Peculiar Thermal Behavior of Diallyl Oxalate Prepolymer

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Synopsis

First, the thermal behavior of diallyl oxalate prepolymer (PDAO) at 130–300°C was preliminarily compared with diallyl phthalate prepolymer; PDAO was self-curable and degraded easily accompanying the evolution of gas. Next, the thermal degradation of PDAO was investigated in detail by TG. The TG curve of PDAO compared with those of various diallyl dicarboxylate prepolymers was peculiar suggesting two stages of thermal degradation processes with two maximum degradation temperatures, although the first stage is relevant to the significant release of carbon dioxide. In addition, the effect of the structural units, involving uncyclized, cyclized, and crosslinked units, on the thermal degradation of PDAO was examined; the thermal degradation rate was reduced with an increase in the cyclized units and was independent of the content of crosslinked units. From these results, the thermal degradation mechanism of PDAO is briefly discussed in terms of a radical mechanism.

INTRODUCTION

We have extensively investigated the radical polymerization of a variety of diallyl dicarboxylates in terms of cyclopolymerization, cyclocopolymerization, and gelation.[1-8] In the course of these investigations, we have found that the polymerization behavior of diallyl oxalate (DAO) is peculiar in comparison with a series of diallyl aliphatic and aromatic dicarboxylates.[4,6] Thus, the polymerization of DAO at elevated temperatures was accompanied by the evolution of carbon dioxide, suggesting the occurrence of the dismutation of the uncyclized growing radical[4]; the significance of this mutation was further demonstrated in the polymerization of several alkyl allyl oxalates[9] and DAO prepolymer (PDAO).[10]

Here it should be noted that the thermal decomposition of some organic oxalates with a central oxalate bond joining two positively polarized atoms[11] has been studied by several investigators[12-19]: For example, the liquid-phase thermal decomposition of dialkyl oxalates of tertiary alcohols containing β hydrogens gave the corresponding alkene and oxalic acid at 150°C, suggesting an ion-pair mechanism, i.e., the intramolecular transfer of a hydrogen atom from each of the β carbon atoms to the adjacent carbonyl group, although the primary and secondary dialkyl oxalates resisted decomposition up to 325°C.[13] Whereas the vapor-phase thermal decomposition of dibenzyl oxalate[15] and diallyl oxalate,[17] whose product radicals possess an appreciable stabilization energy in conjunction with an absence of labile hydrogen atoms at the β carbon atom, gave carbon

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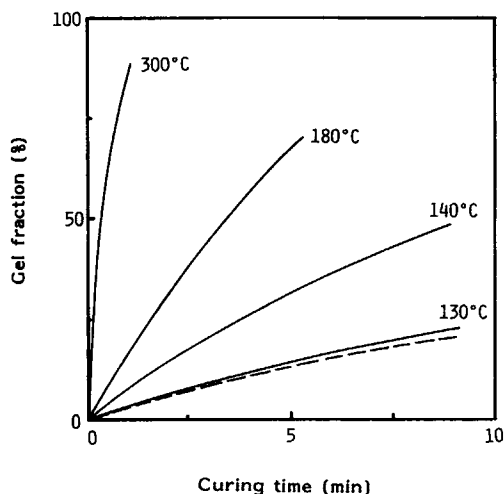* To whom correspondence should be addressed.

Fig. 1. Time dependence of the percentage gel fraction of the cured products in the curing of PDAO-1 at different temperatures: (---) curing result of PDAP at 150°C for comparison.

dioxide and the corresponding radicals by a radical mechanism. The low-pressure vapor phase pyrolysis of di(α-substituted benzyl)oxalates which contain β hydrogen atoms underwent an elimination reaction in addition to homolytic decomposition to α-substituted benzyl radicals.[19]

In this connection, the PDAO and DAO precopolymer were self-crosslink-able,[20] probably due to their post-polymerization initiated by the radicals produced via a homolytic thermal decomposition. Thus, the present article deals with the elucidation of the peculiar thermal behavior of PDAO.

EXPERIMENTAL

Materials. PDAO-1,[21] diallyl malonate prepolymer (PDAM),[21] diallyl succinate prepolymer (PDASu),[21] diallyl phthalate prepolymer (PDAP),[22] diallyl isophthalate prepolymer (PDAI),[23] diallyl terephthalate prepolymer (PDAT),[23] poly(allyl benzoate) (PABz),[24] and poly(allyl methyl oxalate) (PAMO)[9] were prepared at less than 10% conversion by the bulk polymerization using benzoyl peroxide (BPO) as initiator at 80°C, as described previously.

PDAO-2–4 were prepared by the solution polymerizations using benzene as solvent.

Thermogravimetry (TG). A Shimazu DT-30/TG-30 thermal balance was used to obtain TG curves. About 8 mg of each sample was heated in a nitrogen atmosphere from room temperature to 500°C at a heating rate of 10°C/min as the common procedure; otherwise, the conditions of measurements will be given.

RESULTS AND DISCUSSION

Preliminary Thermal Behavior of PDAO Compared with PDAP. The thermal behavior of PDAO was tentatively examined as compared with com-
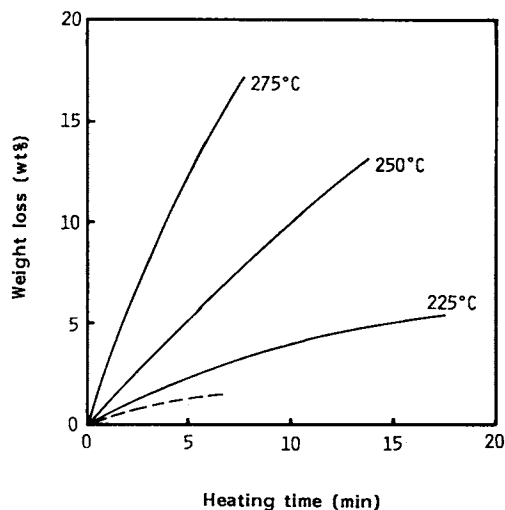
Fig. 2. Time dependence of the weight loss in the isothermal degradation of PDAO-1 at different temperatures: (- - -) thermal degradation of PDAP at 275°C for comparison.

mercially important PDAP.   Figure 1 shows the dependence of the percentage gel fraction of the cured products on the curing time in the curing of PDAO-1 and PDAP at different temperatures without the usual curing agents such as organic peroxides.   The gelation of PDAO was remarkably enhanced compared with PDAP.   In this connection, the decrease in saponification value and the increase in carbon content were observed in the curing of PDAO-1 as opposed to no substantial change in PDAP.

Figure 2 shows the results of the preliminary thermal decomposition in which the prepolymer wrapped up in aluminum foil was heated in an oven, although
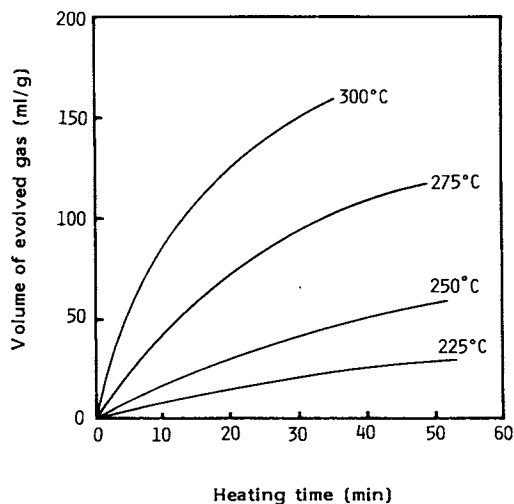

Fig. 3. Time dependence of the volume of the evolved gas in the thermal degradation of PDAO-1 at different temperatures.
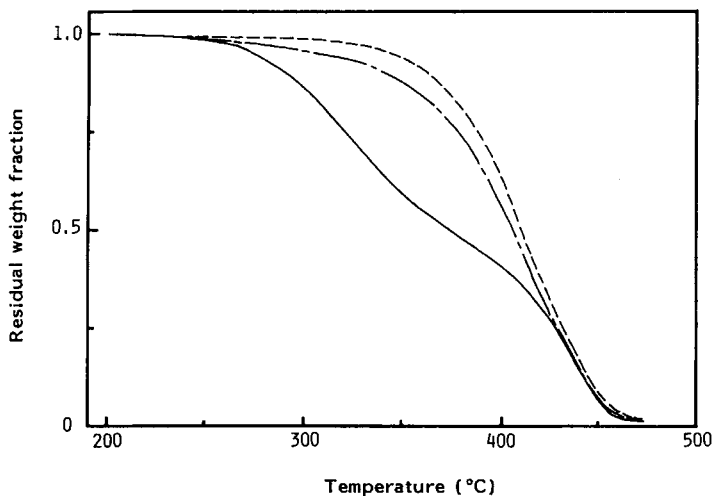
Fig. 4. TG curves for the thermal degradation of: (——) PDAO-1; (---) PDAM; (-----) PDASu. Heating rate 10°C/min.

the detailed thermal degradation behavior was followed by TG as will be described below. In the case of PDAO the decrease in weight was remarkably observed with the elevation of temperature, whereas only 1% weight loss was detected for PDAP in the heat-treatment at 275°C for 5 min. Furthermore, the volume of the evolved gas with the thermal degradation of PDAO-1 was measured as shown in Figure 3, although the analysis of the evolved gas was not done. These results may suggest the possibility of the formation of a new type of foamed thermosetting resins.

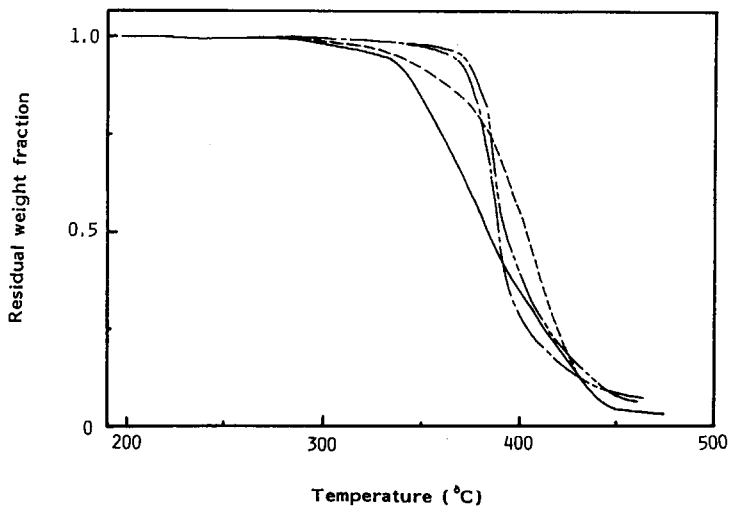Thus, the thermal behavior of PDAO was rather peculiar compared with PDAP

Fig. 5. TG curves for the thermal degradation of: (——) PDAP; (---) PDAI; (----) PDAT, (-----) PABz. Heating rate 10°C/min.
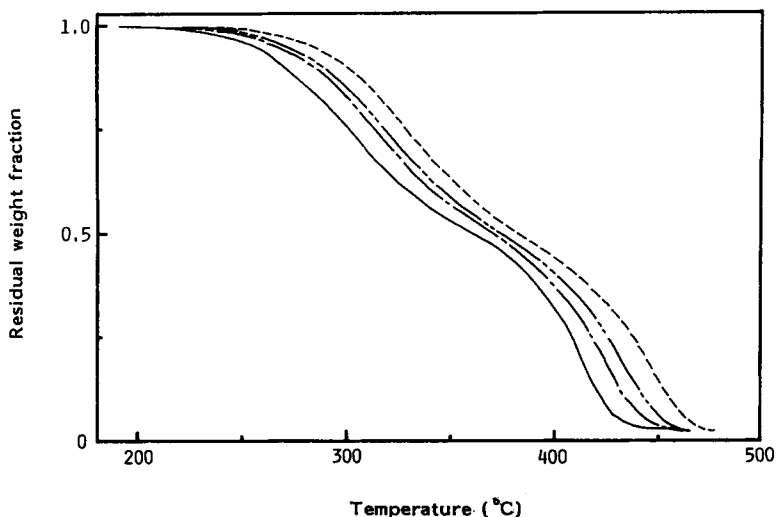
Fig. 6. TG curves for the thermal degradation of PDAO-1 at different heating rates (°C/min): (——) 2; (---) 5; (----) 10; (-----) 15.

and therefore, the thermal degradation of PDAO was followed in detail by TG.

Comparison of TG Curves of Various Diallyl Dicarboxylate Prepolymers. The thermal degradation behavior of PDAO by TG was compared with a variety of diallyl dicarboxylate prepolymers: Figure 4 shows the TG curves for the programmed heating degradation of PDAO-1, PDAM, and PDASu as diallyl aliphatic dicarboxylate prepolymers and in Figure 5 the TG curves of
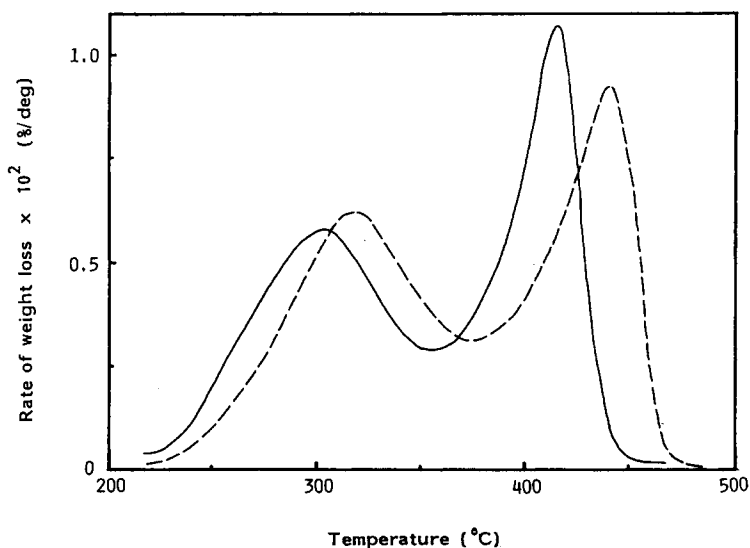

Fig. 7. The rate of weight loss as a function of increasing temperature in the thermal degradation of PDAO-1 at heating rates of (——) 2 and (-----) 10°C/min.
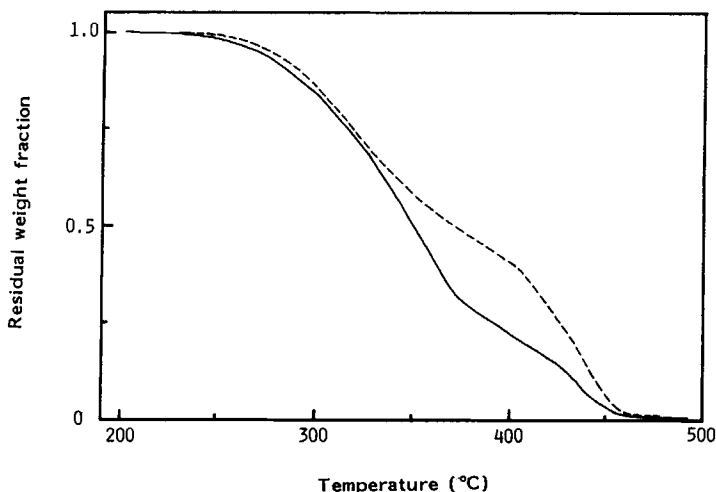
Fig. 8. TG curve for the thermal degradation of PAMO: (- - -) thermal degradation of PDAO-1 for comparison.

PDAP, PDAI, and PDAT as diallyl aromatic dicarboxylate prepolymers are illustrated along with that of PABz as monoallyl aromatic monocarboxylate polymer for comparison. These polymers degraded at a temperature range of 200–500°C and the temperature of onset of degradation increased in the order PDAO < PDAM < PDAP < PABz < PDASu < PDAI < PDAT. Noteworthily, the TG curve of PDAO was peculiar as suggesting two stages of thermal degradation processes with two maximum degradation temperatures at 320°C and 440°C; then, the peculiar thermal degradation of PDAO was examined in detail.

Peculiar Thermal Degradation of PDAO. Figures 6 and 7 show the weight loss and rate of weight loss as a function of increasing temperature in the thermal degradation of PDAO-1 at different heating rates of 2°C/min, 5°C/min, 10°C/min, and 15°C/min. Clearly, two stages of thermal degradation processes were observed; the first stage may correspond to the significant release of carbon dioxide as reasonably expected from the above-mentioned results. In this connection, the PDAO recovered after the programed heating up to 380°C, which is an intermediate point between the first and second maximum degradation temperatures was subjected to elemental analysis giving the carbon and hydrogen contents of 71.9% and 8.8%, respectively, as opposed to those of 56.5% and 5.9% for the original PDAO. The increase in both carbon and hydrogen contents, i.e., the decrease in the oxygen content of the recovered PDAO compared to the original one is in conformity with the occurrence of a significant release of carbon dioxide. Moreover, the thermal degradation of PAMO, the AMO monomer which is a mono-ene counterpart of DAO monomer, was followed by TG, as shown in Figure 8; the thermal degradation process was quite similar to PDAO, and, interestingly, the weight loss after the first stage degradation was around 70% as is in line with the value of 72.2% calculated by assuming that the first stage degradation of PAMO corresponds to the evolution of carbon dioxide and methane.
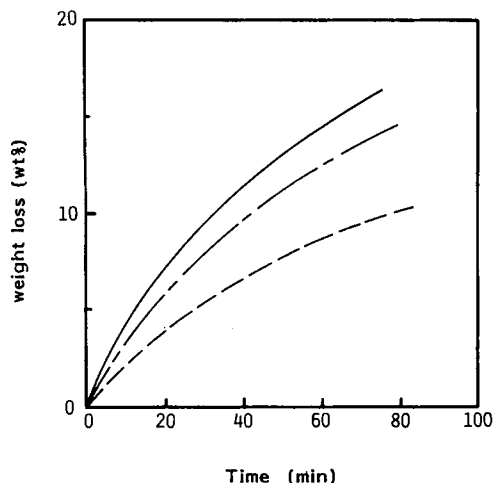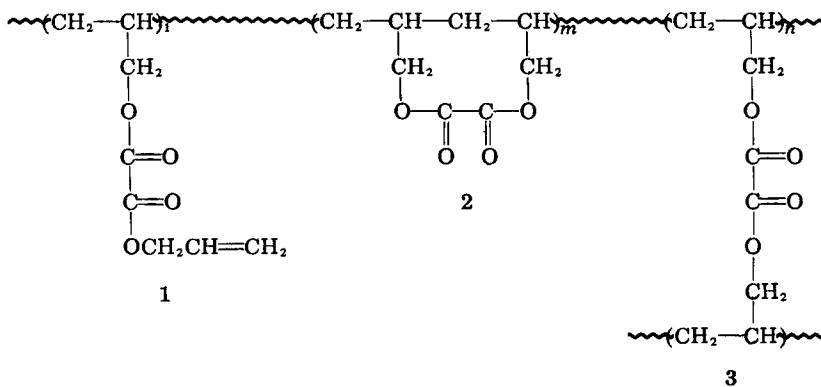
Fig. 9. Time dependence of the weight loss in the isothermal degradation of (——) PDAO-2, (—·—) PDAO-3, and (- - - - -) PDAO-4 carrying different amounts of cyclized units at 250°C.

Effect of Structural Units on Thermal Degradation of PDAO. The structure of PDAO is depicted as follows:

DAO is a cyclopolymerizable monomer, the cyclization constant K_c of which is 3.6 mol/L[21], and thus, the PDAO's carrying different amounts of cyclized units 2 were prepared by the cyclopolymerization in benzene solution using BPO as the initiator at 80°C. Figure 9 shows the time dependency of the thermal degradation of PDAO's of the cyclized unit contents $m/(1 + m + n) = 0.25$(PDAO-2), 0.36(PDAO-3), and 0.63(PDAO-4), at 250°C, the weight loss being measured isothermally by TG. The thermal degradation rate was reduced with an increase in the cyclized units. Next, the effect of the crosslinked units 3 was examined: In the polymerization of DAO the crosslinking reaction between the pendant double bond of the prepolymer produced and the growing chain radical gradually becomes important as the polymerization proceeds.[1] Thus, DAO was polymerized in bulk using 0.05 mol/L of BPO at 80°C for 180 min and the PDAO-5 produced was characterized as follows: conversion, 23.7%; $\overline{P}_n$, 97.4; $\overline{P}_w/\overline{P}_n$, 9.6. The polydispersive PDAO-5 thus obtained was precipitation-fractionated from an acetone–methanol system and the resulting PDAO-5′ ($\overline{P}_n = 44$, $\overline{P}_w/\overline{P}_n = 1.4$)
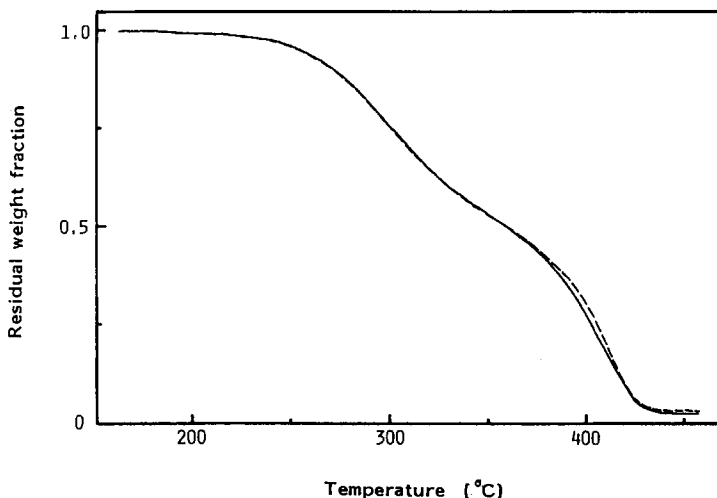
Fig. 10. TG curves for the thermal degradation of (——) PDAO-5' and (-----) PDAO-5'' carrying different amounts of crosslinked units.

and PDAO-5'' ($\overline{P}_n$ = 344, $\overline{P}_w/\overline{P}_n$ = 4.7) were subjected to TG measurement. Figure 10 shows the TG curves; both results were quite coincident, regardless of the degree of polymerization, i.e., the content of crosslinked units.

Mechanistic Discussion. On the basis of the results shown above, we will briefly discuss the thermal degradation mechanism of PDAO. From James and Kambanis's result[17] of the vapor-phase thermal decomposition of diallyl oxalate it is expected that the thermal degradation of PDAO starts at the uncyclized unit 1 since the resulting allyl radical possesses an appreciable stabilization energy. This expectation may coincide with the result of Figure 9 in which the thermal decomposition of cyclized unit was reduced compared to the uncyclized unit. However, the result of Figure 8 is in conflict with the above expectation, in which the thermal degradation of PAMO producing unstable methyl radical were easier compared to PDAO. Here it should be recalled that PDAO was self-crosslinkable. Thus the radicals generated initially by the partial decomposition of uncyclized units may induce the post-polymerization of PDAO converting uncyclized units into crosslinked ones, and, eventually, the thermal decomposition of crosslinked units may become an essential reaction responsible for the first stage degradation of PDAO. This may be in line with the result shown in Figure 10.

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