

# Effect of temperature on the structure of prepolymers of diallyl benzenedicarboxylates

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The effect of bulk polymerization temperature on the structure of prepolymers of diallyl phthalate (DAP), diallylisophthalate (DAI) and diallylterephthalate (DAT) was investigated in the temperature range of 80°C–285°C. The degree of unsaturation of the prepolymers of each of the monomers unexpectedly increased with temperature in the range above 160°C. The average length of linear C–C chain in the prepolymers decreased with temperature. The branching ratio for prepolymers increased with conversion of the monomer at each of the temperatures. The degree of cyclization of monomer units ( $P_c/P$ ) was always arranged in the order: poly(DAP) > poly(DAI) > poly(DAT). But, contrary to expectations, at temperatures above 160°C the  $P_c/P$  values diminished progressively, which was attributed mainly to the diminished probability of cyclization occurring by chain transfer.

(Keywords: allyl polymerization; diallyl benzenedicarboxylates; prepolymers; branching; cyclization; chain transfer reaction)

## INTRODUCTION

In our previous paper<sup>1</sup> we presented results of investigation of the influence of temperature on the reactivity of allyl groups in the polymerization of three isomers: diallyl phthalate, diallyl isophthalate and diallyl terephthalate (DAP, DAI and DAT, respectively).

The polymerization of these monomers is known to take place with one of the allyl groups, leading to unsaturated polymers (prepolymers)<sup>2</sup>. As early as 1946, Simpson, in his study of DAP polymerization<sup>3</sup>, found the degree of unsaturation of the prepolymer lower than that expected for a linear polymer, and he suggested that this effect might be principally due to reactions giving rise to branched macromolecules. Later, together with Holt<sup>4</sup>, he brought about saponification of ester links of DAP prepolymer, and showed that the polymer resulting, despite its branched structure, comprised appreciable amounts of cyclic structures as well. In later investigations<sup>5</sup>, Holt and Simpson proved the capacity for cyclization to be characteristic of the polymerization of diallyl dicarboxylates, dependent, however, on the distance between allyl groups in the monomer molecule.

The probability of occurrence of cyclic structures during polymerization was considered by Haward<sup>6</sup> as well by Dušek and Ilavsky<sup>7</sup>. Matsumoto *et al.*<sup>8,9</sup> recently studied the problem of the formation of eleven-membered rings at an early stage in polymerization of this monomer. They indicated that during polymerization the tendency of DAP to cyclize increases with temperature. As yet, no data have been given to enable comparison between all three isomeric allyl benzenedicarboxylates in their capacity for cyclization and branching in a range of temperatures wider than 60°C–100°C. The purpose of the present work was to investigate the influence of temperature (80°C–285°C) and conversion on the participation of side reactions in structural changes in prepolymers as

well as on the changes in degree of unsaturation and other properties of prepolymers.

## EXPERIMENTAL

### *Materials and polymerization procedure*

Monomers and initiators were prepared, and polymerization and precipitation of polymers were achieved by methods described previously<sup>1</sup>.

### *Analyses of polymers*

The number-average molecular masses  $\bar{M}_n$  were determined by membraneless osmometry at 37°C in chloroform with use of a Hewlett–Packard vapour pressure osmometer. The iodine numbers were determined by the Wijs method. The degree of unsaturation ( $U$ ) was expressed as the ratio of the iodine number of the polymer to that of monomer.

The structure of polymers was investigated by the procedure of Holt and Simpson<sup>4</sup>. So, saponification was effected by refluxing in a nitrogen atmosphere a weighed portion (*ca.* 10 g) of polymer for 24 h with an adequate amount of 0.5 N alcoholic potassium hydroxide (three moles of base per mole of ester groups). At the end of this period, saponification was completed, as was indicated by titration of samples after 20 and 24 h. The solution was then filtered and solid carbon dioxide added until no more salts were precipitated. The alcoholic solution of poly(allyl alcohol) was filtered and the solvent was removed by distillation, under a nitrogen atmosphere. Then ten moles of acetic anhydride per mole of alcoholic groups were added, and refluxed for 10 h under a nitrogen atmosphere.

Excess acetic anhydride was then removed under reduced pressure in the nitrogen atmosphere, the polymer taken up in benzene, washed repeatedly with water and

dried over anhydrous sodium sulphate. The poly(allyl acetate) was finally isolated by distillation under reduced nitrogen pressure and dried *in vacuo* at 25°C.

Following Simpson *et al.*<sup>4</sup>, we propose to describe the structure of branched poly(diallyl esters) by the variables:

$P$ , the degree of polymerization ( $\overline{DP}$ ) of the branched macromolecule expressed in the monomer units from which it is constructed;

$P'$ , the degree of polymerization ( $\overline{DP}$ ) of the linear C–C chain expressed as a number of reacted allyl units per chain;

$U$ , the degree of unsaturation of the polymer expressed as a fraction of the unsaturation of pure monomer;

$B$ , the degree of branching of the macromolecule (number of linear C–C chains from which it is composed);

$P_d$ , the number of doubly reacted monomer units per one macromolecule;

$P_c$ , the number of cyclized monomer units per macromolecule.

The interdependence of these variables is expressed by<sup>4</sup>

$$B = \frac{2P}{P'}(1 - U) \quad (1)$$

$$P_d = BP' - P = P(1 - 2U) \quad (2)$$

$$P_c = P(1 - 2U) - (B - 1) \quad (3)$$

#### Gel permeation chromatography

Measurements were made with the following apparatus and conditions: glass column with Merckogel OR–PVA 6000; tetrahydrofuran solvent; column volume, 300 cm<sup>3</sup>; temperature, 25°C; flow rate, 20 cm<sup>3</sup> h<sup>-1</sup>; ultra-violet (254 nm) spectrophotometer detector (LKB Uvicord 407).

## RESULTS AND DISCUSSION

It is known that the degree of unsaturation of prepolymers ( $U$ ) is the basic quantity to indicate the sharing of cyclization and branching side-reactions in the polymerization process. On analysis of the  $U$  values for DAP, DAI and DAT prepolymers, determined just before the gel point at varying temperatures (80°C–285°C, Figure 1), we found the results rather inconsistent with the literature reports. In agreement with prediction,  $U$  for DAP prepolymers (curve 1) in the whole range of temperatures is markedly lower than for DAI prepolymers (curve 2), which in turn, apart from the highest temperatures, is considerably lower than for DAT prepolymers (curve 3). The arrangement in order of increasing values of  $U$  correlates with the increasing distance between allyl groups in monomer molecules, which is likely to cause the tendency to cyclize to gradually decrease, although it is surprising that at the highest temperatures the difference between DAI and DAT disappears.

However, the temperature dependence of  $U$  values was contrary to that expected. Matsumoto<sup>2</sup> and others found DAP capable of progressive production of the cyclic structures with a rise in temperature. Hence the  $U$  values for prepolymers might be expected to be successively lowered with rising temperature. We proved, however, that Matsumoto's findings are true to some extent only. In

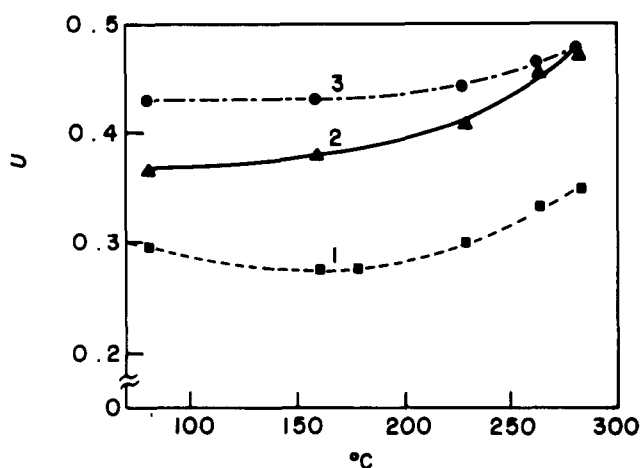


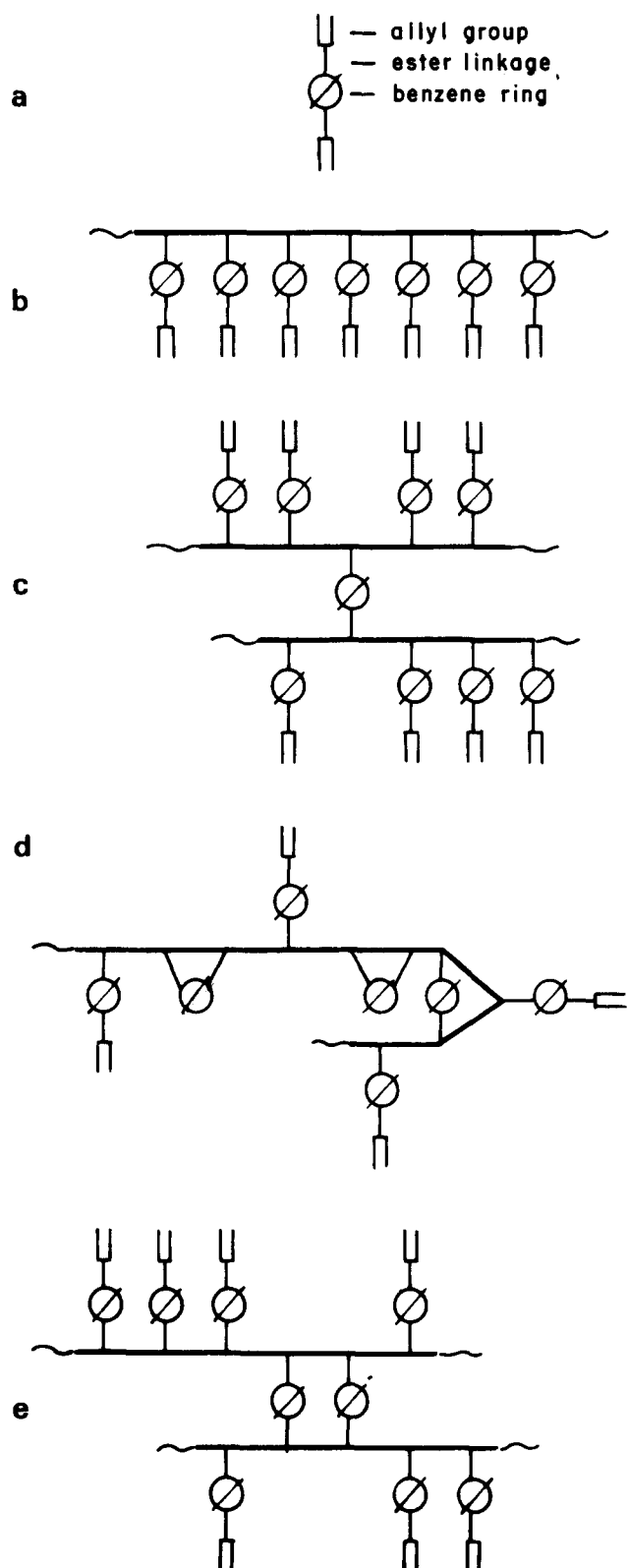
Figure 1 The influence of the polymerization temperature on the degree of unsaturation of prepolymers obtained just before the gel point: curve 1, DAP; 2, DAI; 3, DAT

our experiments,  $U$  for DAP prepolymers was diminished in the range 80°C–160°C, whereas above 180°C it grew with temperature. However, for DAI prepolymers,  $U$  values increased in the whole range of temperatures (80°C–285°C). But for DAT prepolymers, the rise in temperature from 80°C to 160°C did not alter  $U$ , but it grew noticeably at higher temperatures.

This interesting relation between the degree of prepolymer unsaturation and polymerization temperature tempted us to study the polymer structures. The structures resulting from the basic kinds of reactions, involved in polymerization of DAP, DAI and DAT, are shown schematically in Figure 2. It is possible, from each of the structures depicted, to allot the outlines of linear chains of non-saponifiable C–C bonds. After base hydrolysis (saponification) of ester groups, we managed to fix the number of allyl groups: the constituents of the linear C–C chain ( $P'$ ). Simpson and Holt have discussed various possibilities that might interfere with the accuracy of the results of an analysis of poly(allyl esters) by the saponification technique<sup>4</sup>. They have deduced from the results of saponification and re-esterification experiments that no change in degree of polymerization of the linear C–C chain occurred during these operations.

The  $P'$  values, together with those for degree of unsaturation determined before hydrolysis, and values for the number-average degree of polymerization of prepolymers obtained at several double-bond conversions of the polymerization mixture ( $-\Delta[C=C]$ ) are quoted in Tables 1–3. On the preliminary analysis of the  $P$ ,  $P'$  and  $U$  values for prepolymers of allyl esters examined, one can easily observe that at each of the polymerization temperatures: the average number of allyl groups involved in production of linear C–C chains is diminished by only a quite small degree during polymerization; the average number of monomer units in the prepolymer increases to a large extent in the process of polymerization, while the degree of unsaturation ( $U$ ) is lowered.

These facts led to the conclusion that, irrespective of temperature, the higher the polymer content in a reaction mixture, the higher the content of macromolecules built of a few linear C–C chains. This conclusion has been supported by the results from calculating the values for



**Figure 2** Basic types of reaction leading to various structures of the prepolymers of diallyl benzenedicarboxylates: (a) monomer; (b) 'ideal' prepolymer; (c) branching; (d) chain cyclization; (e) interchain cyclization

average branching ratio ( $B$ , Tables 1–3), by the use of Simpson's equation<sup>1</sup>.

At each of the polymerization temperatures the value of  $B$  increases markedly as the process develops. The branching ratios for diallyl phthalate, isophthalate and terephthalate in the polymerization process usually increase by a factor of 3–4.

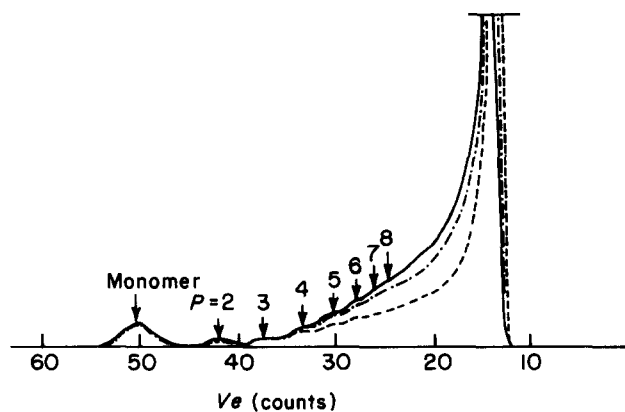
The formation of branched macromolecules during polymerization was confirmed by gel permeation chromatography analysis of DAI prepolymers (Figure 3). The chromatographic column exhibited a high resolution in the range of molecular weights up to 3000 (corresponding to  $V_e = 17$  counts), particular oligomers with degree of polymerization up to 8 being recorded in the form of individual peaks.

It can be seen in Figure 3 that the same polymers resulting from higher conversion, at stable temperature, contain decreased amounts of oligomers (up to  $P = 8$ ) and enlarged quantities of macromolecular fractions. This indicates that the formation of branched macromolecules occurs in the process of conversion, the molecules building into their own structures the unsaturated polymeric products generated earlier. The details of gel permeation chromatography analyses will be presented elsewhere.

Because of the very complicated spatial structure of diallyl benzenedicarboxylate prepolymers, it is practically impossible to define the kinds and numbers of rings being formed at various stages of monomer conversion. We have, therefore, made attempts to calculate the ratio of monomer units of diallyl esters involved in the production of the cyclic structure ( $P_c$ ), to the total number of monomer units included in the macromolecule of the prepolymer ( $P$ ). To evaluate the ratio  $P_c/P$ , we have first calculated the number of monomer units in which both double bonds have been reacted ( $P_d$ ).

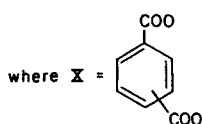
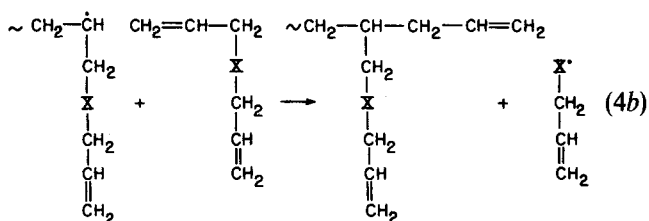
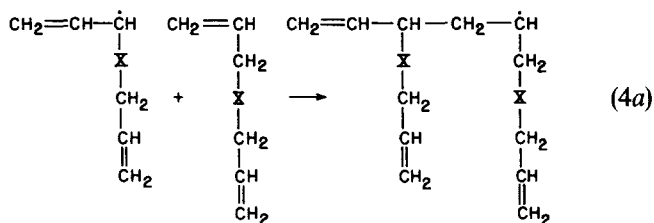
It is known that allyl esters polymerize with difficulty, giving products of low  $\bar{M}_n$ , which is caused by the specific role of the chain transfer to monomer molecule. This chain transfer reaction can be 'degradative'<sup>10</sup>, terminating the kinetic chain, or 'effective'<sup>11</sup>, when a generated radical is able to initiate the polymerization reaction with another monomer molecule.

When they deduced equation (2), Holt and Simpson<sup>4</sup> disregarded the possibility of the 'effective' chain transfer. In our previous publication<sup>1</sup>, we pointed out, however, that the 'effective' transfer plays an important role even at 80°C. On account of the 'effective' transfer it is possible to incorporate a monomer unit into the prepolymer chain without consuming any of the double bonds of the monomer molecule (reinitiation by an allylic radical, formula (4a)), or to terminate the chain by the non-reacted



**Figure 3** Gel permeation chromatography curves of DAI prepolymers obtained at polymerization temperature 230°C; the effect of the double bond conversions: (i) —, 3.7% ( $\bar{M}_n = 3100 \pm 300$ ); (ii) ---, 7.7% ( $\bar{M}_n = 3500 \pm 400$ ); (iii) - · - ·, 14.3% ( $\bar{M}_n = 4100 \pm 400$ )

allyl group (radical displacement reaction<sup>11,12</sup>, formula (4b)).



Thus a correction including the effects of the above reactions (4a) and (4b), the 'effective' chain transfer, has been inserted by us into the equation (2) applied by Simpson:

$$P_d = BP' - \left( P - B \frac{k_e}{k_d + k_e} \right) = P(1 - 2U) + B \left( \frac{k_e}{k_d + k_e} \right) \quad (5)$$

where  $k_e/(k_d + k_e)$  represents the participation of effective

chain transfer in the total transfer reaction. Then, equation (3) will be

$$\begin{aligned}
 P_c &= P(1 - 2U) + B \left( \frac{k_e}{k_e + k_d} \right) - (B - 1) \\
 &= P(1 - 2U) - B \left( \frac{k_d}{k_e + k_d} \right) + 1
 \end{aligned} \quad (6)$$

The share of cyclized monomer units may be expressed by the equation

$$\frac{P_c}{P} = 1 - 2U - \frac{B}{P} \left( \frac{k_d}{k_d + k_e} \right) + \frac{1}{P} \quad (7)$$

Because of the shortage of published values for the initiation effectivity coefficients ( $f$ ) in systems investigated, we have estimated the value  $k_d/(k_e + k_d)f$  in place of  $k_d/(k_e + k_d)$ . However, since the former expresses the maximum possible participation of the 'degradative' chain transfer ( $f \leq 1$ ), we have acknowledged that it may be applied in the place of the latter, without lessening the part of 'degradative' transfer. On assuming this, we have calculated the values  $P_c/P$  for the temperature 80°C (Tables 1-3).

In our previous paper<sup>1</sup>, we compared the participation of 'degradative' transfer at 80°C and 230°C and found the degradative transfer share at 230°C negligible by comparison with that at 80°C. To ascertain whether the fraction  $k_d/(k_e + k_d)$  is still significant at 160°C, we have continued studying it at this temperature according to the procedure given in reference 1. Accordingly, further

**Table 1** Characteristics of the DAP prepolymers structure

Temp. (°C)	Initiator (mol dm <sup>-3</sup> )	-Δ[C=C] (%)	U	P	P'	B	P <sub>c</sub> /P (%)
80	AIBN; 0.01	6.0	0.303	39.8	27.2	2.0	38.3
80	AIBN; 0.035	16.5	0.298	69.9	23.7	4.2	37.3
160	CHP; 0.0025	5.7	0.295	38.2	23.3	2.3	43.6
160	CHP; 0.0025	11.0	0.291	48.0	22.6	3.0	43.9
160	CHP; 0.0025	19.7	0.276	104.1	22.0	6.8	45.8
230	thermal	6.5	0.328	21.5	13.0	2.2	39.1
230	thermal	22.7	0.308	31.3	12.5	3.5	41.6
230	thermal	29.2	0.303	42.7	11.8	5.0	42.6
285	thermal	5.5	0.370	12.6	7.9	2.0	33.9
285	thermal	42.5	0.351	36.6	7.3	6.5	32.5

AIBN, 2,2'-azo-bis-isobutyronitrile; CHP, cumene hydroperoxide; -Δ[C=C], double-bond conversion of the polymerization mixture from which the prepolymer has been separated; other symbols as in the text. These definitions also apply to Tables 2 and 3

**Table 2** Characteristics of the DAI prepolymers structure

Temp. (°C)	Initiator (mol dm <sup>-3</sup> )	-Δ[C=C] (%)	U	P	P'	B	P <sub>c</sub> /P (%)
80	AIBN; 0.01	3.4	0.416	24.8	25.1	1.2	18.6
80	AIBN; 0.01	6.5	0.371	42.7	22.6	2.4	25.6
80	AIBN; 0.02	13.8	0.366	77.2	20.2	5.0	25.2
160	CHP; 0.0025	2.9	0.428	15.4	18.5	1.0	19.9
160	CHP; 0.0025	7.6	0.395	21.9	16.6	1.6	25.5
160	CHP; 0.0025	15.8	0.382	51.6	16.5	3.9	25.5
230	thermal	3.7	0.469	12.6	11.7	1.1	14.1
230	thermal	7.7	0.460	14.2	11.7	1.3	15.0
230	thermal	14.2	0.420	16.7	11.6	1.7	22.0
230	thermal	32.5	0.410	47.5	11.8	4.8	20.1
285	thermal	4.0	0.520	7.4	8.4	0.9	7.6
285	thermal	29.7	0.475	19.9	7	3.0	10.0

**Table 3** Characteristics of the DAT prepolymers structure

Temp. (°C)	Initiator (mol dm <sup>-3</sup> )	-Δ[C=C] (%)	U	P	P'	B	P <sub>c</sub> /P (%)
80	AIBN; 0.01	3.7	0.463	21.9	25.8	1.0	9.5
80	AIBN; 0.02	13.2	0.431	50.8	18.8	3.1	12.7
160	CHP; 0.0025	3.7	0.489	17.8	19.0	1.0	7.8
160	CHP; 0.0025	7.2	0.456	26.2	-	-	12.6
160	CHP; 0.0025	15.6	0.433	40.6	15.0	3.1	15.9
230	thermal	3.6	0.519	9.3	9.7	1.0	6.9
230	thermal	12.8	0.496	12.2	9.7	1.3	9.0
230	thermal	23.0	0.445	42.7	9.3	4.9	13.3
285	thermal	3.5	0.569	6.6	6.4	1.0	1.4
285	thermal	29.3	0.482	16.7	6.0	2.9	9.6

**Table 4** Influence of the monomer structure on the kinetic chain length and the degradative transfer<sup>a</sup> share at the polymerization temperature 160°C

Monomer	$\nu f$	$\frac{k_d}{k_e + k_d} \frac{1}{f}$
DAP	524	0.044
DAI	566	0.033
DAT	537	0.035

<sup>a</sup> Initiated by cumene hydroperoxide (0.001 mol dm<sup>-3</sup>); symbols as in the text

polymerization initiated by cumene hydroperoxide at a concentration of 0.001 mol dm<sup>-3</sup> has been made until reaction of the initiator is completed.

The results of comparative determination of the length of kinetic chain ( $\nu f$ ) and the share of the degradative transfer are presented in Table 4. These results show that, increasing the temperature from 160°C, even with the assumption that the initiation effectivity coefficient  $f=1$ , the participation of degradative transfer in the total transfer reaction does not exceed a small percentage. Thus, starting from this temperature, the penultimate term in equation (7) may be dropped. With this consideration, the values  $P_c/P$  at temperatures above 160°C have been calculated (Tables 1–3).

It will be seen, for DAP prepolymers (Table 1), that degree of cyclization of monomer units ( $P_c/P$ ) is, at each of the temperatures (80, 160, 230 and 285°C) independent of the conversion. This fact coincides with results obtained by Matsumoto and his coworkers<sup>2,8</sup>, who have proved that for DAP (*ortho* isomer) the rings generally result from the reaction of growing radical with the double bond of the same monomer unit. With such an intramolecular mechanism of chain cyclization, the degree of cyclization of DAP monomer units would depend only to a very slight degree on the polymer concentration in a reaction mixture. We have observed that the values of  $P_c/P$  for DAP prepolymers will change with the polymerization temperature. So at temperatures elevated from 80°C to 160°C, the ratio will be augmented from 38% to ca. 44%, and then reduced to about 41% at 230°C and about 33% at 285°C.

According to Oiwa and Matsumoto<sup>2</sup>, the increase of cyclization with temperature might be caused by a slightly higher activation energy of the intramolecular addition (cyclization) than the activation energy of the intermolecular addition (propagation). We would suggest that the chain transfer might also have an effect on the number of cyclic structures. In the range of temperatures up to 160°C, this reaction interferes with  $P_c/P$ , but only to

a negligible extent, since the ratio of the total rate of double-bond addition (cyclization and propagation) to the transfer reaction rate undergoes quite small changes, exemplified by comparatively small alterations in  $P'$  (Table 1). The  $P'$  value will, however, be markedly decreased if the temperature is elevated above 160°C. Accordingly, it is suggested that the transfer reaction rate would be increased in comparison with the total rate of addition reaction, which may be interpreted as a result of a higher activation energy of the transfer reaction. Hence the chain transfer is likely to become competitive with the cyclization reaction to cause the observed effect of decreasing the cyclic structure content.

The ratio of cyclized monomer units ( $P_c/P$ , Table 2) for DAI prepolymers will be smaller than that for DAP prepolymers; moreover it increases markedly, at any given temperature, as the conversion proceeds. These results indicate that for DAI (*meta* isomer), the cyclic structures arising from multiple interchain bonds (Figure 2) are of greater importance than those of the *ortho* isomer (DAP).

The decrease of  $P_c/P$  for DAI prepolymers with increasing temperature, visible at an early stage in polymerization ( $-\Delta[C=C] \leq 4\%$ ) in the range of temperature above 160°C, might be interpreted as the minor probability of the cyclization taking place due to the increase in the rate of the chain transfer reaction with temperature.

The degree of cyclization of monomer units, at each of the temperatures, is evidently lower for DAT prepolymers than for DAP and DAI, respectively (Table 3). Values of  $P_c/P$  at an early stage of polymerization, at which the simple chains are predominant ( $B=1$ ), are quite small at each of the temperatures, and decrease with rising temperature from ca. 9.5% at 80°C to ca. 1.4% at 285°C. Because the cyclization within one diallyl terephthalate monomer unit is impossible<sup>5</sup>, the chain cyclization for DAT is likely to occur only as a reaction of a growing free radical chain end with earlier attached monomer units. Accordingly, the decrease in  $P_c/P$  with a rise in temperature, at an early stage in polymerization, is the first consequence of diminished probability of this cyclization type as the chain shortening proceeds. The competitive chain-transfer reaction, increasing in rate with temperature, might also be of some significance for the decrease in  $P_c/P$  values of DAT prepolymers likely, as for DAP and DAI. In addition to this, the values increase distinctly, at each temperature, with increasing double-bond conversion. Likewise, for DAI, this may be interpreted as an increased number of cyclic structures arising from the formation of interchain bonds.

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