. Relationship between $\log(1/r_1)$ and $\log Q_2$ for the copolymerizations of CMVK (M_1) with vinyl monomers (M_2) at 60°C , $[\text{AIBN}] = 4 \times 10^{-3}$ mole/liter: (\circ) this report; (Δ) obtained in our previous paper [9]. The Q_2 values were given by Young [32]: (a) vinyl acetate; (b) vinylidene chloride; (c) acrylonitrile, (d) methyl methacrylate; (e) α -methylstyrene; (f) styrene.

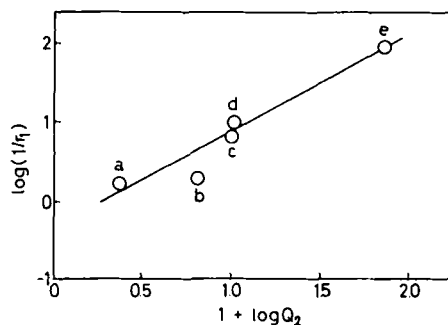


FIG. 8. Plot of $\log(1/r_1)$ against $\log Q_2$ for the copolymerizations of MIPK (M_1) with vinyl monomers (M_2). The r_1 and Q_2 were obtained from the literature: (a) vinylidene chloride [33]; (b) acrylonitrile [32]; (c) α -methylstyrene [32]; (d) styrene [32]; (e) chloroprene [34].

Copolymerizations of CMVK with Vinyl Monomers

Table 5 represents the results of radical copolymerizations of CMVK (M_1) with vinyl monomers (M_2). The copolymer composition curves obtained are shown in Fig. 6, and the monomer reactivity ratios (r_1 and r_2) are listed in Table 6. The logarithms of relative reactivities, $\log(1/r_1)$, of vinyl monomers toward the poly(CMVK) radical were correlated with the Q_2 values of M_2 monomers used rather than e_2 values, as shown in Fig. 7. Similar relationships were also observed for the reactivities of vinyl monomers toward the polymer radicals of MIPK [32-34] and MVK [9, 32, 35-37] which were calculated from the monomer reactivity ratios reported for their radical copolymerizations. These plots are also shown in Figs. 8 and 9.

From Figs. 7-9, the slopes of the resulting straight lines are 1.6, 1.2, and 0.7 for the attack of polymer radicals of CMVK, MIPK, and MVK, respectively. The order in these values for CMVK, MIPK and MVK radicals is in agreement with that of k_D values for cyclodimerizations (Table 1), and also of Q_1 values (2.07 for CMVK [9], 1.49 for MIPK [32-34], and 1.12 for MVK [9] of the respective ketone monomers. These observations seem to suggest that the more stable vinyl ketone radical is easily dimerized.

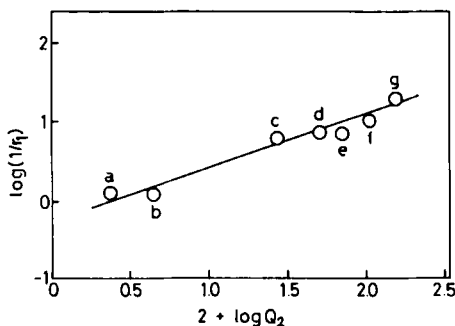


FIG. 9. Plot of $\log(1/r_1)$ against $\log Q_2$ for the copolymerizations of MVK (M_1) with vinyl monomers (M_2). The r_1 and Q_2 were obtained from the literature: (a) vinyl acetate [36]; (b) vinyl chloride [35]; (c) vinylidene chloride [35]; (d) butyl acrylate [32]; (e) acrylonitrile [37]; (f) styrene [9]; (g) 2,5-dichlorostyrene [35].

The results shown above suggest that the cyclodimerizations of vinyl ketones seem to proceed via a concerted two-stage or an unconcerted biradical mechanism. Although it is difficult to distinguish clearly whether either mechanism is valid, on the basis of the observed low activation enthalpies and large negative activation entropies and the pronounced effect of the α -methyl group of vinyl ketones on their cyclodimerizations, the former mechanism seems to be more probable than the latter.

Consequently, we conclude that cyclodimerizations proceed via a concerted mechanism including a biradical intermediate and asymmetric bond closure.

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Accepted by editor July 14, 1976

Received for publication July 22, 1976