CYCLOPOLYMERIZATION OF BIFUNCTIONAL MONOMERS

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ABSTRACT

Cyclopolymerization of some divinyl compounds and dialdehydes is discussed. First, the polymerization results with *o*-divinylbenzene are reviewed, together with the introductory discussion on some problems of cyclopolymerization of divinyl compounds in general. In all of the radical, cationic and anionic polymerizations of *o*-divinylbenzene, the intramolecular cyclization reaction possesses higher activation energies than the intermolecular propagation, where both reactions are competitive. Catalyst and solvent effects are demonstrated for the cyclization process in the ionic polymerization, loose propagating ion pairs apparently increasing the extent of cyclization. And propagation mechanisms are suggested which take into consideration the catalyst effect and the solvent effect.

In the following sections, it is shown that some dialdehydes, which are expected to form five or six membered ring by cyclization, polymerize readily to give highly cyclized polymers. The cationic polymerization of *o*-phthalaldehyde is shown to involve a "living" growing cation, and the steric structure of poly(*o*-phthalaldehyde) varies with the polymerization conditions. The capacity to cyclize, i.e. to form five or six-membered rings, is considered to be an important driving force for the polymerization of aromatic dialdehydes, e.g. *o*-phthalaldehyde and *o*-formylphenylacetaldehyde, in contrast to the non-polymerizability of benzaldehyde.

Generally speaking the structural characteristics, when the two functional groups are present at the vicinal position (*ortho* position) of the six-membered ring, provide great steric advantages for cyclopolymerization with all the monomers studied. However, propagation schemes are quite different among these monomers. Stepwise propagation is proposed for the cationic polymerization of *o*-divinylbenzene, and an intermediate or concerted scheme for those of dialdehydes and 1,2-divinylcyclohexane. Moreover, it is concluded that both of these reaction schemes probably coexist in the cationic polymerization of *o*-divinylbenzaldehyde, depending on the kind of cation produced.
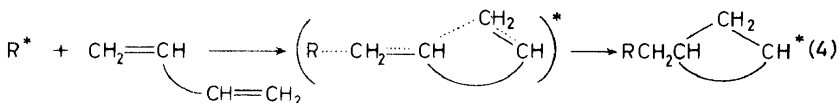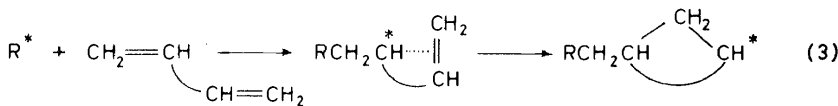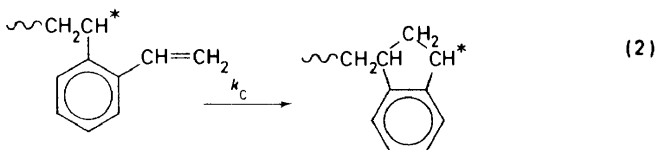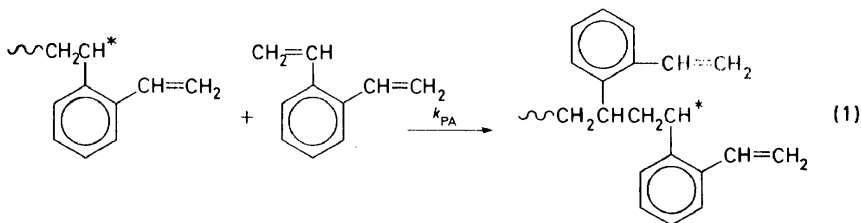
INTRODUCTION

Since Butler and Angelo reported cyclopolymerization of diallylammonium salt in 1957[1], a large number of investigations have been made on cyclopolymerization. The concept of cyclopolymerization, not being limited to polymerizations of divinyl compounds, was extended to polymerizations of other bifunctional monomers, such as dialdehydes, dinitriles, diisocyanates

and diepoxides. The first example among these monomers was cyclopolymerization of glutaraldehyde in 1962[2-5]. It is the purpose of this paper to discuss some factors which affect cyclization in the cyclopolymerization of o-divinylbenzene together with some problems of cyclopolymerization of divinyl compounds in general. The cyclopolymerization of bifunctional monomers with two heteroatom–carbon multiple bonds is also discussed with particular emphasis on dialdehydes.

SOME ASPECTS OF CYCLOPOLYMERIZATION OF DIVINYL COMPOUNDS

Three topics were selected concerning the cyclopolymerization of divinyl monomers. The first is concerned with the scheme of cyclization in the cyclopolymerization. When the extent of cyclization increases with dilution of the polymerization system, the cyclization of and the monomer addition to an uncyclized active species are thought to be competitive. The polymerization scheme for o-divinylbenzene belongs to this case, as shown in equations 1 and 2. Other cyclization schemes are the intermediate and concerted types, which are shown as equations 3 and 4, respectively.

(1)

(2)

$$R^* + CH_2\!\!=\!\!CH\big(CH\!\!=\!\!CH_2\big) \longrightarrow RCH_2\overset{*}{CH}\!\!\cdots\!\!\underset{CH}{\overset{CH_2}{\big\|}} \longrightarrow RCH_2CH\big\langle\overset{CH_2}{\underset{}{}}\big\rangle\overset{*}{CH} \qquad (3)$$

$$R^* + CH_2\!\!=\!\!CH\big(CH\!\!=\!\!CH_2\big) \longrightarrow \Big(R\!\cdots\!CH_2\!\cdots\!CH\big\langle\overset{CH_2}{}\big\rangle CH\Big)^* \longrightarrow RCH_2CH\big\langle\overset{CH_2}{}\big\rangle\overset{*}{CH} \quad (4)$$

It is not easy to prove the occurrences of these latter processes. However, when the extent of cyclization is quite high or when the reactivity of divinyl compounds is much higher than that of the corresponding monovinyl monomer, these processes are conceivable. In cases where some kinds of interaction take place between two double bonds, as for example, the elec-

tronic interaction as reported by Butler[6], the latter processes may be expected in the propagation process.

The second aspect is the steric factors. This seems to be one of the most important factors to enhance intramolecular cyclization. For example, cis-1,2-divinylcyclohexane gave rise to completely cyclized polymers. The complete cyclization was ascribed to the fixation of the two vinyl groups at the vicinal position[7]. In some cases, the presence of a bulky group in the penultimate position may facilitate the cyclization in the terminal unit.

The third topic is the structure of cyclopolymers. The cyclization does not necessarily involve the head-to-tail addition of the two vinyl groups. For example, it was reported that the poly(divinylformal) contained 20–30 per cent of the 5-membered ring and 65–75 per cent of the 6-memberd ring
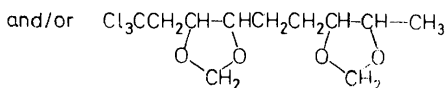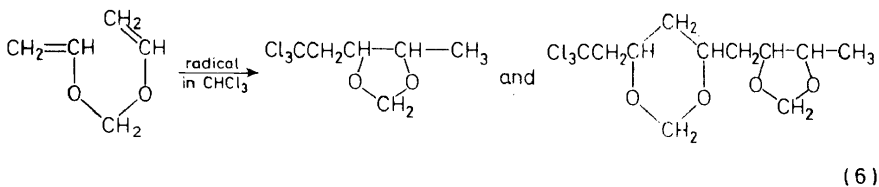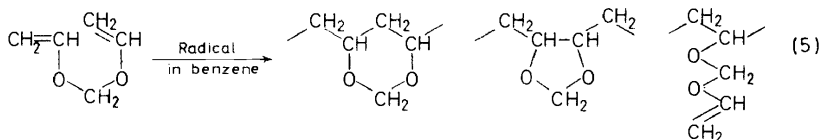
(equation 5)[8,9]. In order to obtain information on the structure of the cyclo-polymer, we carried out telomerization of divinylformal in chloroform and obtained monomeric and dimeric telomers. Both telomers possessed the 5-membered ring due to the head-to-head addition in the cyclization[10], as shown in equation 6. Thus, the correspondence between the cyclization reactions in telomerization and in polymerization may not necessarily be satisfactory.

SOME FACTORS AFFECTING CYCLIZATION IN THE POLYMERIZATION OF o-DIVINYLBENZENE

Among the three aspects mentioned above, I will discuss more fully the competition between cyclization and propagation in the case of o-divinyl-benzene. The propagation process for this monomer consists of competitive reactions—equations 1 and 2. Here, r_c is defined as the ratio of the rate constant of unimolecular cyclization k_c to that of the bimolecular propagation $k_{p,A}$. This ratio can be generally used as a measure for the cyclization capacity, as already used by Holt and Simpson in the case of polymerization of diallyl-esters[11].

Assuming the steady-state concentration for the growing end, equation 7 was obtained[12]. It can be also derived from a statistical steady-state assumption[13].

$$\frac{-\mathrm{d}(m)}{\mathrm{d}(M)} = \frac{2(M)}{2(M) + r_c} \tag{7}$$

$$r_c = k_c/k_{pA}$$

$(m) = $ Concentration of pendant double bond (mole/l)

$(M) = $ Concentration of unreacted monomer (mole/l)

If the conversion is low, r_c is calculated by equation 7 using the initial monomer concentration $(M)_o$ for (M) and the percentage of the pendant double bond in polymer for $-\mathrm{d}(m)/\mathrm{d}(M) \times 100$, respectively. At high conversions, the integration of equation 7 is necessary. Using the integrated equation (equation 8), r_c was calculated by trial-and-error or with the help of a computer[12–16]

$$\frac{(m)}{(M)_o X} = 1 - \frac{r_c}{2(M)_o x} \ln\left[\frac{2(M)_o + r_c}{2(M)_o(1 - x) + r_c}\right] \tag{8}$$

x: Conversion

$(M)_o$: Initial concentration of monomer.

The polymerization of o-divinylbenzene was carried out with radical, cationic and anionic catalysts and the r_c values obtained were compared[12–16]
Some examples of the polymerization results are shown in *Table 1*. The

Table 1. Several examples of polymerization of o-divinylbenzene with different catalysts

Catalyst m.mole/l		Monomer $(M)_0$ mole/l	Solvent	Temp. °C	Time h	Conversion[a] %	PDB[b] %	r_c mole/l	Reference
AIBN	10	2·62	Benzene	70	1·8	I: 12·1 S: 5·0	60	3·14	12
AlCl₃	50	2·57	Toluene	0	5·0	I: 13·5 S: 12·6	48	4·8	13
SnCl₄	50	2·64	Toluene	0	12	63	65	1·9	13
$(C_6H_5)_3CBF_4$	10·5	0·72	Methylene-chloride	0	1·2	57	68	0·47	16
$(C_6H_5)_3CBF_4$[c]	9·3	0·72	Methylene-chloride	0	1·3	9	80	0·36	16
Na-Naph[d]	40	0·75	THF	−40	1·0 min.	96	78	0·16	15

[a] I: Insoluble fraction, S: Soluble fraction.
[b] PDB: Pendent double bond.
[c] Et₄NBF₄ was added as additive (additive catalyst = 2·8).
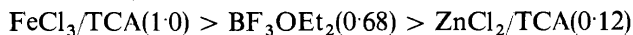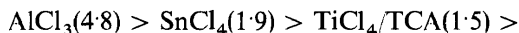[d] Sodium naphthalene.

content of the pendant double bond in polymers decreased with increase in conversion, as expected. It also depended on the polymerization conditions. The extent of cyclization is low in the anionic polymerization and rather high in the cationic polymerization. The variation of the cyclization constant r_c with polymerization conditions can be used as a measure for polymerization mechanisms.

In the anionic polymerization, r_c values, as shown in *Table 1*, are smaller than those in the radical polymerization When anionic polymerizations with alkali-metal naphthalenes were carried out in several solvents at 20°, the value of r_c(mole/l) obtained varied depending on the counter cation and solvent used as follows:

(a) $Li^+(0.8) > Na^+(0.56) > K^+(0.54)$ in THF

(b) $Li^+(0.27) < Na^+(0.41) < K^+(0.70)$ in Dioxane.
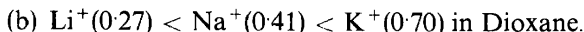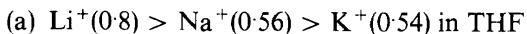
Values for r_c decreased with increase in the ionic radius of the counter cation in THF, but this tendency was reversed in dioxane[15]. Szwarc and co-workers[17] suggested that the reactivity of the growing ion pair of the styryl anion was determined in THF by the solvation of the counter cation and the most strongly solvated Li^+ gave the most reactive ion pair. In dioxane the coulombic interaction of the ion pair was considered to determine its reactivity and Li^+ gave the least reactive ion pair. An analogous explanation may apply for the r_c variation on the basis of the assumption that r_c increases with the reactivity of the ion pair. Therefore, Li^+ gave the largest r_c value in THF, and the smallest value in dioxane. Some decrease of r_c values on addition of sodium-tetraphenyl-borate ($NaBPh_4$) was observed in the polymerization with sodium-naphthalene. This was considered to indicate the propagation via the uncyclized free anion and a higher cyclization reactivity of a free ion than that of an ion pair[15].

The catalyst and solvent affected the extent of cyclization, in the cationic polymerization, as well. The catalyst exerted particularly great influences and the following r_c values (mole/l) were obtained in toluene at $0°((M)_o = 2.5-2.9$ mole/l).

$$AlCl_3(4.8) > SnCl_4(1.9) > TiCl_4/TCA(1.5) >$$
$$FeCl_3/TCA(1.0) > BF_3OEt_2(0.68) > ZnCl_2/TCA(0.12)$$

It was concluded that a strong Lewis acid promoted the cyclization and the above-mentioned order of catalysts is similar to that of the first ionization potential of metals ($Al > Ti > Sn > Fe > B > Zn$) and to the order of effectiveness of Friedel-Crafts catalysts in acylation[18] or in alkylation[19]. This catalytic effect was interpreted previously in terms of the tightness of ion pairs[13]. A strong Lewis acid will form a loose ion pair, while a weak Lewis acid will form a tight ion pair. A tight ion pair was considered to be less reactive, because the activation energy of cyclization was greater than that of propagation and a smaller r_c value was obtained with a weak Friedel-Crafts catalyst.

The following solvents are arranged according to the order of dielectric

constants and r_c values with mole/l unit are given in parenthesis, as obtained using $(C_6H_5)_3CBF_4$ catalyst at $0°$ (monomer concentration: 1 mole/l):

$C_6H_5CH_3(1\cdot10)$, $CHCl_3(1\cdot15)$, $C_6H_5Cl(0\cdot82)$, $CH_2Cl_2(0\cdot47)$,

$$C_2H_5NO_2(0\cdot41), C_6H_5NO_2(0\cdot76), CH_3CN(0\cdot27)$$

Solvent effects on r_c were rather small. The variation of r_c cannot be explained simply in terms of the tightness of ion pair, since polar solvents should render an ion pair looser and accordingly give a higher r_c[16].

In order to explain these results structurally the uncyclized growing cation was conceived. The vinyl π-orbital cannot be simultaneously coplanar with the p-orbital of the cation and the π-orbital of the ring. As the carbonium ion

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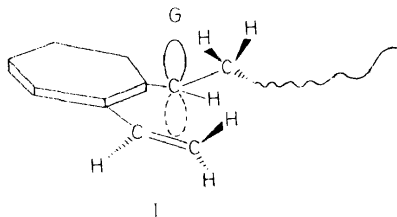
is stabilized by resonance with the benzene ring, the vinyl group will be correspondingly pushed out of the plane. The positive p-orbital can interact both with the vinyl group and with the counter anion located on the other side of the vinyl group. In a loose ion pair, the positive charge is less shielded by the counter anion. Thus, the carbonium ion becomes more reactive and interacts more with the neighbouring vinyl group. Accordingly, higher r_c values result due to the increased reactivity of the growing cation and/or to the increased p-π interaction. In a polar (or higher solvating) medium, the carbonium ion forms a loose ion pair by solvation. At the same time, the interaction with the vinyl group may be replaced by that with polar solvent

Table 2. Activation parameters[a] for several systems of cyclopolymerization of o-divinylbenzene

No.	Catalyst	Solvent	A_c/A_{pA}	$\dfrac{E_c - E_{pA}}{K_{cal}/\text{mole}}$	Reference
1	Free radical	Benzene	50	1·9	[12]
2	BF_3OEt_2	Toluene	$2\cdot2 \times 10^4$	5·3	[14]
3	$(C_6H_5)_3CBF_4$	Methylene-chloride	5×10^4	6·2	[16]
4	Na-naphthalene	THF	66	2·8	[15]
5	Na-naphthalene with NaBPh₄ (ion pair)	THF	15	2·2	[15]

[a] Calculated from the following equation:

$$r_c = k_c/k_{pA} = (A_c/A_{pA}) \exp\{(-E_c + E_{pA})/RT\}.$$

Dimension of r_c = mole/l.

molecules. Therefore, for a given ion pair, r_c will decrease with polarity of the solvent used[16].

Table 2 shows activation parameters for several systems of cyclopolymerization of *o*-divinylbenzene[12, 14—16]. In all cases, the intramolecular cyclizations require higher activation energies than the intermolecular propagations of the uncyclized growing end. The pre-exponential terms tends to compensate for the difference in the activation energies.

It should be noted that *cis*-1,2-divinylcyclohexane gave almost completely cyclized cyclopolymers with cationic catalysts[7]. This monomer is structurally similar to *o*-divinylbenzene, but the polymerization rate is very much slower than for *o*-divinylbenzene. A growing cation derived from divinylcyclohexane may be less stable than that of divinylbenzene due to localization of the positive charge and would interact more strongly with the adjacent double bond. Therefore, the cationic polymerization of divinylcyclohexane may proceed through a concerted or intermediate manner unlike that for *o*-divinylbenzene[7].

SOME ASPECTS OF CYCLOPOLYMERIZATIONS OF DIALDEHYDES

The cyclopolymerization of bifunctional monomers possessing heteroatom-carbon multiple bonds is undoubtedly an interesting subject of investigation. Some dinitriles[20, 21], diisocyanates[22—24], dialdehydes[2—5, 25—31] and diepoxides[32—35], which are expected to form a five or six-membered ring during the course of polymerization, gave highly cyclized cyclopolymers. Conceivable problems for these monomers are similar to those in the divinyl compounds: i.e. reaction schemes, steric factors, the structure of the cyclized unit, and so on. Since the functional groups in these monomers are polarized, the interaction (such as dipole–dipole, hydrogen bond etc.) between the two functional groups in a monomer molecule becomes probable. Furthermore, except for the cases of several dinitriles reported by Liepen and co-workers[21], these monomers usually polymerize with ionic catalysts. Thus expected are the ease of interaction between a propagating ionic chain end and the adjacent functional group and the subseqent prevalence of the cyclization reaction. For some of these monomers, therefore, the progation of the two adjacent functional groups within a molecule may occur in a concerted or intermediate manner rather than as a stepwise process. Formation of highly cyclized polymers supports this view. The polymerization of some dialdehydes will be discussed in this section.

Glutaraldehyde[2—4] and succinaldehyde[25] polymerized spontaneously to oligomeric cyclopolymers. The spontaneity of polymerization, apparently initiated by contaminating water as a proton donor, seems to be one of the


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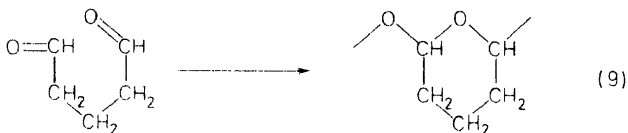
characteristics of these dialdehydes. These dialdehydes were also cyclo-polymerized with several catalysts such as BF_3OEt_2 or $AlEt_3/H_2O$, as shown in equation 9. The ease of cyclopolymerization and the spontaneity of polymerization may suggest the presence of the interaction between two aldehyde groups. The effect of dilution on the shift of the $C{=}O$ stretching band in the IR spectrum was smaller for these dialdehydes than for the corresponding monoaldehydes. This difference probably suggests the presence of the intramolecular interaction between both aldehyde groups of dialdehydes[36]. The dipole–dipole interaction, the presence of which was pointed out from IR spectra by Schneider and Bernstein[37] in the case of formaldehyde, was presumed in the above case. The existence of such interaction will promote cyclization.
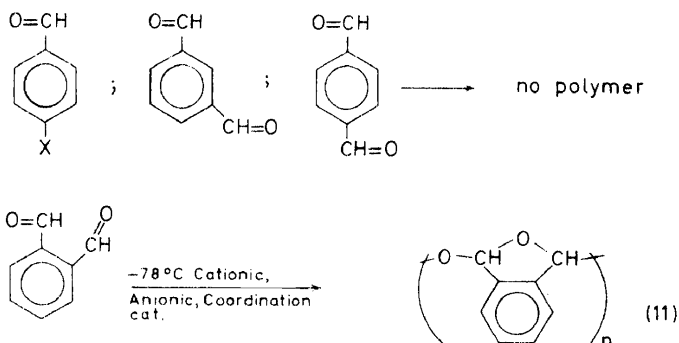
Cyclopolymerizations of various dialdehydes were investigated. Those aldehydes that are expected to form 5- or 6-membered ring by cyclization—succinaldehyde[25], malealdehyde[26], glutaraldehyde[2-5] and its 3-methyl and 3-phenyl derivatives[4,27], cyclohexene-cis-4,5-dicarboxyaldehyde and its 2-methyl derivative[31] and o-phthalaldehyde[29,30]—polymerized readily to give highly cyclized polymers, showing usually an extent of cyclization of over 90 per cent.

On the other hand, polymerization of adipaldehyde with BF_3OEt_2 gave a cross-linked polymer along with a small amount of the soluble fraction catalyst. The soluble fraction had a low extent of cyclization of only 30 per cent and the cyclic unit formed was conceivably the 7-membered ring[28]. Koral and Smolin mentioned that suberaldehyde might undergo cyclo-polymerization to some extent[38]. The smallest ring derivable therefrom would have been the nine-membered ring, and the content of the cyclized unit in the polymer was probably small. Therefore, the size of the ring formed in the polymer seems important in determining the ease of the cyclopoly-merization of dialdehydes, as in the case of divinyl compound. When adipalde-hyde was copolymerized with chloral, the copolymer obtained possessed a nearly equimolar composition and highly cyclized adipaldehyde units. The extent of cyclization of the adipaldehyde unit reached about 96 per cent. This may be an example where cyclization is promoted by steric hindrance of a bulky penultimate (trichloromethyl) group toward monomer addition, as seen in equation 10.

It was remarkable that o-phthalaldehyde could be polymerized readily[29,30],

$$(10)$$
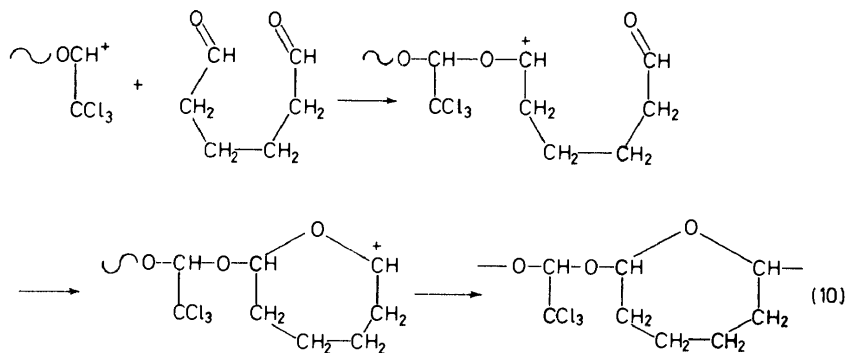
because aromatic aldehydes, such as benzaldehyde, isophthalaldehyde and terephthalaldehyde, did not polymerize with common ionic catalysts. Although the latter aldehydes could be copolymerized with styrene by cationic catalysts, sequences of more than one aromatic aldehyde unit were not found in copolymers[39, 40]. In addition, the poly-(o-phthalaldehyde) obtained was

O=CH   O=CH   O=CH

(benzaldehyde with X) ; (isophthalaldehyde, CH=O) ; (terephthalaldehyde, CH=O) ⟶ no polymer

$$\text{o-phthalaldehyde} \xrightarrow[\substack{\text{Anionic, Coordination} \\ \text{cat.}}]{-78^\circ\text{C Cationic,}} \left(-O-CH\overset{O}{\diagup}CH- \right)_n \qquad (11)$$

composed of only cyclic structures, as shown in equation 11. These results suggest that the driving force of the polymerization of o-phthalaldehyde is apparently attributable to the formation of five-membered rings in the course of the cyclopolymerization. Therefore, the importance of the fixed *cis* arrangement of the two aldehyde groups is to be noted. In general, the reactivity of bifunctional monomers, such as dialdehydes, diepoxides and others, may be enhanced by the favourable steric arrangement of two functional groups within a monomer molecule.

CYCLOPOLYMERIZATIONS OF o-PHTHALALDEHYDE AND RELATED COMPOUNDS

Some examples of polymerization results of o-phthalaldehyde are given in *Table 3*. The extent of cyclization reached almost 100 per cent in every case.

The cationic polymerization of o-phthalaldehyde was quite fast at low temperatures, e.g. -78°, and the conversion reached saturation values at the respective polymerization temperature. The conversion was determined by the final polymerization temperature, when the temperature was changed during polymerization, as shown in *Table 3*. These results indicated that the monomer and polymer were in equilibrium in this polymerization system. The ceiling temperatures of o-phthalaldehyde was calculated to be -43° from the relationship between the equilibrium concentration of the monomer and polymerization temperature[29].

One of the interesting results obtained in the cationic polymerization is that the molecular weight of the polymer was proportional to conversion[29]. This phenomenon suggested the occurrence of the 'living' polymerization. In a typical living polymerization, the molar ratio of monomer to the growing end is equal to the degree of polymerization. However, some deviation from the theoretical value was noted and it was probably due to the fact that the concentration of the living end was somewhat smaller (about 75 per cent) of

Table 3. Selected examples of polymerization of o-phthalaldehyde with various catalysts at −78°.

Catalyst	mole %	Monomer g/ml	Solvent	Polymerization Time h	Conversion %	$[\eta]$ in C_6H_6 at 30°C	$M_n \times 10^{-3}$	Softening point °C	cis content %
γ-ray[a]		0·1			24		—	130–132	87
BF₃OEt₂	(1·0)	0·1	CH₂Cl₂	115	87	0·06	11·7	—	66
BF₃OEt₂	(1·3)	0·1	CH₂Cl₂	12[d]	73	0·31	16·5	—	—
BF₃OEt₂	(1·3)	0·1	CH₂Cl₂	[e]	77	0·28	14·2		—
Ph₃CBF₄	(0·5)	0·1	CH₂Cl₂	24	87	0·32	8·6	125–127	77
t-BuOLi	(1·6)	0·1	THF	22	24	0·11	—	117–120	56
Na-Naph	(3·7)[b]	0·1	THF	21	80	0·13	—	113–116	60
AlEt₃/TiCl₄	(4)[c]	0·02	toluene	70	28	0·13	—	152–154	37

[a] dose: 9·27 × 10⁶ r.
[b] sodium naphthalene.
[c] Al/Ti = 2, Al mole %.
[d] The reaction mixture was kept at −50° for 2 h and then at −78° for 1 h.
[e] The reaction mixture was kept first at −78° for 1 h, secondly at −20° for 1 h and last at −78° for 1 h.

the catalyst molecules) than the initial catalyst concentration. The rate constant for propagation k_p was obtained using equation 12, where (P^*) was the concentration of the living growing end and $(M)_o$, $(M)_e$, and $(M)_t$ denoted the monomer concentration at the initial state, at the equilibrium conversion and at time t, respectively. (P^*) was 7.5×10^{-3} mole/l at $-78°$ $((M)_o = 0.746$ mole/l, $BF_3OEt_2 = 0.01$ mole/l in methylene chloride).

$$k_p(P^*)t = \ln[\{(M)_0 - (M)_e\}/\{(M)_t - (M)_e\}] \qquad (12)$$

Then k_p could be calculated to be 0.18 l/mole sec by dividing the slope of the line of *Figure 1* by (P^*). It was greater than that of 1,3-dioxolane $k_p = 4.3 \times 10^{-2}$ l/mole sec $(Et_3OBF_4$ catalyst, $30°$, methylene chloride solvent)[41].

It was of interest to investigate the cationic copolymerization of o-phthalaldehyde and styrene at temperatures above and below the ceiling temperature
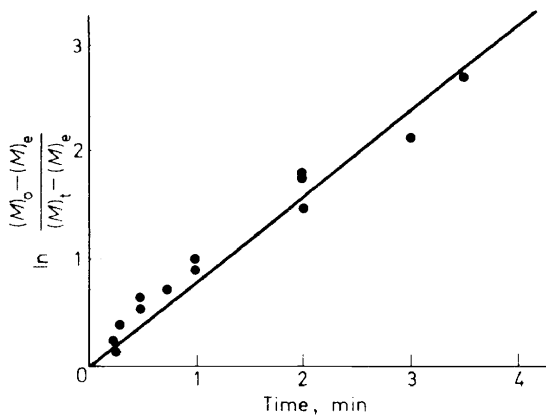

Figure 1. First-order plots of the polymerization of o-phthalaldehyde in methylene chloride at $-78°$. $[M]_o = 0.746$ mole/l; $BF_3OEt_2 = 0.01$ mole/l; Solvent: CH_2Cl_2.

$(-43°)$ of homopolymerization of the former monomer. Benzaldehyde copolymerized with styrene readily at $0°$[39], a temperature much higher than the presumed ceiling temperature $(-160°$[29]). The copolymerization temperature selected were $0°$ and $-78°$, and the copolymer composition changed with temperature used, as shown in *Table 4*[40].

The copolymer obtained at $0°$ consisted of three structural units, that is, a cyclized phthalaldehyde unit, an uncyclized phthalaldehyde unit (the unit possessing a pendant aldehyde group) and a styrene unit. Since reaction of o-phthalaldehyde with BF_4OEt_3 at room temperature gave a monomeric cyclized product, the formation of which is shown schematically in equation 13, the cyclization reaction must also be the preferred course in the addition reaction of phthalaldehyde to a propagating cation during the copolymerization even at temperatures above the ceiling temperature. The existence of long sequences of phthalaldehyde units, may however be improbable, since the depropagation should be extensive at $0°$. When the penultimate unit is styrene, the reverse reaction produces an uncyclized phthalaldhyde unit

Table 4. Selected examples of copolymerization of styrene (M_1) with
o-phthalaldehyde (M_2) in methylene chloride

| (M_2) in monomers mole %	Monomer g/cc	BF_3OEt_2 mole %	Temp. °C	Time h	Conversion %	(m_2) in copolymer mole %
29·1	0·20	5·0	0	2	25·6	36·0
76·6	0·18	5·0	0	240	11·6	66·8
30·5	0·16	2·7	−78	0·3	27·3	100
29·7	0·16	2·7	−78	22·7	79·6	29·5

(II in equation 14), the propagation which will give rise to the pendant alde-hyde group.

$$(13)$$
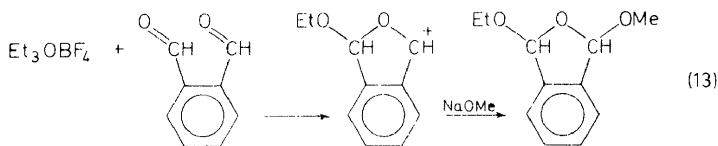
On the other hand, the polymer obtained at $-78°$ does not possess pendant aldehyde groups. The content of the o-phthalaldehyde unit in the copolymer was quite high at low conversions, and decreased with increasing conversions, as is apparent in Table 4. It was concluded from solubility and

$$(14)$$
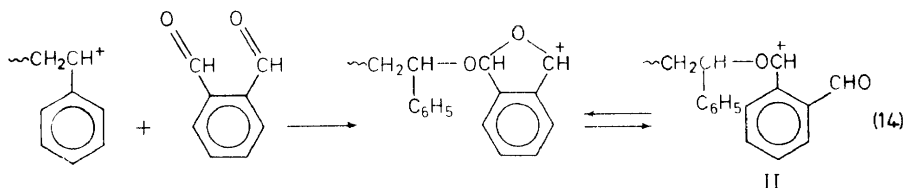
saponification results that the copolymer was not a mixture of homopolymers of styrene and phthalaldehyde, but a block copolymer, as shown, for example, by the following structure III.

(Cyclized phthalaldehyde unit)$_{40-45}$—(Styrene unit)$_{16}$

(Cyclized phthalaldehyde unit)$_{1-2}$—(Styrene unit)$_{16}$
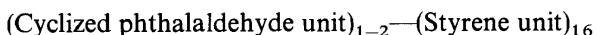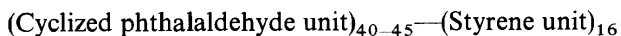
III

Formation of the block copolymers was explained by assuming that o-phthalaldehyde polymerized preferentially in the presence of styrene until the amount of phthalaldehyde monomer reached the equilibrium con-centration and then styrene added to the living end. The polymerization processes at these two temperatures are consistent with the homopoly-merization behaviour of phthalaldehyde with cationic catalysts.

The steric structure of poly(o-phthalaldehyde) was also investigated[30]. The recurring unit of polymer is composed of cis- (IV) and/or trans-oxy-phthalan ring V.

cis – configuration

(ee ⇌ aa)

trans – configuration

(ea ⇌ ae)

◯,Oxygen,   ●,Carbon,   O,Hydrogen,
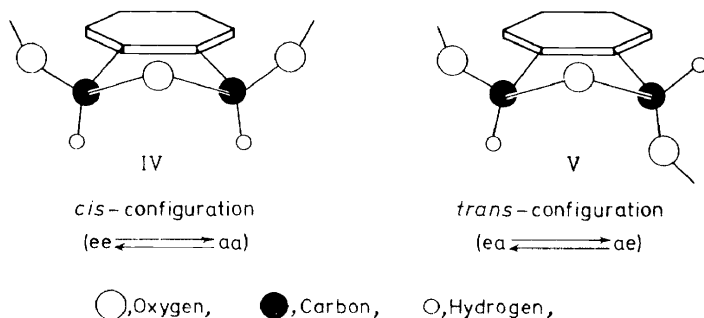
In order to determine the steric structure of the ring in the polymer, NMR spectra of 1,3-dialkoxyphthalans, which were considered as models of the cyclic units in the polymer, were compared with those of polymers. cis- and trans-dialkoxyphthalans gave methine peaks with different chemical shifts: for example, the cis-isomer of diethoxyphthalan showed the methine peak at 6.08 ppm in dimethylsulphoxide and the trans-isomer at 6.33 ppm. From comparison with these model compounds, peaks at 6.59 ppm and 6.90 ppm of poly(o-phthalaldehyde) were assigned to methine protons of the cis and trans structures, respectively. The content of cis and trans rings in the polymer was determined by comparing the methine peak areas in NMR spectra. Figure 2 shows the steric structures of polymers obtained with different catalysts. In general, the coordination catalysts gave trans-rich polymers, the highest trans content being 88 per cent. On the other hand,
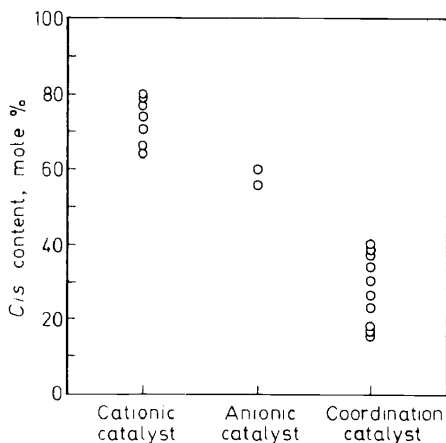

Figure 2. Effect of catalysts on the configuration of poly(o-phthalaldehyde).

cis-rich polymers were usually obtained in the cationic polymerization. The latter result is consistent with the fact that the *cis*-rich 1,3-diethoxy-phthalan (*cis* 60 per cent) was obtained in 70 per cent yield by reacting *o*-phthalaldehyde with excess Et_3OBF_4 and then by adding an ethanol solution of sodium-ethoxide, as shown schematically in equation 13. The polymer obtained by γ-ray irradiation, probably a cationic process, gave the highest *cis* content of about 87 per cent.

The cationic propagation of *o*-phthalaldehyde may be represented by one of the three mechanisms, that is, the competitive, intermediate or concerted schemes. This situation is quite similar to the case of cyclopolymerization of divinyl compounds, which was already explained in the first section of this paper. In the stepwise reaction, additions of the two carbonyl groups in a monomer occur as separate elementary processes with similar activation energies. In the concerted addition, two aldehyde groups in a monomer simultaneously undergo the $C=O$ double bond opening. In the intermediate-type addition, the initially-formed carbonium ion is stabilized by interaction with the second aldehyde group. Enhanced reactivity of *o*-phthalaldehyde over those of benzaldehyde and its derivatives and the complete cyclization of poly(*o*-phthalaldehyde) strongly suggest that the cationic propagation proceeded by the intermediate or concerted scheme. The precise discussions were done previously by using thermodynamic constants obtained for the cationic polymerization[29].

The cationic polymerization scheme is shown in equation 15. Since a five-membered ring ether oxygen is nearly planar and the carbonium ion is placed between an ether oxygen and a phenyl ring, cation VI may be a sp^2-hybridized or of a quite shallow pyramidal type. Accordingly, the direction of approach of a new monomer to the cyclic cation VI determines the configuration of the ring of the polymers, *cis* IV or *trans* V.
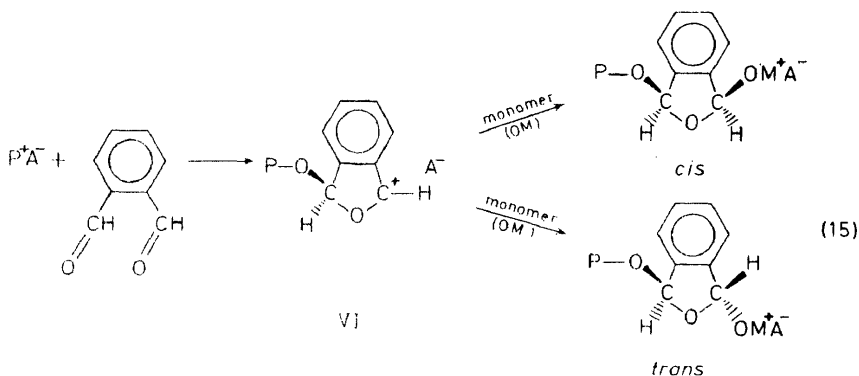
Two different explanations are put forward for the preferred formation of the *cis* structure in the cationic polymerization[30]. One of them is based on the mechanism of isotatic propagation, which was proposed previously by our research group for the cationic polymerization of vinyl compounds[42]. The counteranion A^- is assumed to be present at the lower side of the carbonium ion (below the plane of this paper), so as to avoid the steric repulsion

with the penultimate unit. The monomer molecule reacts with the cyclic cation VI from the upper side (remote from the counteranion) and the *cis* structure is formed preferentially. The other explanation is based on the difference in the stability of the cyclic unit. Since the free energy of propagation was found to be small, -0.82 kcal/mole at $-78°$, the difference in the stability of the phthalan ring formed may be reflected in the transition state. If the transition state leading to the *cis* ring is more stable, the *cis* structure is formed preferentially.

The ring formation in anionic polymerization proceeds in a different way. It should be pointed out that the stereochemical structure of the cyclic unit is determined during the intramolecular cyclization, because the cyclic anion may be a sp^3-hybridized type.

The polymerizations of *cis*-cyclohexene-4,5-dicarboxyaldehyde and the 1-methyl derivative were carried out in comparison with the polymerization of *o*-phthalaldehyde, because the former two monomers have partially hydrogenated benzene rings. These monomers polymerized readily with various catalysts to yield highly cyclized polymers[31]. The extent of cyclization reached over 98 per cent. Films made of these polymers were rather flexible. On the other hand, cyclohexene-4-monoaldehyde gave only a cyclic trimer (m.p. 176°) with BF_3OEt_2 catalyst at $-78°$. The formation of high polymers from these dialdehydes indicate strongly the presence of the cooperative effect of the aldehyde groups as in the case of *o*-phthalaldehyde. The ease of cyclopolymerizations of these dialdehydes led us to assume the presence of a similar propagation scheme to that of *o*-phthalaldehyde; i.e. concerted or intermediate-type propagation. However, the ceiling temperature for polymerization of *cis*-cyclohexene-4,5-dicarboxyaldehyde determined by NMR spectra was about $+60°$ in the cationic polymerization, a much higher value than that of *o*-phthalaldehyde. Generally speaking, the ceiling temperatures of cyclopolymerization of aliphatic dialdehydes including the above cyclohexenedialdehydes lie above room temperature, because these compounds cyclopolymerized spontaneously or with ionic catalysts at room temperature.

o-Formylphenylacetaldehyde is an unsymmetrical dialdehyde monomer and possesses two different kinds of aldehyde groups. That is, one is an aromatic aldehyde group and the other is aliphatic. The cylization reaction was expected to give a six-membered ring. The polymer obtained with anionic catalysts contained a small amount of pendant aldehyde group. According to the spectral observation, the amount of the pendant aromatic aldehyde group was greater than that of the aliphatic aldehyde group and this difference reflects the higher reactivity of the aliphatic aldehyde group.

BF_3OEt_2 catalyst gave a highly cyclized polymer at $-78°$. The extent of cyclization was higher than 90 per cent (equation 16). Interestingly, phenylacetaldehyde did not copolymerize with benzaldehyde. Therefore, the capacity to cyclize, i.e. to form a six-membered ring, is considered to be a driving force for the polymerization of *o*-formylphenylacetaldehyde. The polymerization process may be considered as follows. First a propagating cation will attack an aliphatic aldehyde group, because it is more reactive than the aromatic aldehyde group. Next, the carbonium ion derived will attack intramolecularly

the adjacent aromatic aldehyde, considering the ease of formation of six-membered rings. An interesting cyclic trimer (crystalline: m.p. 284°) was obtained when the reaction of this monomer was carried out with BF_3OEt_2 at room temperature, VII in equation 17[43].

VII
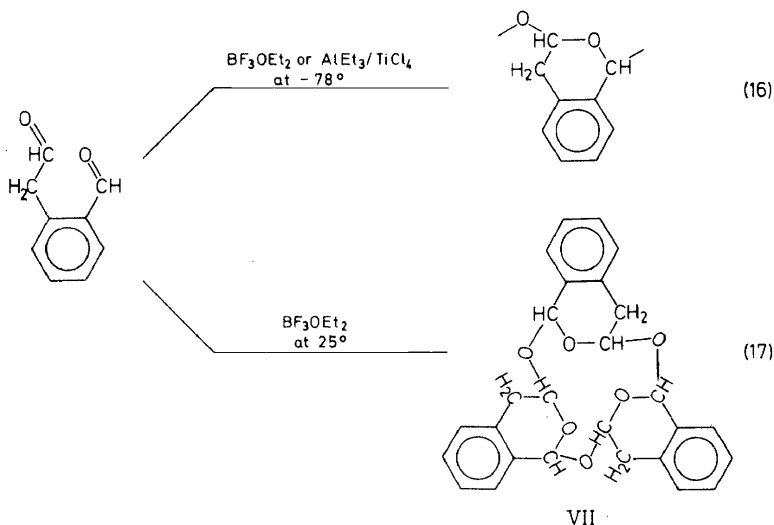
Since the aromatic aldehyde group was found to be capable of under-going propagation from the adjacent carbonium ion, as seen in cationic polymerizations of o-phthalaldehyde and o-formylphenylacetaldehyde, it was an interesting problem to study the polymerization behaviour of o-vinylbenzaldehyde[44]. The cationic polymerization of o-divinylbenzene proceeded in a stepwise manner and gave cyclopolymers possessing 40 to 100 per cent of the double bond, depending on the polymerization condition[13]. Therefore, if the cation adds first to the aldehyde group of o-vinylbenzalde-hyde, the subsequent cyclization with the adjacent vinyl group may compete with monomer addition. Cationic polymerization of this monomer gave a cyclopolymer possessing about 20 per cent of the pendant double bond and a
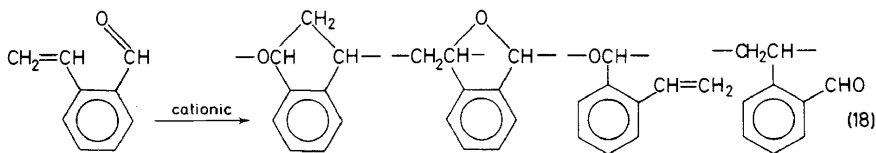
few per cent of aldehyde groups (equation 18). In addition, when *o*-vinyl-benzaldehyde was reacted with excess Et_3OBF_4 at 0° and then treated with sodium ethoxide, *o*-vinyldiethylbenzal was obtained in 25 per cent yield, together with the polymeric product (25 per cent yield) which contained 15 per cent pendant vinyl groups. Thus, this monomer appears to react with the propagating cation preferentially at the aldehyde site.

On the other hand, the presence of a few per cent of the aldehyde group in the cyclopolymer suggests that the cyclization occurred predominantly when a cation first attacked the vinyl group of *o*-vinylbenzaldehyde. This interpretation is consistent with the behaviour of the aromatic aldehyde group in the cationic polymerizations of phthalaldehyde and *o*-formyl-phenylacetaldehyde.

Accordingly, two different schemes of propagation, i.e. stepwise and concerted or intermediate schemes, are considered to coexist in the cationic polymerization of *o*-vinylbenzaldehyde, depending on the kind of the cation produced.

CONCLUSION

The bifunctional monomers discussed in this paper can be classified into three groups: (a) Monomers possessing two carbon–carbon multiple bonds (*o*-divinylbenzene and *cis*-1,2-divinylcyclohexane). (b) Monomers possessing two heteroatom–carbon multiple bonds (*o*-phthalaldehyde, *cis*-cyclohexene-4,5-dicarboxyaldehyde, and *o*-formylphenylacetaldehyde). (c) Monomers possessing one heteroatom–carbon multiple bond and one carbon–carbon multiple bond (*o*-vinylbenzaldehyde). The two functional groups in these monomers are present at the vicinal position (*ortho* position) of the six-membered ring (*o*-formylphenylacetaldehyde excluded). These structural characteristics are of great steric advantage for cyclopolymerization. However, propagation schemes are quire different among these monomers. The cyclopolymerizability of bifunctional monomers depends greatly on the nature of monomer. The stepwise propagation was proposed for the cationic polymerization of *o*-divinylbenzene, and the intermediate or concerted scheme for those of *cis*-1,2-divinylcyclohexane, *o*-phthalaldehyde and *cis*-cyclohexene-4,5-dicarboxyaldehyde. Moreover, both of these reaction schemes probably coexist in the cationic polymerization of *o*-vinylbenzalde-hyde, depending on the kind of cation produced. In the case of stepwise reaction, the investigation of the influence of polymerization conditions on cyclization gives useful information in connection with the polymerization mechanism of the related monofunctional monomers. Studies on the structure of cyclic units in cyclopolymers and on telomerization of bifunctional monomers may also give valuable information for cyclopolymerization.

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