

Oligoethylenes in High Pressure Polyethylenes

II. Production Mechanism

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Summary

Elucidation of the mechanism for the production of a variety of oligoethylenes produced in high pressure ethylene polymerization revealed important features of actually occurring radical reactions. Several definite types of radical cyclization reactions are found to be very common in high pressure ethylene polymerization.

Introduction

In the preceding paper (TAKAHASHI et al. 1980) we reported a variety of oligoethylenes extracted from commercial samples of high pressure polyethylene. The production mechanism of those oligoethylenes is discussed in this paper.








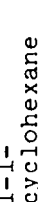
Experimental Facts

Table 1 shows the kinds (structures) and the relative amounts of the oligoethylene homologues present in some representative commercial samples of high pressure polyethylene. The relative amounts were roughly estimated on the basis of integrator readings of GC peak areas. The oligoethylenic compositions varied greatly among the resins and the oligoethylenes fell into three types. The first type appeared in only particular resins, the second in almost all the resins, and the third was the hybrid of the both, i.e., it appeared in almost all the resins, but its amount was unusually high in particular resins.

The differences in the structures and amounts of oligoethylenes are supposed to be the reflections of the differences in the reactions producing them. The first type of oligoethylenes is considered to be due to the particular chain transfer agent, the second one to the common component of polymerization, i.e., the ethylene monomer itself, and the third one to both origins.

TABLE 1 Oligoethylene Compositions (%) of Various Commercial Samples of High Pressure Polyethylene

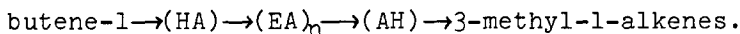
Oligoethylenes	Polyethylene Samples													
	A	B	C	L	E	F	G	H	I	N				
alkane (even carbon numbers)	41	11	15	11	10	10	15	7	6	8				
do. (odd)	2	22	7	10	17	13	13	6	5	10				
2-methylalkane	-	23	-	-	-	-	-	-	-	-				
3-methylalkane	3	2	35	2	3	3	2	3	5	3				
5-methylalkane	1	-	-	19	3	1	5	-	2	1				
3-ethylalkane	1	-	-	4	3	2	1	1	4	2				
4-ethylalkane	1	-	-	14	3	2	7	-	2	-				
5-ethylalkane	1	1	4	3	4	2	4	1	3	1				
2,2-dimethylalkane	-	-	3	-	-	-	5	-	-	-				
5,5-diethylalkane	3	7	5	4	6	3	3	4	6	10				
3-ethyl-3-methylalkane	2	1	4	2	2	3	1	4	3	3				
5-ethyl-5-methylalkane	1	-	2	1	2	1	1	-	1	1				
1-alkene (even)	9	2	4	3	7	4	3	-	4	4				
1-alkene (odd)	3	2	3	2	5	23	-	5	4	1				
2-alkene	-	-	-	-	-	-	6	-	-	-				

2-methyl-1-alkene	$C=C-C-(C-C)_n$	-	-	-	-	-	-	-	-	-	30	-	-
2-ethyl-1-alkene (even)	$C=C-C^2-(C-C)_n$	4	5	-	3	5	2	2	-	-	5	6	-
do. (odd)	$C=C-C-C-(C-C)_n$	2	4	4	4	4	3	2	2	4	4	4	-
3-methyl-1-alkene	$C=C-C-C-(C-C)_n$	-	-	-	-	-	-	5	-	-	-	-	-
alkylcyclopentane		9	11	14	15	16	12	14	15	25	27	-	-
alkylcyclohexane (odd)		-	-	-	-	1	5	-	-	-	-	-	-
2-cyclohexylalkane		-	-	-	-	-	-	6	-	-	-	-	-
1-alkyl-trans-2-methylcyclohexane		-	-	-	-	-	-	1	-	-	-	-	-
1-alkyl-cis-2-methylcyclohexane		-	-	-	-	-	-	1	-	-	-	-	-
1-alkyl-1-methylcyclohexane		-	-	-	-	-	-	-	-	2	-	-	-
1-alkyl-1-ethylcyclohexane		-	-	-	-	-	-	1	3	-	-	-	-
2-methyl-2-alkanol	$HO-C-C-(C-C)_n$	-	-	-	-	-	-	-	-	-	6	-	-
4-alkyl-5-propyl-5-pentanolid		-	-	-	-	-	-	-	-	-	-	12	-
Miscellaneous including Unidentified		17	9	0	3	9	11	2	17	15	7	-	-
Total		100	100	100	100	100	100	100	100	100	100	100	100

Mechanism of Production of Oligomers

In the following discussion, the abbreviations shown in Table 2 are used for space-saving. An example of the production mechanism belonging to the first type is shown in Scheme 1, where five reaction paths starting from butene-1 as chain transfer agent leading to six kinds of oligoethylene homologues are shown. The relative contributions of individual reaction paths may be calculated from the relative amounts of the final products. Based on the data of resin G shown in Table 1, the relative contributions were calculated, which are included in Scheme 1.

The route (1) of Scheme 1 may be expressed as follows.



This type of reaction route seems quite common. For example, 2-methylalkanes, 3-methylalkanes, or 2-methyl-2-alkanols have been found in Resins B, C, or I, respectively, whose productions are assumed to be due to the chain transfer agents of propane, n-butane or

Scheme 1 Oligoethylenes from Butene-1 as Chain Transfer Agent

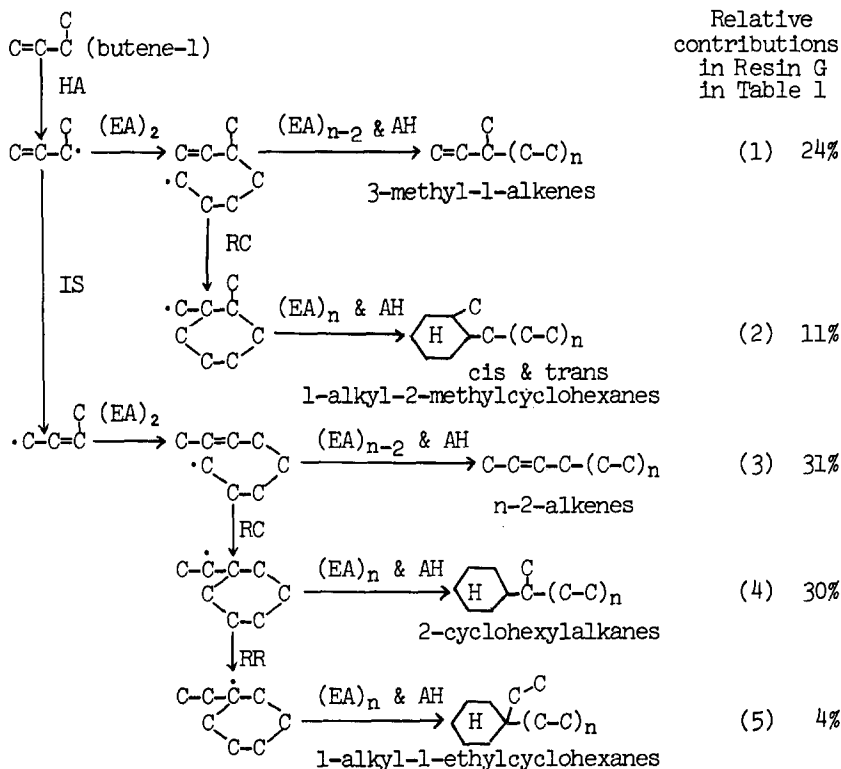


TABLE 2 Elementary Reactions

<u>Abbreviations</u>	<u>Elementary Reactions</u>	<u>Remarks</u>
AH	Acceptance of Hydrogen	$R\cdot \rightarrow R-H$
BS	β -Scission	
EA	Ethylene Addition	$(EA)_1, (EA)_2 \dots (EA)_n$ mean additions of 1,2...n molecules of ethylene
HA	Hydrogen Abstraction	$RH \rightarrow R\cdot$
IS	Isomerization	
RC	Radical Cyclization	intramolecular addition to double bond
RR	Radical Rearrangement	1,2-shift of hydrogen or methyl group
BB	Backbiting	

2-propanol, respectively.

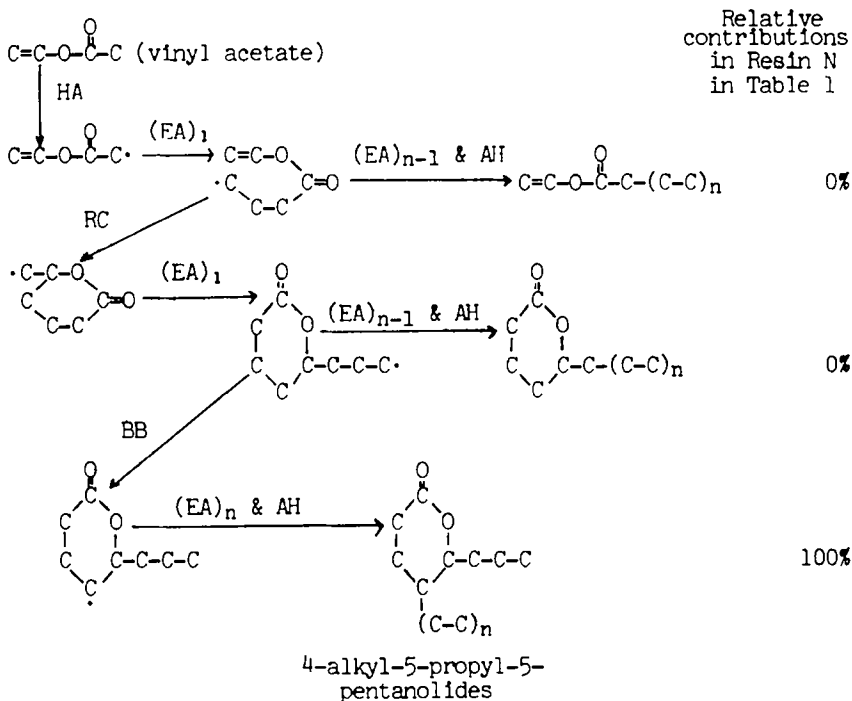
The routes (2) and (4) involve an interesting radical cyclization process (JULIA 1971) which also occurs in the case of other olefinic chain transfer agents. For propylene and isobutylene as chain transfer agents, the reaction routes are expressed as follows.

	Relative contributions in Resin F or H in Table 1
propylene	
↓ (HA)	
↓ (EA) ₂ → (EA) _{n-2} → (AH) → n-1-alkenes (odd)	80%
↓ (RC) → (EA) _n → (AH) → alkylcyclohexanes (odd)	20%
isobutylene	
↓ (HA)	
↓ (EA) ₂ → (EA) _{n-2} → (AH) → 2-methyl-1-alkenes	85%
↓ (RC) → (EA) _n → (AH) → 1-alkyl-1-methylcyclohexanes	7%
↓ (RR) → (EA) _n → (AH) → 1-alkyl-1-ethylcyclohexanes	8%

The reaction route (5) involves a radical rearrangement involving 1,2-hydrogen shift, and in the case of isobutylene as chain transfer agent, 1,2-shift of methyl group is assumed. The radical rearrangements involving 1,2-shift of hydrogen or alkyl group have not been well established (PRYOR 1966, SHIMAMURA et al. 1971), and the above proposed mechanisms need further studies.

The resin designated as N in Table 1 was actually ethylene-vinyl acetate copolymer manufactured in high pressure process, and quite unexpectedly 4-alkyl-5-propyl-5-pentanolides were found in this type of copolymer. The production mechanism was then assumed as shown in Scheme 2. It is characterized by high selectivity of the combination of RC and BB processes.

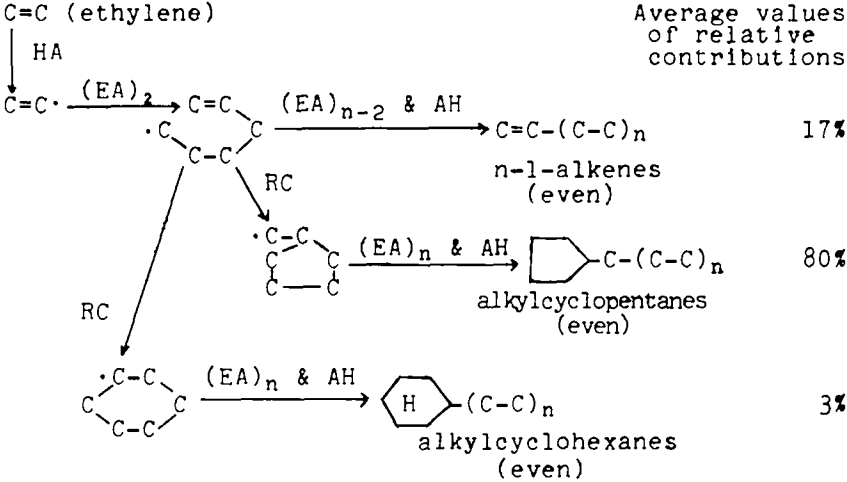
Scheme 2 Production Mechanism of 4-alkyl-5-propyl-5-pentanolide



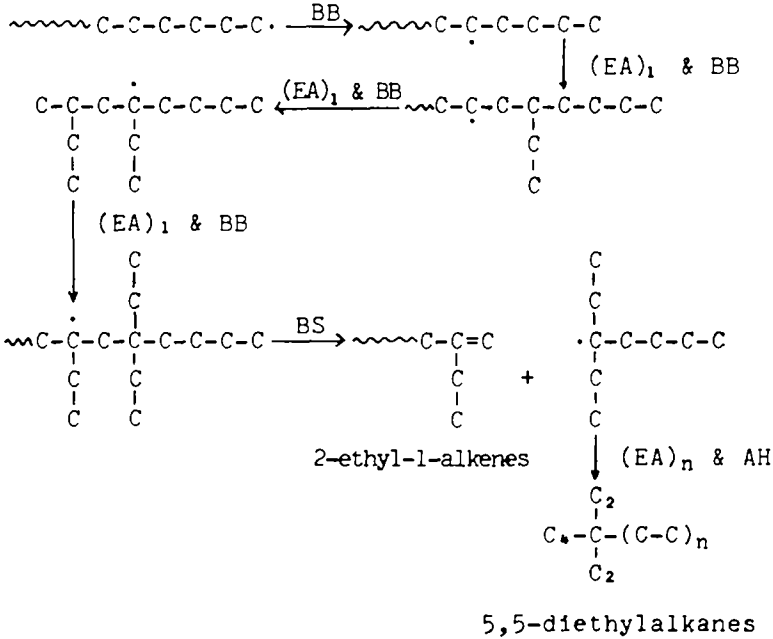
As can be seen in Table 1, the most popular oligo-ethylenes commonly appeared in all the samples are n-alkanes (odd and even carbon numbers), n-1-alkenes (odd and even), alkyl-cyclopentanes (even) and 5,5-diethyl-alkanes (odd). The productions of n-alkanes and n-1-alkenes were expected, whereas those of the latter two, i.e., alkylcyclopentanes (even) and 5,5-diethylalkanes (odd) were quite unexpected. In Scheme 3, the production mechanisms for the latter two oligo-ethylenes are proposed.

Scheme 3 Production Mechanisms of Oligoethylenes
Derived From Ethylene Only

(1) Alkylcyclopentanes of even carbon numbers



(2) 5,5-Diethylalkanes of odd carbon numbers



For the production of alkylcyclopentanes, the hydrogen abstraction from ethylene monomer is assumed first (TROTMAN-DICKENSON et al. 1951). The vinyl radical thus formed grows to 5-hexenyl radical which in turn cyclizes to the pentane ring (JULIA 1971, LAMB et al. 1963). Average values of relative contributions for the productions of n-1-alkenes, alkylcyclopentanes and alkylcyclohexanes (even) have been estimated as shown in Scheme 3.

For the production of 5,5-diethylalkanes, successive selective backbiting reactions (WU et al. 1972) must be assumed as shown in Scheme 3. Other oligoethylenes such as 3-ethylalkanes (odd) and 5-ethylalkanes (odd) are to be produced in the similar way, and another group of common oligoethylenes of 2-ethyl-1-alkenes (odd and even) are expected to be produced simultaneously with these branched alkanes as shown in Scheme 3.

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