Polymer Bulletin 4, 497–504 (1981)

Polymer Bulletin

Oligoethylenes in High Pressure Polyethylene
3. Alkylated Cycloheptanes

Mikio Takahashi, Tetsuo Satoh and Tomohiro Toya

Central Technical Research Laboratory, Nippon Oil Co., Ltd., Yokohama, 231, Japan

Summary

Series of several alkylated cycloheptanes were detected in some commercial samples of high pressure polyethylene. The structures of the alkylated cycloheptanes were found closely related to the chain transfer agents used in the polymerization process. A probable mechanism involving radical cyclization to cycloheptane structures was presented.

Introduction

In a previous paper (TAKAHASHI et al. 1980b), we reported the existence of a series of 1-alkyl-1-ethylcyclohexanes among other series of oligomers in two different categories of commercial high pressure polyethylene (HPPE) resins, that is, the one is the sample manufactured with isobutylene as a chain transfer agent and the other is the one with butene-1. A mechanism for the formation of 1-alkyl-1-ethylcyclohexanes was assumed, which required unusual reactions of 1,2-displacement of methyl or hydrogen radical. Because the identification of 1-alkyl-1-ethylcyclohexanes was ambiguous, we reexamined it and have found that they are two series of alkylated cycloheptanes instead of 1-alkyl-1-ethylcyclohexanes.

Experimental

Pertinent authentic samples were synthesized as shown briefly in Scheme 1. Their retention indices and mass spectra were measured as described earlier (TAKAHASHI et al. 1980a) and compared with those of the oligomers separated from HPPE.

Results and Discussions

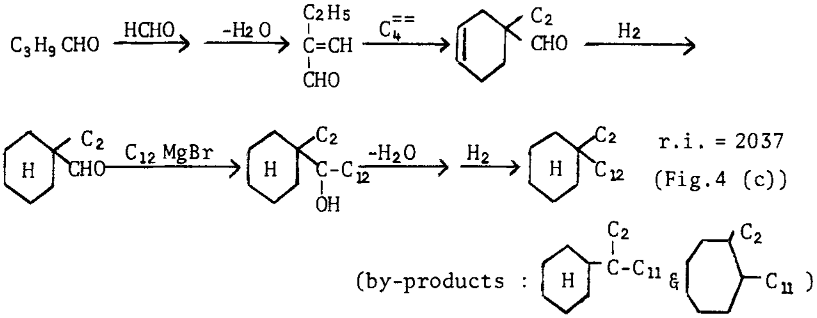
Gaschromatograms (RIC=reconstructed ion chromatogram) and masschromatograms of the oligomeric extracts from three commercial HPPE resins are shown in Figures 1, 2 and 3.

In Fig. 1, three characteristic series of peaks

0170-0839/81/0004/0497/$01.60

Scheme 1 Syntheses of Authentic Samples

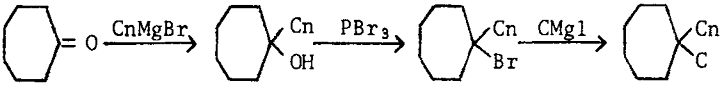
1-Alkyl-1-ethylclohexanes :



r.i. = 2037

(Fig.4 (c))

1-Alkyl-1-methylcycloheptanes :

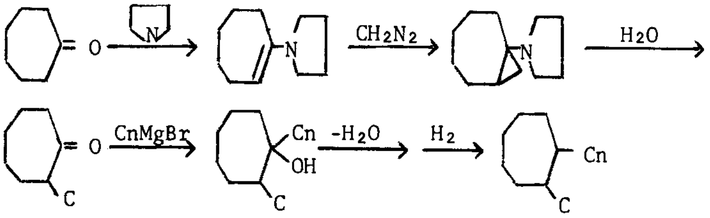


n = 8 r.i. = 1647

n = 12 r.i. = 2064

(Fig.4 (a))

1-Alkyl-2-methylcycloheptanes :

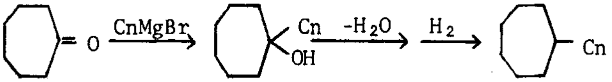


n = 8 r.i. = 1646 & 1661

n = 12 r.i. = 2062 & 2077

(Fig.4 (e))

n-Alkylcycloheptanes :



n = 8 r.i. = 1590

n = 12 r.i. = 2004

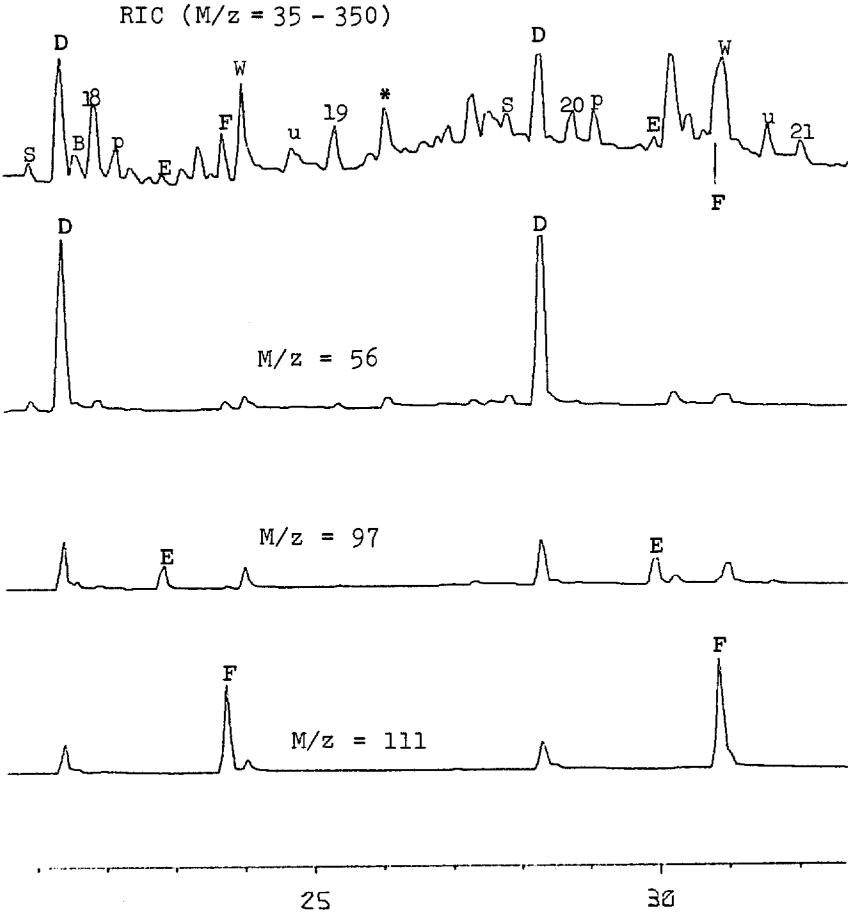
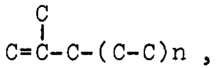
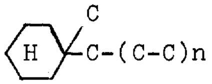
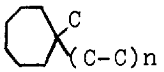


Fig. 1 Masschromatograms of Oligomers from a commercial HPPE resin (MI = 5, d = 0.924)

D : 
$\mathrm{C{=}\overset{C}{\overset{|}{C}}{-}C{-}(C{-}C)n}$,

E : 

F : 

18, 19, 20 and 21 : n-alkanes with indicated carbon number

S : 3-methylalkanes , p : 5,5-diethylalkanes

W : n-alkylcyclopentanes , * : contaminants

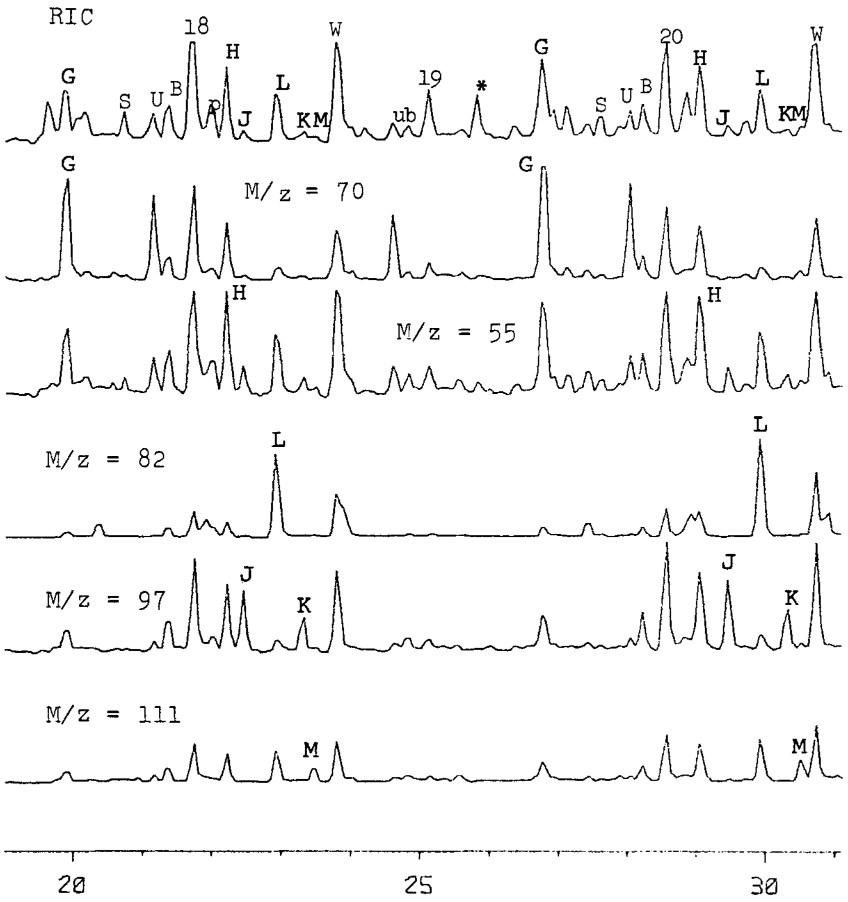
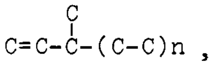
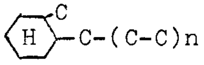
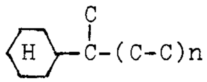


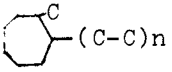
Fig. 2 Masschromatograms of Oligomers from a commercial HPPE resin (MI = 1.5, d = 0.927)

G : 
$C{=}C{-}\overset{\displaystyle C}{\overset{|}{C}}{-}(C{-}C)n$,

H : C-C=C-C-(C-C)n

J
K :  ,

L : 

M : 

U & u : 2-ethyl-1-alkenes (even & odd carbon)

B & b : n-1-alkenes (even & odd carbon)

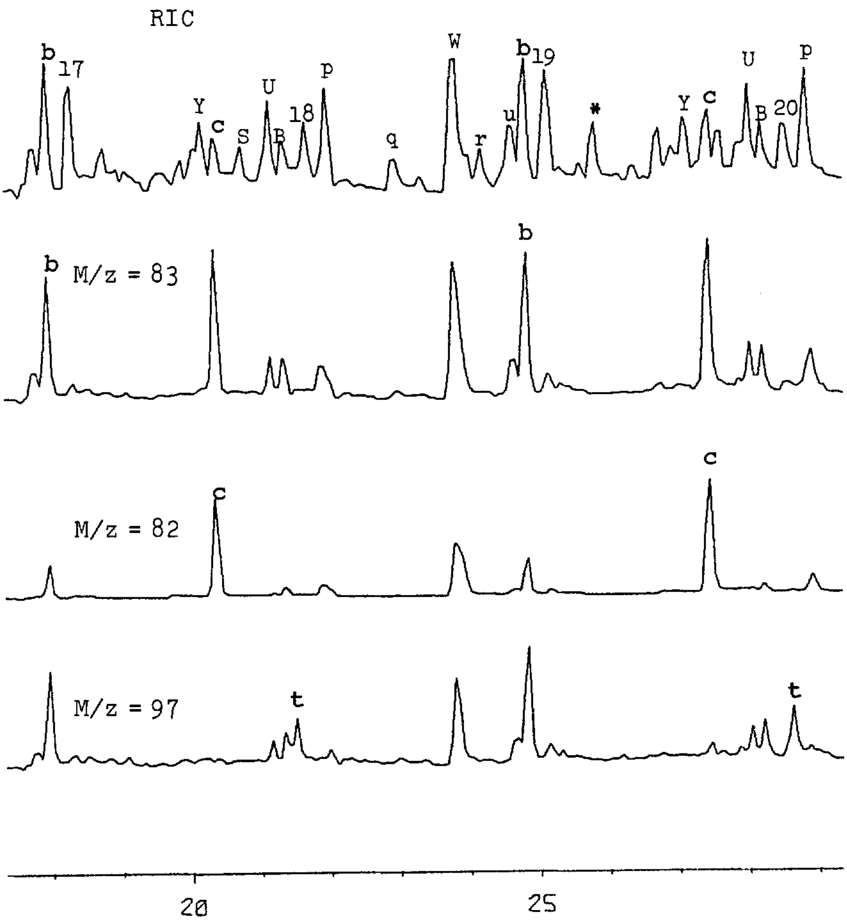
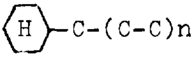
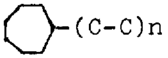


Fig. 3 Masschromatograms of Oligomers from a commercial HPPE resin (MI = 3.5, d = 0.919)

b : C=C-C-(C-C)n ,

c : 

t : 

q : 5-ethylalkanes ,

r : 3-ethylalkanes

Y : 3-ethyl-3-methylalkanes

can be recognized. Series of peaks marked D and E are 2-methyl-1-alkenes and 1-alkyl-1-methylcyclohexanes respectively, as reported earlier (T. 1980b). Peaks F are the ones which were previously assigned to 1-alkyl-1-ethylcyclohexanes, but now they have been found to be 1-alkyl-1-methylcycloheptanes. The structure of F was established by the comparison of mass spectra and retention indices with some reference compounds as shown in Fig. 4.

Non characteristic series of peaks are also shown with common marks in Figures 1, 2 and 3. Their chemical names as reported earlier (T. 1980a) are included in the legends of the figures.

In Fig. 2, six characteristic series of peaks can be recognized. Peaks G, H, J, K, and L have the structures as shown in the figure. Peaks M are the ones which were assigned erroneously to 1-alkyl-1-ethylcyclohexanes in the previous report (T. 1980b). In the present study, peaks M have been shown to be 1-alkyl-2-methylcycloheptanes (lower boiling, therfore, maybe trans isomer). The experimental supports are presented also in Fig. 4.

In Fig. 3, three characteristic series of peaks can be recognized. Peaks b and c are n-1-alkenes and n-alkylcyclohexanes respectively as shown in Fig. 3 and reported earlier (T. 1980b). Peaks t are now found to be n-alkylcycloheptanes.

We have independent information for the fact that the commercial HPPE resins, from which oligomers of Figs. 1, 2 and 3 were extracted, were manufactured using isobutylene, butene-1 and propylene, respectively as chain transfer agents. As the consequence, the formation mechanism of the afore-mentioned variety of oligomers are supposed as depicted in Scheme 2.

A radical transferred onto a chain transfer agent grows to oligomers (or to high polymers), and at the initial stage of chain growth there seems to exist appreciable probability of the intramolecular addition to double bond (the cyclization) leading to the six-membered ring or seven-membered ring structures. The former is well known in organic chemistry of radical reactions (ex. JULIA 1967 and 1971, BUTLER 1978, and BECKWITH et al. 1979), the latter seems rarely reported.

Acknowledgements

The authors wish to thank Nippon Oil Co., Ltd. and Nippon Petrochemicals Co., Ltd. for permission to publish this work. They also gratefully acknowledge the helpful discussion of Prof. Takeo Saegusa of Kyoto University.

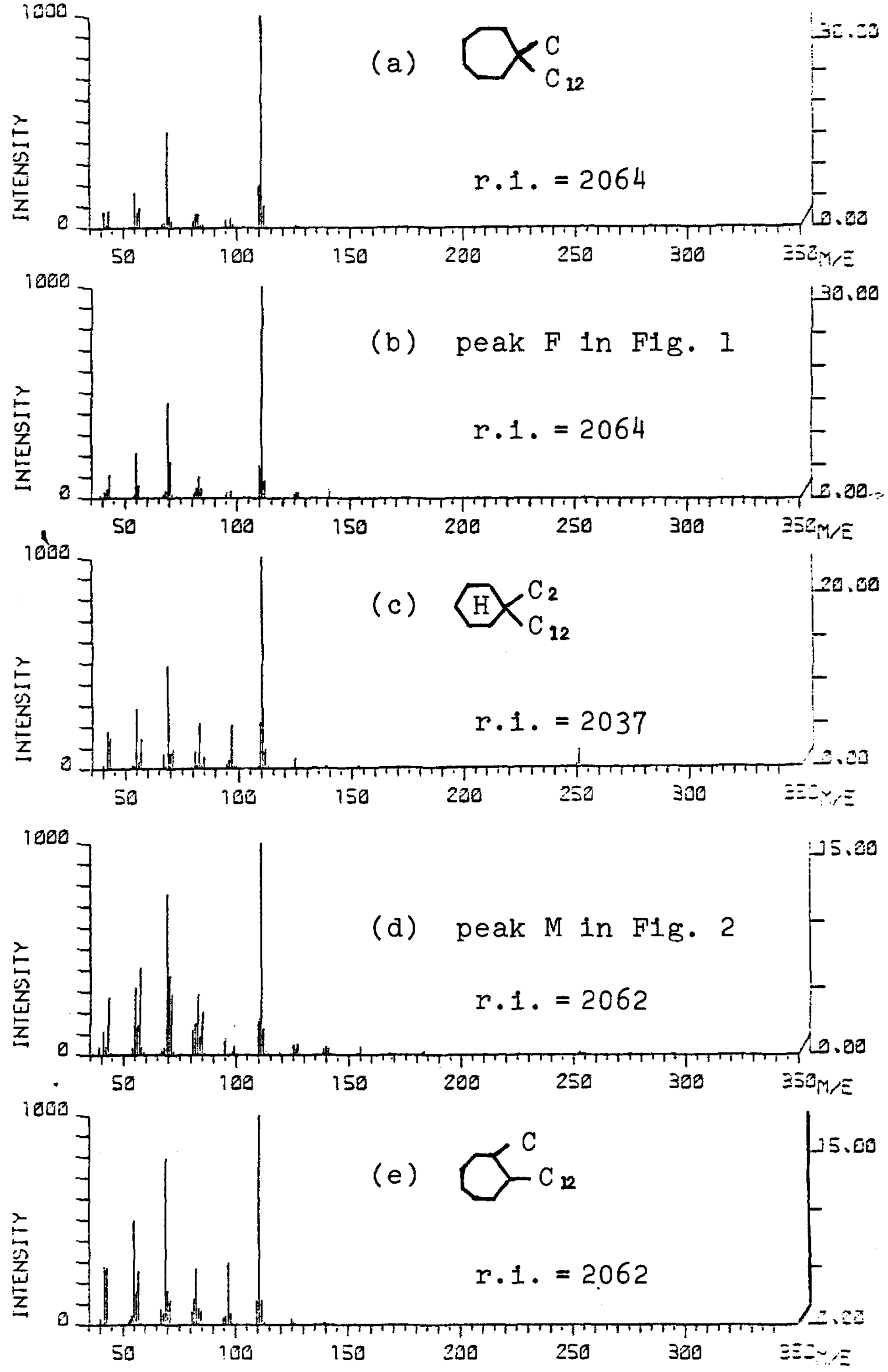
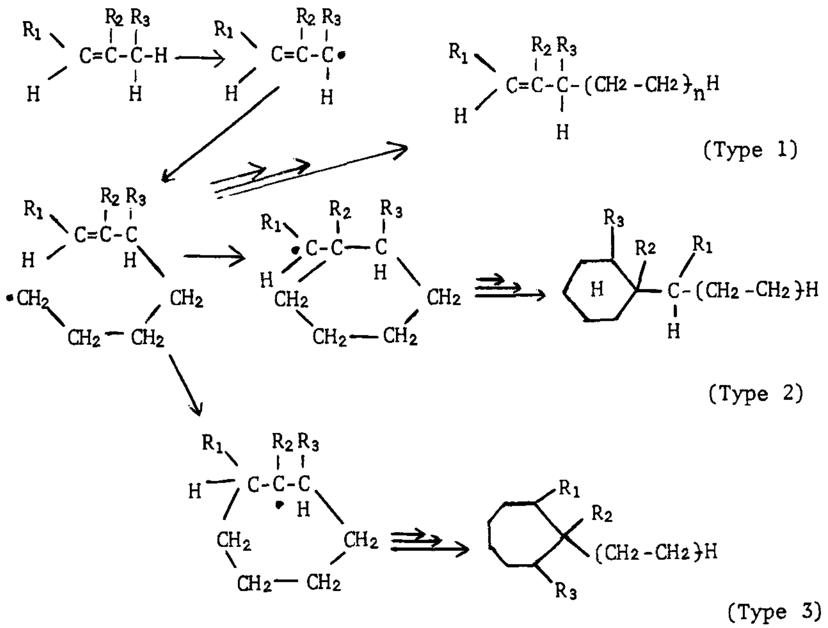


Fig. 4 Comparison of Mass Spectra and Retention Indices (MW = 280)

Scheme 2 Formation Mechanism of Oligomers



chain transfer agents				corresponding oligomer peaks				
	R_1	R_2	R_3	in Fig.	Type 1	Type 2	Type 3
propylene	H	H	H	3	b	c	t
isobutylene	H	CH_3	H	1	D	E	F
butene-1	H	H	CH_3	2	G	J , K	M
butene-2	CH_3	H	H	2	H	L	M

References

BECKWITH, A.L. and LAWRENCE, T. : J. Chem. Soc., Perkin II, 1535 (1979).

BUTLER, G.B. : J. Polymer Sci., Polymer Symp. 64, 71 (1978).

JULIA, M. : Pure Appl. Chem. 15, 167 (1967).

JULIA, M. : Accounts Chem. Res. 4, 386 (1971).

TAKAHASHI, M., SATOH, T. and TOYA, T. : this Bulletin 2, 215 (1980a).

TAKAHASHI, M., SATOH, T. and TOYA, T. : this Bulletin 2, 643 (1980b).

Received March 12/ Accepted March 27, 1981