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The Polymerizations of 2-Vinyl-4-acryloxy-1,3-dioxolane and 2-Vinyl-4-methacryloxy-1,3-dioxolane

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The polymerizations of 2-vinyl-4-acryloxy-1,3-dioxolane(VADO) and 2-vinyl-4-methacryloxy-1,3-dioxolane (VMDO), and the copolymerizations of those divinyl cyclic acetals with styrene (St) and acrylonitrile(AN), have been carried out at 60°C, using 2,2′-azobisisobutyronitrile as the initiator. They were discussed kinetically. The following results were obtained: 1) The polymerizations of the above cyclic acetals containing allylidene and vinyl groups proceeded primarily on the acryl or methacryl group, and the allylidene group was extinguished a little by means of cyclization; the ratios of the rate constant of the unimolecular cyclization reaction to that of the bimolecular propagation reaction of the uncyclized radical were 0.065 mol/*l* (VADO) and 0.114 mol/*l*(VMDO). 2) The following monomer reactivity ratios were obtained at 60°C: VADO(M_1)-St(M_2) $r_1=0.22$, $r_2=0.81$; VADO(M_1)-AN(M_2) $r_1=0.89$, $r_2=0.95$; VMDO(M_1)-St(M_2) $r_1=0.51$, $r_2=0.49$. The Q and e values of the two monomers were calculated from these values: VADO, $Q=0.41$, and $e=0.65$; VMDO, $Q=0.81$ and $e=0.38$.

In previous papers, the polymerizations of cyclic acetal compounds containing two equivalent functional groups were kinetically investigated, but the difference in reactivity between allylidene and vinyl groups has not been discussed in detail.[1-4)]

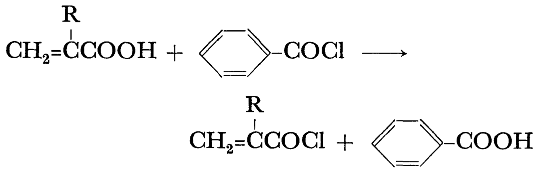
In the present experiment, the polymerization of 2-vinyl-4-acryloxy-1,3-dioxolane (VADO) was carried out; by employing the kinetic equation derived in a previous paper,[2)] we will kinetically discuss our results in view of the difference in reactivity between the allylidene and acryl groups.

The polymerization of 2-vinyl-4-methacryloxy-1,3-dioxolane (VMDO) was further carried out; we will investigate the influence of the α-methyl group on the vinyl group.

The copolymerizations of the above divinyl cyclic acetals with styrene (St) or acrylonitrile (AN) were also carried out, and the reactivity ratios were estimated.

Experimental

Materials. The oxochlorides were prepared by the reactions of acrylic and methacrylic acids with benzoyl chloride in the presence of anthraquinone, according to the procedure of Stempel *et al*:[5)]

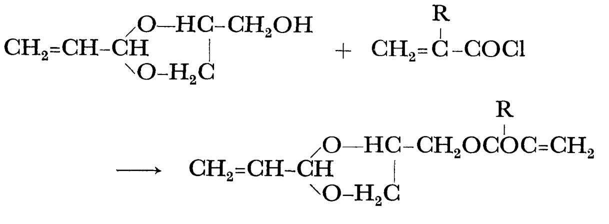


R=H, CH_3

The oxochlorides (1 mol) were slowly dropped into a mixture of 1 mol of 2-vinyl-4-hydroxymethyl-1,3-dioxolane (VHDOL), 1 mol of trimethylamine as a catalyst, 0.1 wt% anthraquinone as an inhibitor, and benzene (1500 m*l*) as a solvent at 0—3°C over a 5-hr period; the mixtures were then washed with water to remove any unreacted VHDOL, oxochlorides, and the $((C_2H_5)_3N\cdot HCl)$ salt.

The products remaining in the benzene layer were separated, dried over calcium carbonate, and then distilled *in vacuo*; VADO bp 87—89°C/2mmHg, VMDO bp 95—98°C/3mmHg. The yields were 20—25%.

The final products were confirmed to be the new monomers of VADO and VMDO by a determination of the infrared spectrum, the molecular weight (MW), the saponification value (SV), and the bromine value (BV).



R=H, CH_3

VADO Found: C, 57.89; H, 6.31%; MW, 184.6; BV, 172.2; SV, 302.5. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57%; MW, 184.2; BV, 173.5; SV, 304.6.

VMDO Found: C, 60.67; H, 7.21%; MW, 200.1; BV, 159.8; SV, 281.8. Calcd for $C_{10}H_{14}O_4$: C, 60.60; H, 7.12%; MW, 198.2; BV, 161.2; SV, 283.1.

The St, AN, 2,2′-azobisisobutyronitrile (AIBN), benzene, and dimethylformamide (DMF) used as the solvents were purified by conventional methods.

Polymerization Procedure. A glass ampoule was charged with the prescribed amount of each monomer, a solvent, and AIBN; it was then degassed, sealed off under a vacuum, and set in a thermostatted water bath at 60±0.1°C. The reaction solution was poured into a large amount of methanol, and the polymer thus separated was filtered and then dried *in vacuo* until it reached a constant weight. The conversion was less than 10%. The homopolymers of these divinyl acetals were purified from benzene-methanol.

The copolymers obtained on VADO or VMDO-St and VADO-AN systems were also reprecipitated from benzene-methanol and DMF-methanol respectively.

Analyses of the Polymer and Copolymer. The overall residual double bonds of the polymer and the copolymer

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1) T. Ouchi and M. Oiwa, *Kogyo Kagaku Zasshi*, **72**, 746 (1969).

2) T. Ouchi, Y. Imase, and M. Oiwa, This Bulletin, **43**, 2863 (1970).

3) Y. Minoura and M. Mitoh, *J. Polym. Sci., Part A-1*, **3**, 2149 (1965).

4) S. G. Matsoyan, *ibid.*, **52**, 189 (1961).

5) G. H. Stempel, R. P. Cross, and R. P. Mariella, *J. Amer. Chem. Soc.*, **72**, 2299 (1950).

(allylidene+acryl) were calculated by means of the bromine values measured by the method of Siggia (BV_{a+v});⁶⁾ the residual allylidenic double bonds were then calculated by means of those determined according to the usual bromite-bromate method (BV_a).⁷⁾

The composition of the copolymer was determined by C, H, and N elementary analyses.

The infrared spectra were measured on a Shimadzu infrared spectrophotomerte, Model IR-27.

The infrared spectra of the resulting monomer and polymer are shown in Fig. 1. The absorption peaks at 1598, 1740, and 1200—1040 cm^{-1} may be assigned to C=C, >C=O, and cyclic acetal respectively.

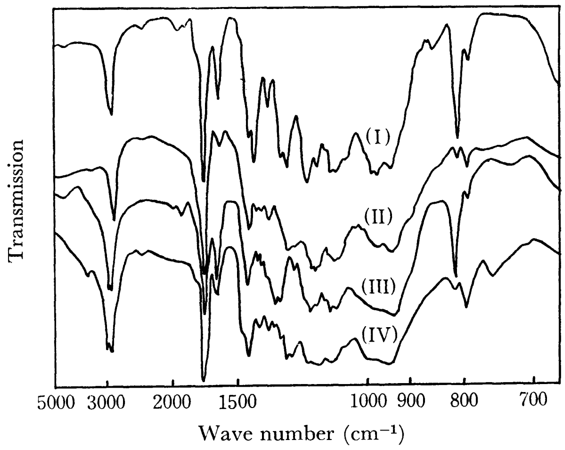

Fig. 1. Infrared spectra of VADO, VMDO monomer and polymer.
(I) VADO monomer, (II): VADO polymer, (III): VMDO monomer, (IV): VMDO polymer

Results and Discussion

Homopolymerization. The VADO and VMDO polymerizations were carried out under different initiator and monomer concentrations at 60°C. The results are given in Tables 1 and 2, in which the values of BV_{a+v} and BV_a are estimated by extrapolating to zero at yield.

TABLE 1. POLYMERIZATION OF VADO AT 60°C

(I) (×10^{-3} mol/l)	(M) (mol/l)	R_p (×10^{-4} mol/l·sec)	$BV^{a)}_{a+v}$	$BV^{a)}_{a}$	$2R^{b)}_{us}$
0.61	2.01	0.633	84.07	84.06	0.969
1.22	2.01	2.60	84.11	84.07	0.970
1.83	2.01	3.48	84.06	84.05	0.969
2.44	2.01	4.02	84.09	84.09	0.969
3.66	2.01	4.92	84.05	84.02	0.969
1.83	1.15	1.93	82.15	82.13	0.947
1.83	1.34	2.26	82.76	82.72	0.954
1.83	1.61	2.74	83.45	83.44	0.962
1.83	2.68	4.69	84.75	84.71	0.977

TABLE 2. POLYMERIZATION OF VMDO AT 60°C

(I) (×10^{-3} mol/l)	(M) (mol/l)	R_p (×10^{-4} mol/l·sec)	$BV^{a)}_{a+v}$	$BV^{a)}_{a}$	$2R^{b)}_{us}$
1.22	2.01	2.54	76.47	76.45	0.948
1.83	2.01	3.40	76.42	76.40	0.947
2.44	2.01	3.92	76.45	76.41	0.947
3.66	2.01	4.81	76.43	76.42	0.947
4.88	2.01	5.55	76.48	76.41	0.948
1.83	1.15	1.87	73.36	73.35	0.909
1.83	1.34	2.21	74.57	74.55	0.924
1.83	1.61	2.68	75.45	75.43	0.935
1.83	2.68	4.65	77.39	77.33	0.959

a) The values were obtained by extrapolating to zero for the conversion.
b) $2R_{us}=BV_{a+v}/BV_{id}$.

As can be seen from Tables 1 and 2, the residual unsaturation of the polymer, $2R_{us}$, is not equal to 1.00, and it does not depend on the initiator concentration, but decreases with a decrease in the monomer concentration. Accordingly, the polymerizations of these monomers may proceed by a mechanism of cyclopolymerization such as that of DβMPP.²⁾ Since the value of BV_a is nearly equal to that of BV_{a+v}, it may be considered that the pendant double bonds in the polymer almost corresponded to the allylidene groups; since the reactivity of acryl is larger than that of allylidene, it can be pointed out that the usual propagation is assumed to be related to the acryl and that the cyclization is related to the acryl and the allylidene.

The results of these homopolymerizations were then analyzed by the kinetic equations according to the following reaction scheme:

$$\left.\begin{array}{lll} & & \text{Rate const.} \\ \text{Decomposition of initiator} & I \rightarrow 2R\cdot & k_d \\ \text{Initiation} & R\cdot + M \rightarrow M\cdot & k_i \\ \text{Cyclization} & M\cdot \rightarrow M_c\cdot & k_c \\ \text{Propagation} & M\cdot + M \rightarrow M\cdot & k_p \\ & M_c\cdot + M \rightarrow M\cdot & k_{cp} \\ & M_c\cdot + M_c\cdot \rightarrow P_c & \alpha^2 k_t \\ \text{Termination} & M_c\cdot + M\cdot \rightarrow P_c' & \alpha\beta k_t \\ & M\cdot + M\cdot \rightarrow P & \beta^2 k_t \end{array}\right\} \quad (1)$$

If a steady-state condition is assumed, Eqs. (2)—(6) can be obtained.

When the monomer concentration is kept constant, the relation of the rate of polymerization, R_p, to the initiator concentration, (1), can be written by Eq. (2):

$$R_p/(\mathrm{I})^{1/2} = A(\mathrm{I})^{1/2} + B \tag{2}$$

where:

$$\left.\begin{aligned} A &= (k_{cp}/k_c)(2fk_d)(k_p/k_{cp}-\beta/\alpha)(\mathrm{M}) = \text{const.} \\ B &= (k_{cp}/\alpha)(2fk_d/k_t)^{1/2}(\mathrm{M})\{(k_p/k_{cp}-\beta/\alpha) \\ &\quad \times (k_{cp}/k_c)(\mathrm{M})+1\} = \text{const.} \end{aligned}\right\} \quad (3)$$

Similarly, when the initiator concentration is kept constant, the relation between R_p and the monomer concentration, (M), can be written by Eq. (4):

$$R_p/(\mathrm{M}) = C(\mathrm{M}) + D \tag{4}$$

where:

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6) S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," 3rd ed., J. Wiley & Sons, New York and London (1963), p. 301.

7) I. P. Losev and O. Y. Fedotoba, "Praktikum po Khimii Vysokopolimernykh Soedinenii," Gosudarstvennoe Nauchno-Tekhnicheskoe Izdatelstvo Khimicheskoi Literatury, Moskova.

$$\left.\begin{aligned} C &= (k_{cp}/\alpha)(2fk_d/k_t)^{1/2}(k_p/k_{cp}-\beta/\alpha) \\ &\quad \times (k_{cp}/k_c)(\mathrm{I})^{1/2} = \text{const.} \\ D &= (k_{cp}/k_c)(2fk_d)(k_p/k_{cp}-\beta/\alpha)(\mathrm{I}) \\ &\quad + (k_{cp}/\alpha)(2fk_d/k_t)^{1/2}(\mathrm{I})^{1/2} = \text{const.} \end{aligned}\right\} \quad (5)$$

On the other hand, the residual unsaturation of the polymer, $2R_{\mathrm{us}}$, is given by:

$$(1-2R_{\mathrm{us}})^{-1} - (1+E(\mathrm{I})^{1/2}/(\mathrm{M}))^{-1} = \frac{k_p}{k_c}(\mathrm{M}) \quad (6)$$

where:

$$E = \alpha(2fk_dk_t)^{1/2}/k_{cp}$$

Influence of the Initiator and Monomer Concentrations on the Rate of Polymerization. When the monomer concentration is varied, it may be kinetically expected from Eq. (2) that the plots of $R_p/(\mathrm{I})^{1/2}$ *vs.* $(\mathrm{I})^{1/2}$ will have straight lines. Similarly, if the initiator concentration is kept constant and the monomer concentration is varied, a linear relationship between $R_p/(\mathrm{M})$ and (M) may be expected on the basis of Eq. (4). The results are plotted in Fig. 2, in which the fit of the experimental data to the linear relationship is fairly good. From the slopes and intercepts of the straight lines shown in Fig. 2, the A, B, C, and D of VADO were estimated to be 5.97×10^{-6}, 8.13×10^{-3}, 4.90×10^{-6}, and 1.62×10^{-4} respectively; the corresponding values of VMDO were found to be 3.05×10^{-6}, 7.94×10^{-3}, 6.94×10^{-6}, and 1.55×10^{-4} respectively. Accordingly, the ratios of the rate constant, as calculated from the above values, are shown in Table 3.

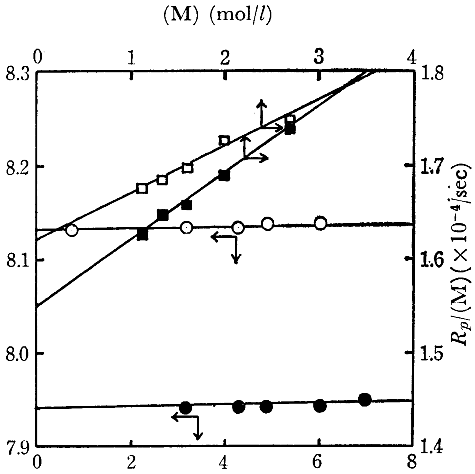

Fig. 2. Plots of $R_p/(\mathrm{I})^{1/2}$ *vs.* $(\mathrm{I})^{1/2}$ and R_p (M) *vs.* (M).
○, □: VADO; ●, ■, VMDO

Table 3. The parameters of polymerization

Monomer	$2fk_d$ ($\times10^{-5}$ sec^{-1})	$k_{cp}/k_t^{1/2}$ ($\times10^{-1}$ mol$^{1/2}/l^{1/2}\cdot$sec$^{1/2}$)	$(k_p/k_{cp}-\beta/\alpha)$ (k_{cp}/k_c) ($\times10^{-2}l$/mol)	E ($\times10^{-2}l^{1/2}$/mol$^{1/2}$)
VADO	9.34	3.92	3.18	2.47
VMDO	3.39	6.22	4.48	9.36×10^{-1}
DβMPP	6.95	0.57×10^{-1}	2.26	1.46×10^{2}

Here, the $2fk_d$ value of the order of 10^{-5} seems to be pertinent when AIBN is used as an initiator.

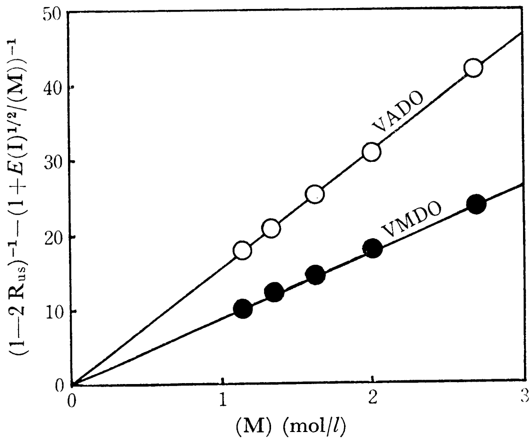

Fig. 3. Plots of $\{(1-2\mathrm{R_{us}})^{-1}-(1+E(\mathrm{I})^{1/2}/(\mathrm{M}))^{-1}\}$ *vs.* (M).

On the other hand, the $k_{cp}/\alpha k_t^{1/2}$ values of VADO and VMDO were larger than that of DβMPP; the termination between the two $\mathrm{M}_c\cdot$ values in the polymerizations of VADO and VMDO might be slower than that of the DβMPP polymerization.

The Residual Unsaturation. The plots of $\{(1-2\mathrm{R_{us}})^{-1}-(1+E(\mathrm{I})^{1/2}/(\mathrm{M}))^{-1}\}$ *vs.* (M) are shown in Fig. 3; there is a good linear relationship, as was predicted by Eq. (6). The ratios of the rate constant of the unimolecular cyclization reaction to that of the bimolecular propagation of the uncyclized radical, k_c/k_p, were estimated to be 0.065 mol/l(VADO), and 0.114 mol/l(VMDO) from the slopes of the straight lines. The results show that the pendant double bonds in polymers are almost not cyclized at all because the acryl double bond is more active than the allylidene double bond. The difference between VADO and VMDO could not be seen in these polymerizations; the influence of methyl groups could not be observed, either.

Therefore, although VADO and VMDO both undergo cyclopolymerization, they act as monofunctional monomers rather than as bifunctional monomers.

Copolymerization. The composition and the unsaturation of polymer as functions of the monomer

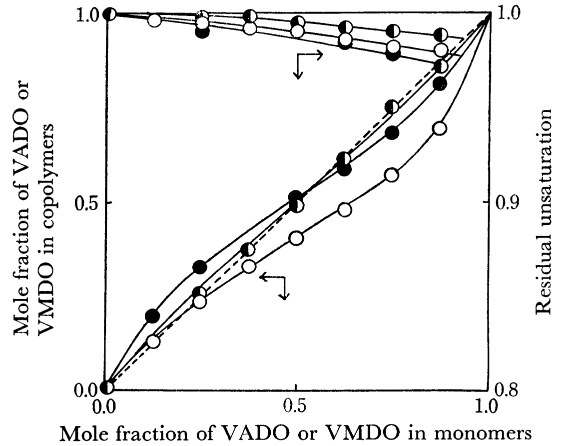

Fig. 4. Relation of the copolymer composition and the residual unsaturation to the monomer composition.
○: [VADO+St]=3.49 mol/l, ◑: [VADO+AN]=6.10 mol/l, ●: [VMDO+St]=3.49 mol/l, —: calculated curve

composition are shown in Fig. 4. It may be seen in the figure that the residual unsaturations of the copolymer thus obtained decreased slightly with an increase in the comonomer composition until they became nearly constant at 1.0. Accordingly, the cyclization may be approximately negligible, the ratio being obtainable by the well-known Fineman-Ross method; the results are summarized in Table 4.

Table 4. Reactivity ratios for VADO or VMDO (M_1)-monovinyl compounds(M_2) systems

M_1	M_2	r_1	r_2	Q_1[10]	e_1[10]	Q_2	e_2
VADO	St	0.22	0.81	1.00	−0.80	0.43	0.51
VADO	AN	0.89	0.95	0.60	1.20	0.39	0.79
VMDO	St	0.51	0.49	1.00	−0.80	0.80	0.30

In Fig. 4 the theoretical solid curves as calculated from the resulting reactivity ratios agreed well with the results of the experimental measurements.

The average values of Q and e for VADO, VMDO were estimated as follows: VADO, $Q=0.41$, and $e=0.65$; $Q=0.80$, and $e=0.30$.

These values are not equal to Q, e values of diallylidene cyclic acetals[8–9] but those of DβMPP,[2] methyl acrylate[10] and methyl methacrylate.[10] Consequently, VADO and VMDO may be suggested to be polymerized as same as monoacryl and methacryl esters.

The Q value for VMDO was larger than that for VADO; it might be influenced by the hyperconjugation of methyl group.

On the other hand, the e value of VMDO was more negative than that of VADO; it might be contributed to the methyl group which was a proton donor.

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[8] T. Ouchi, S. Yamamoto, Y. Akao, Y. Nagaoka, and M. Oiwa, *Kogyo Kagaku Zasshi*, **71**, 1078 (1968).

[9] T. Ouchi, S. Tatasuno, T. Nakayama, and M. Oiwa, *ibid.*, **73**, 607 (1970).

[10] J. Brandrup and E. H. Immergut, "Polymer Handbook," J. Wiley & Sons, New York (1966).