Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Studies of the Polymerization of Diallyl Compounds. XL. Correlation between Addition Modes and Evolution of Carbon Dioxide in the Polymerization of Diailyl Oxalate

Masataka Yamawaki[a]; Manabu Kikuta[a]; Akira Matsumoto[a]; Masayoshi Oiwa[a]
[a] Department of Applied Chemistry Faculty of Engineering, Kansai University, Suita, Osaka, Japan

To cite this Article Yamawaki, Masataka , Kikuta, Manabu , Matsumoto, Akira and Oiwa, Masayoshi(1984) 'Studies of the Polymerization of Diallyl Compounds. XL. Correlation between Addition Modes and Evolution of Carbon Dioxide in the Polymerization of Diailyl Oxalate', Journal of Macromolecular Science, Part A, 21: 2, 207 — 214

To link to this Article: DOI: 10.1080/00222338408056549

URL: http://dx.doi.org/10.1080/00222338408056549

J. MACROMOL. SCI.–CHEM., A21(2), pp. 207-214 (1984)

Studies of the Polymerization of Diallyl Compounds. XL. Correlation between Addition Modes and Evolution of Carbon Dioxide in the Polymerization of Diallyl Oxalate

MASATAKA YAMAWAKI, MANABU KIKUTA,
AKIRA MATSUMOTO,* and MASAYOSHI OIWA

Department of Applied Chemistry
Faculty of Engineering
Kansai University
Suita, Osaka 564, Japan

ABSTRACT

The occurrence of head-to-head (HH) addition in the radical polymerization of diallyl oxalate (DAO) was examined under various polymerization conditions. The content of HH linkage in poly(DAO) was reduced in comparison with allyl acetate and diallyl succinate; this may be ascribed to the high polarity of DAO inducing a polar effect on the intermolecular propagation of the growing polymer radical, resulting in reduced HH addition. The correlation between addition modes and evolution of carbon dioxide characteristic of DAO polymerization at elevated temperatures is mechanistically discussed in detail, with special focus on the solvent effect and the reduced dismutation of the cyclized radical compared to the uncyclized one.

---

*To whom correspondence should be addressed.

0022-233X/84/2102-0207$3.50/0

INTRODUCTION

In our earlier articles [1-4] it was found that in the radical polymerization of allyl compounds a remarkable anomalous head-to-head (HH) addition occurs compared with common vinyl monomers. This has been interpreted by considering that allyl compounds are typical unconjugated monomers and, therefore, the difference in the resonance stability between two types of intermediate radicals, the secondary or tertiary head and primary tail radicals, formed through head-to-tail (HT) and HH additions is small, implying reduced reaction selectivity governed by the thermodynamic stability of the resulting radicals in comparison with the cases of common vinyl monomers. Thus the selectivity of addition modes is governed significantly by other factors than the thermodynamic stability of the resulting radicals. The occurrence of HH addition was enhanced by an increase in the bulkiness of the acid moiety of monoallyl carboxylates as reflected in the side group steric hindrance of the resulting polymers [1-3]. The intramolecular addition modes in the cyclopolymerization of diallyl and dimethallyl dicarboxylates were the cases studied. In the cyclopolymerization of diallyl phthalate only the cyclic polymer of an 11-membered ring was obtained [5], whereas 10-membered ring formation was observed in diallyl aliphatic dicarboxylates, including diallyl succinate (DASu) and diallyl cis-1,2-cyclohexanedicarboxylate (DACH) [2]. Also, in the cyclopolymerization of dimethallyl dicarboxylates the intramolecular HH addition was highly enhanced compared with the corresponding diallyl dicarboxylates [3].

On the other hand, the polymerization of diallyl oxalate (DAO) at elevated temperatures was accompanied by the evolution of carbon dioxide due to the dismutation of the uncyclized growing polymer radical to yield the allyl radical, carbon dioxide, and a polymer carrying a terminal double bond [6]. Here it should be noted that the unimolecular dismutation inevitably competes with intramolecular or intermolecular HT or HH propagations as reactions of the uncyclized growing polymer radical.

The present article is concerned with the elucidation of addition modes in the radical polymerization of DAO. The correlation between HH addition and evolution of carbon dioxide is discussed.

EXPERIMENTAL

Purification of DAO and DASu as monomers, benzoyl peroxide (BPO) and dicumyl peroxide (DCPO) as initiators, and diethyl phthalate (DEP) and benzonitrile (BN) as solvents, polymerization procedure, analysis of polymers, and determination of evolved gas and reacted allyl groups were conducted as described previously [6].

The determination of HH linkage in the poly(DAO) was made according to the method described in our previous article [5]; thus poly(DAO) was converted to poly(allyl acetate) (poly(AAc)) which was subsequently subjected to ^{13}C-NMR analysis to estimate HH linkage.

RESULTS AND DISCUSSION

Dependence of Addition Modes on Polymerization Temperature

Bulk polymerizations of DAO were carried out at 80, 100, 130, and 150°C, and the polymers obtained at around 15% conversion were subjected to a determination of the HH linkage content. The derived poly(AAc)'s had number-average degrees of polymerization of 31.4, 24.2, 17.4, and 15.9, respectively. This decreasing tendency with temperature was discussed in our previous article [6].

Figure 1 shows the dependence of the percentage of HH linkage in the polymer on the polymerization temperature for the bulk polymerization of DAO, along with the results of AAc [1] and DASu for com-

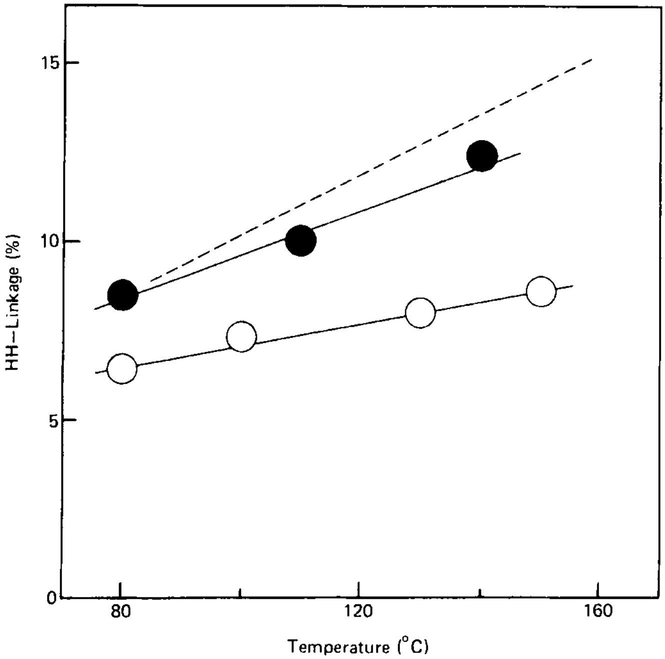

FIG. 1. Dependence of the percentage of HH linkage in the polymer on polymerization temperature for the bulk polymerizations of (○) DAO, (●) DASu, and (- -) AAc.

parison. That HH addition is enhanced with temperature is a reflection of the higher activation energy of HH addition than of HT addition. The difference in activation energy, $E_{HH} - E_{HT}$, is 1.75 kcal/mol for vinyl acetate polymerization [7] and 2.5 kcal/mol for AAc polymerization [1]. Moreover, HH linkage content in the poly(DAO) was appreciably reduced compared to AAc and DASu. Here it should be recalled that in the polymerization of allyl compounds as typical unconjugated monomers, the reaction selectivity for HT or HH addition is small and, thus, the selectivity of addition modes is significantly governed by factors other than the thermodynamic stability of the resulting radicals, as mentioned in the Introduction. In this connection, the high polarity of DAO as compared to AAc and DASu may be relevant to the reduced HH addition because the transition state formed through the interaction of a polar growing polymer head radical with the tail site of a monomer is more stable than that with the head site of monomer as a result of the reduced electrostatic repulsion of the former compared to the latter.

Correlation between Addition Modes and Evolution of Carbon Dioxide

The polar effect on the intermolecular propagation of a growing polymer radical, as mentioned above, may be concerned with the evolution of carbon dioxide at the elevated temperatures characteristic of the polymerization of DAO [6]. Here the unimolecular dismutation of the uncyclized growing polymer head radical, i.e., Eq. (1), essentially competes with the intramolecular or intermolecular HT or HH additions, i.e., Eqs. (2)-(5), as depicted in Fig. 2.

Thus the reaction in Eq. (1) may reflect the reduced occurrence of intermolecular propagations, i.e., Eqs. (4) and (5); this provides another type of driving force for the occurrence of dismutation in the polymerization of DAO at elevated temperatures, in addition to the release of stable carbon dioxide molecules and the allyl radical [6]. In this connection, the solvent effect on the evolution of carbon dioxide was examined because the increased occurrence of dismutation is expected in a polar medium.

Solution polymerizations of DAO were carried out in DEP and BN using 0.01 mol/L of DCPO at 130°C; Figs. 3 and 4 show the time dependence of the consumption of carbon-carbon double bonds and the evolution of carbon dioxide, respectively. The ratio of the rate of evolution of carbon dioxide to that of the consumption of carbon-carbon double bond, $\{d[CO_2]/dt\}/\{-d[C{=}C]/dt\}$, estimated from the initial slopes of Figs. 3 and 4, were obtained as 0.140 in DEP and 0.192 in BN; the high value obtained in BN as a polar solvent is in conformity with our expectation. Moreover, the low rate of polymerization in BN, as shown in Fig. 3, may be relevant to the polar effect on the intermolecular propagation of the growing polymer radical.

The above discussion is also concerned with the fact that the cy-

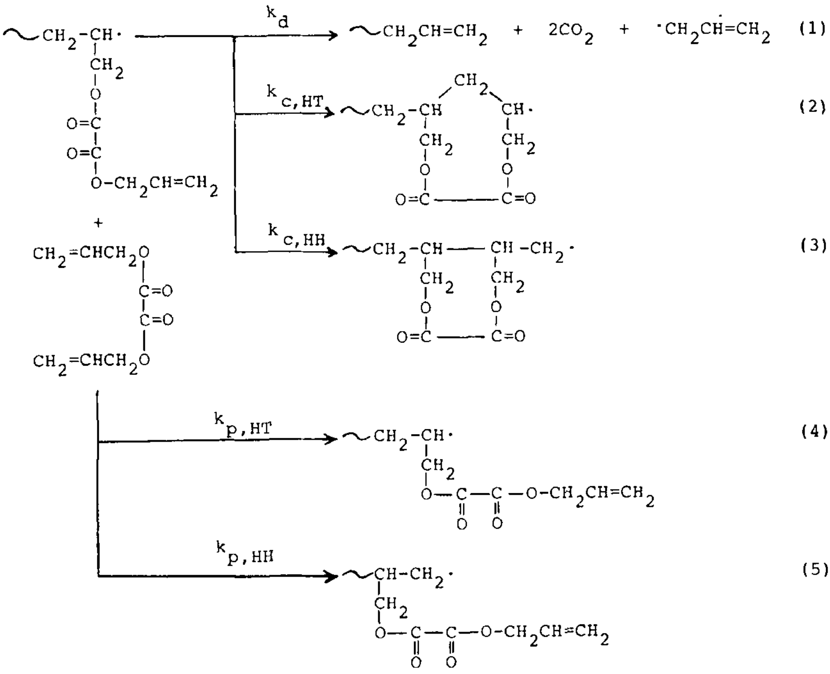

FIG. 2. Reaction scheme of the uncyclized growing polymer head radical.

clized growing polymer radical is reluctant to evolve carbon dioxide [6]. Here it should be noted that two types of cyclized radicals in Eqs. (2) and (3) are present. The favored formation of cyclized radical in Eq. (3), as was reasonably expected from the polymerization results of DASu and DACH [2, 3], inevitably leads to the reduced evolution of carbon dioxide because the β scission of the cyclized tail radical in Eq. (3) must occur with difficulty at carbon-carbon bonds compared to the β scission of cyclized head radical in Eq. (2) at carbon-oxygen bonds followed by the release of stable carbon dioxide molecules. In this connection, the favored occurrence of Eq. (3) should result in the increased incorporation of HH linkages into the polymer chain and, thus, the HH linkage content in the poly(AAc)'s derived from poly(DAO)'s obtained at different monomer concentrations was examined (Fig. 5). Surprisingly the HH linkage content was nearly constant and independent of monomer concentration, although the content of cyclized units in poly(DAO) increased with a decrease in monomer concentration [8], characteristic of cyclopolymerization. On the other hand, the unimolecular dismutation of another type of cyclized head

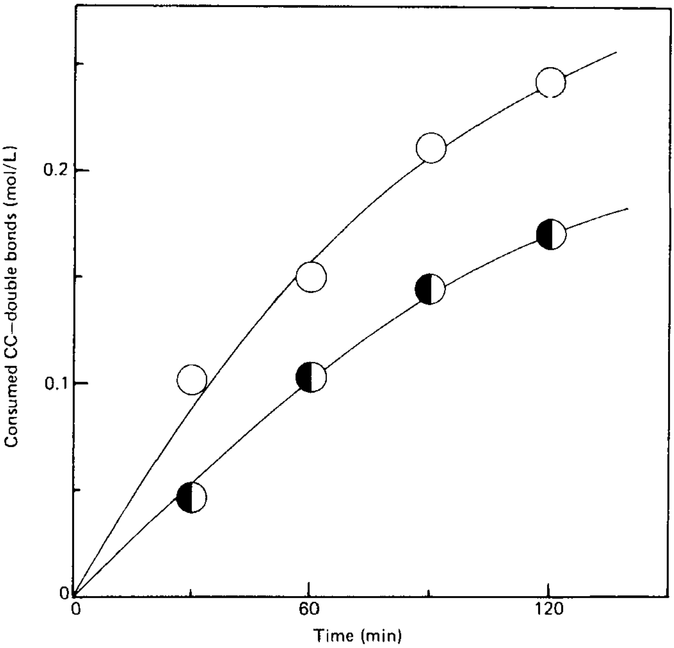

FIG. 3. Time dependence of the consumption of carbon-carbon double bonds in the solution polymerizations in (○) DEP and (◐) BN using 0.01 mol/L of DCPO at 130°C.

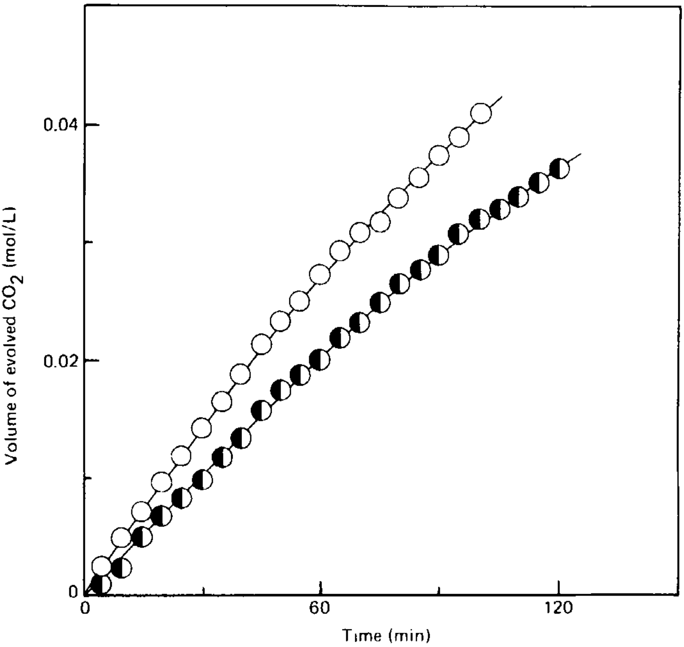

FIG. 4. Time dependence of the evolution of carbon dioxide in the solution polymerizations in (○) DEP and (◐) BN using 0.01 mol/L of DCPO at 130°C.

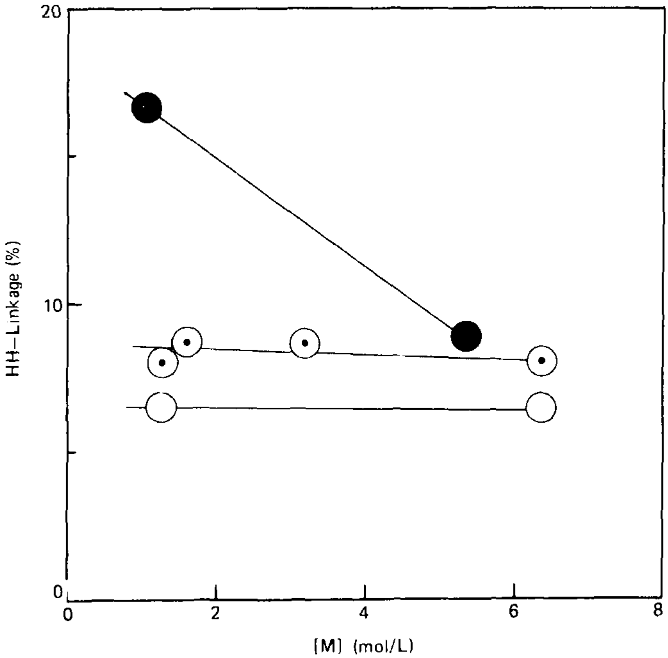

FIG. 5. Dependence of the percentage of HH linkage in the polymer on monomer concentration for the polymerizations of DAO at (○) 80 and (⊙) 130°C as compared with that of DASu at (●) 80°C, DEP being used as a solvent.

radical formed via Eq. (2) may be somewhat suppressed compared to uncyclized head radical as a reflection of the promotion of the competitive, bimolecular propagation with DAO monomer, since the incorporation of a cyclized structure into the polymer chain would somewhat reduce the steric crowding and polar nature of the growing polymer radical because the carbon numbers of a backbone polymer chain increases by four with the formation of a cyclized unit.

REFERENCES

[1] A. Matsumoto, K. Iwanami, and M. Oiwa, J. Polym. Sci., Polym. Lett. Ed., 18, 211 (1980).
[2] A. Matsumoto, K. Iwanami, and M. Oiwa, J. Polym. Sci., Polym. Chem. Ed., 19, 213 (1981).
[3] A. Matsumoto, K. Iwanami, and M. Oiwa, J. Polym. Sci., Polym. Lett. Ed., 19, 497 (1981).

[4] A. Matsumoto, K. Iwanami, N. Kawaguchi, and M. Oiwa, Technol. Rep. Kansai Univ., 24, 183 (1983).

[5] A. Matsumoto, K. Iwanami, and M. Oiwa, J. Polym. Sci., Polym. Lett. Ed., 18, 307 (1980).

[6] A. Matsumoto, I. Tamura, M. Yamawaki, and M. Oiwa, J. Polym. Sci., Polym. Chem. Ed., 17, 1419 (1979).

[7] K. Hayashi and T. Otsu, Makromol. Chem., 127, 54 (1969).

[8] A. Matsumoto and M. Oiwa, J. Polym. Sci., Part A-1, 8, 751 (1970).

Accepted by editor June 15, 1983
Received for publication July 13, 1983