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Reactive propylene oligomers

I. Propylene oligomers with isopropenyl end group by thermolysis

Sándor Nemes, János Borbély, Jenö Borda, and Tibor Kelen*

L. Kossuth University, Insitute of Applied Chemistry, P.O. Box 1, H-4010 Debrecen, Hungary

SUMMARY

Propylene oligomers containing isopropenyl end group have been prepared by thermolysis of atactic polypropylene.

The chain-end structures and the number-avarage isopropenyl chain end functionality was determined in the product by C-13 NMR spectroscopy. Molecular weight of the oligomers were between 300 and 1000, as characterized by GPC.

Conditions leading to the formation of propylene oligomers with number-average isopropenyl chain end functionality of 1.0, have been worked out.

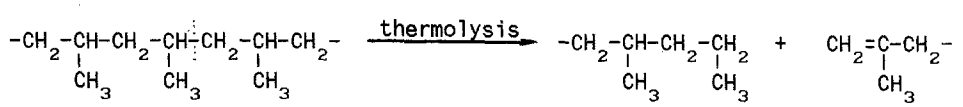
I. INTRODUCTION

End-reactive oligomers serve as intermediates in preparative polymer chemistry. Furthermore, they can be of interest in their own right as additives for plastics, coatings, adhesives etc. (1-2).

In this work, thermolysis has been used as a preparative method to prepare propylene oligomers containing isopropenyl end group. The isopropenyl-ended material is a valuable intermediate that can be converted to a variety of functional oligomers.

The thermolysis of polypropylene (PP) has been studied by several authors (3-7) with the main purpose of clarifying the mechanism of fragmentation and analyzing the low molecular weight volatile products by using mass spectrometry (4) and gas chromatography (5-7). This topic has been reviewed several times (4,8-9). A short work on the C-13 NMR analysis of thermally prepared propylene oligomers has been published (10). Based on the kinetic scheme proposed in a comprehensive product investigation study (5), it seemed feasible that propylene oligomers containing isopropenyl end group can be prepared by thermolysis.

The initiation reaction occurs by random scission of the main chain, yielding primary and secondary radicals. The formation of isopropenyl and n-propyl end groups is the result of various reactions of these radicals (5,9). Schematically:



The presence of saturated chain-end structures is indifferent in respect of the applications we are concerned with.

We have developed a simple, convenient preparative thermolysis method not requiring costly equipment. The oligomers are directly obtained without any additional experimental handling, in absence of solvents or contaminating agents.The increase of flow rate of carrier gas flow introduced into the molten polymer allows control of the oligomer molecular weights.

*Corresponding author

II. EXPERIMENTAL

a/ Materials

A commercial grade of unstabilized atactic polypropylene (APP) (Tipplen APP-A, TVK, Hungary; $\bar{M}_n \approx 3000$, $\bar{M}_w/\bar{M}_n \approx 11$, softening point >145 °C) was used as received. Tipplen APP-A is produced as a byproduct during of the industrial production with $TiCl_3/Al(C_2H_5)_2Cl$ catalyst system of isotactic polypropylene (Tipplen PP)..

b/ Apparatus and preparative procedure

Scheme of the apparatus is shown in Figure 1.

A complete set-up includes: a 100 ml three-neck round-bottom reaction flask equipped with N_2 inlet tube, thermometer and a twice bent glass tube; condenser; 100 ml two-neck round-bottom receiver flask having an outlet tube filled with glass wool.

In the reaction flask 20 g APP was placed. The material was rapidly heated to and thermolyzed at 400 °C. Temperature controller maintained temperature within ± 5 °C. Rotameter was used to measure rate of N_2 flow. Thermolysis products carried by a stream stream of N_2 passed through the twice bent glass tube and condenser, and were collected in the ice-cooled receiver flask. The aim of the outlet tube filled with glass wool is to hinder of the escape of the volatile fragments.

The products were characterized and used in further reactions without any additional handling.

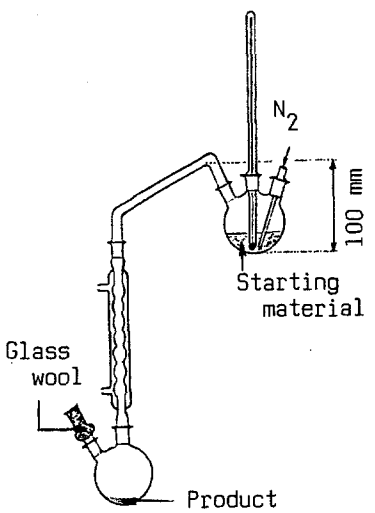


Figure 1. Apparatus used for the preparation of propylene oligomers by thermolysis.

c/ Characterization methods

The H-1 and C-13 NMR spectra were recorded on a Bruker 200 SY spectrometer at 50 °C in $CDCl_3$.

The quantitative C-13 NMR spectra were obtained by using the inverse gated mode of decoupling in order to obtain signals without nuclear Overhauser enhancement (11-12).

When necessary, the assignments were checked by APT (attached proton test) experiment (13).

The chemical shifts are expressed on the TMS (tetramethylsilane) scale.

Molecular weight of the oligomers dissolved in THF were determined with a Shimadzu C-R3A high pressure GPC instrument equipped with RI detector and five LiChrogel columns. The calibration curve was constructed by using narrow molecular weight distribution polyisobutylene standards.

III. RESULTS AND DISCUSSION

a/ Preparation studies

During the thermal degradation of polypropylene the average molecular weight and softening point decrease, and the molecular weight distribution becomes narrower (3,8).

Isotactic polypropylene begins to decompose at about 250 °C, the atactic polymer at about 270 °C. At any given temperature, the stereoregular polymer undergoes thermolysis to a greater extent than the atactic material (7). Volatilization is unimportant below 300 °C (8).

During the thermolysis of isotactic polypropylene an epimerization of considerable degree takes place and products tend to be practically identical with those obtained from atactic polypropylene.

The conditions and results of the preparation of propylene oligomers are presented in Table 1 and Figures 2 and 3. Atactic polypropylene was thermolyzed at 400 °C in a carrier stream of N_2. The regulation of the rate of gas flow introduced into the polymer melt allows fairly reliable control of reaction time and of molecular weight of oligomers: Reaction time decreases, oligomer molecular weight increases with increasing flow rate. Some typical gel perme-

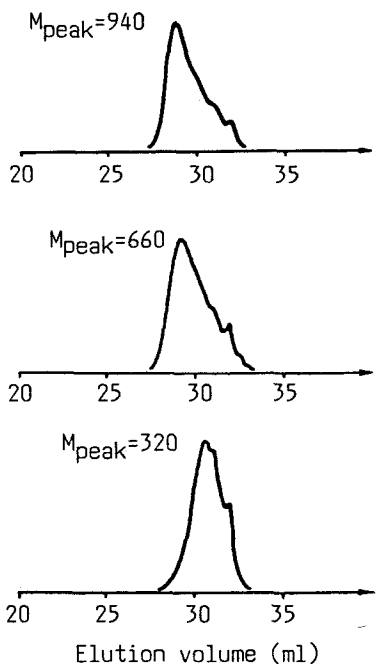


Figure 2. GPC traces of propylene oligomers prepared by thermolysis.

TABLE 1
Conditions and Results of the Preparation of Propylene Oligomers with Isopropenyl End Group by Thermolysis at 400 °C.*

Rate of N_2 flow (ml/s N_2 /g APP)	Reaction time (h)	M_{peak}**	$\bar{F}_n$***
0.174	3.5	320	0.94
0.260	2.3	520	0.97
0.347	1.8	660	0.98
0.416	1.5	730	0.99
0.486	1.5	800	1.01
0.555	1.5	850	1.01
0.694	1.3	940	1.03

* Amount of starting material: 20g APP (M_{peak}=7000, free of unsaturation).

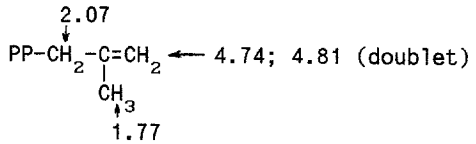
** Yield of oligomers in the range: 73-66 %.
M_{peak} is the molecular weight corresponding to the maximum of the elution profile by GPC.

*** Number-average isopropenyl chain end functionality by C-13 NMR spectroscopy.

ation chromatograms of propylene oligomer mixtures prepared by thermolysis are shown in Figure 2. Since distinct shoulders and side-peaks are present on the low molecular weight side of the elution profiles, the molecular weight corresponding to the maximum of the elution profile (M_{peak}) was calculated.The M_{peak} range explored was 320-940. The molecular weight of the highest molecular weight oligomers present in the samples increases from 1400 to 3000. When $M_{peak}>500$, the appearance of the oligomer mixture is pasty at ambient temperature. Yield varies from 73 to 66 %. A small increase of the number-average isopropenyl chain end functionality ($\bar{F}_n$) with increasing flow rate can be observed but the deviation from $\bar{F}_n = 1.0$ is not essential.

b/ Chain end functionality

In the H-1 NMR spectra of propylene oligomers the following resonances diagnostic for the isopropenyl end group, were found (the numbers are chemical shifts in ppm):



Only traces of resonances were detected for other possible unsaturated end groups in the H-1 NMR spectra of the condensed volatile products.

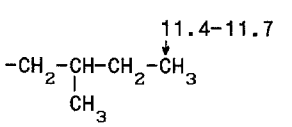
Detailed analysis is possible only by C-13 NMR spectroscopy. The quantitative C-13 NMR spectrum of a propylene oligomer mixture (Entry 1 in Table 1) is shown in Figure 3. The complex spectral features arise from the tacticity splitting, from the abundance of chain-end structures and from the presence of low molecular weight compounds.

The C-13 NMR analysis of polypropylene (14-21) and related model compounds (22-30) has been subject of numerous publications due to the commercial importance of this material. Thus sufficient amount of information exists for peak identification in the open literature. We have identified all chain ends occurring in the propylene oligomer mixture by comparison with previous assignments reported in the literature (14,17,21,29). The assignments were aided by comparison with information on decomposition products previously obtained by mass spectrometry (4) and gas chromatography (5-7).

The only chain ends found are shown in structures I-IV. The intensities (**I**) of these well-separated resonances can be used to determine the number-average isopropenyl chain end functionality:

$$\bar{F}_n = \frac{2\ \mathbf{I}(\text{isopropenyl chain end})}{\mathbf{I}(\text{isopropenyl chain end}) + \mathbf{I}(\text{saturated chain ends})}\ .$$

The numbers in I-IV structures indicate integration limits for the observed chemical shifts in the C-13 NMR spectra. Other predicted chemical shifts are also assigned but cannot be separated due to spectral overlap.



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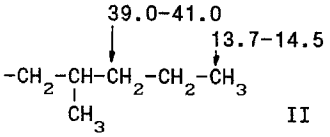


II

Among the chain-end structures found, structures II and IV are dominant. The resonances of any other unsaturated structures (25) are present at about the detection limit of C-13 NMR spectrosopy.

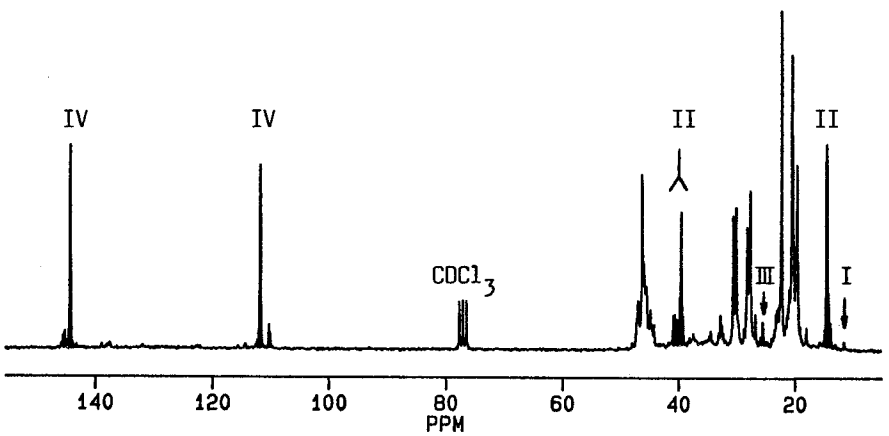
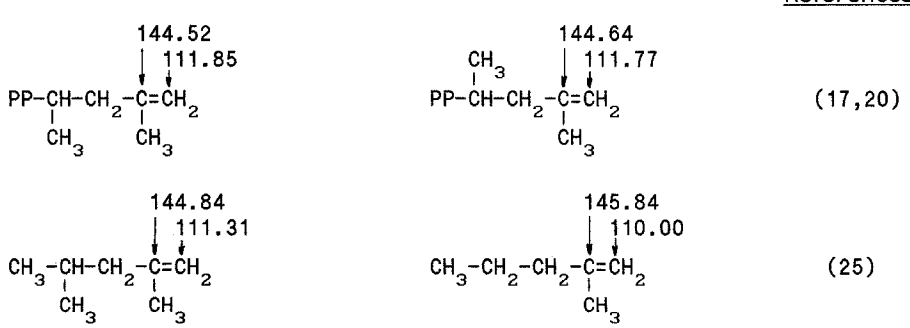


Figure 3. Quantitative C-13 NMR spectrum of propylene oligomers (Table I, Entry 1).

The multitude of chain-end structure resonances can be interpreted on the basis of tacticity splitting and the presence of low molecular weight compounds. For example, in the case of isopropenyl end group the following assignations are known from the literature (the numbers are C-13 NMR chemical shifts in ppm):



References:

(17,20)

(25)

The resonance intensities used for functionality calculations are as follows:
I(saturated chain ends) = 1/2[I(39.0-41.0 ppm) + I(13.7-14.5 ppm)] +
I(25.4-26.1 ppm) + I(11.4-11.7 ppm)
from the structures I,II and III;
I(isopropenyl chain end) = 1/2[I(143.0-145.2 ppm) + I(110.0-112.7 ppm)]
from structure IV.

In conclusion these results strongly support that isopropenyl and n-propyl end groups were formed in one-to-one ratio during the thermolysis of polypropylene.

REFERENCES

1. Synthesis and Reactions of Oligomers and End-Reactive Polymers, Special issue of J. Macromol. Sci., Chem., Vol. A21, Numbers 8-9, 1984.
2. V. PERCEC, C. PUGH, O. NUYKEN and S.D PASK, Macromonomers, Oligomers and Telechelic Polymers, in Comprehensive Polymer Science, G. ALLEN and J.C. BEVINGTON, Eds., Pergamon , Oxford, 1989, Vol. 6, Chap. 9, p. 339.
3. T.E. DAVIS, R.L. TOBIAS and E.B. PETERLI, J. Polym. Sci., 56, 485 (1962)
4. S.L. MADORSKY, Thermal Degradation of Organic Polymers, Interscience, New York, 1964, p. 117.
5. Y. TSUCHIYA and K. SUMI, J. Polym. Sci. Part A-1, 7, 1599 (1969)
6. M. SEEGER and H.-J. CANTOW, Makromol. Chem., 176, 2059 (1975)
7. J.K.Y. KIANG, P.C. UDEN and J.C.W. CHIEN, Polym. Degradation Stab., 2, 113 (1980)
8. C. DAVID, Thermal Degradation of Polymers, in Chemical Kinetics, C.H. BAMFORD and C.F.H. TIPPER, Eds., Elsevier, Amsterdam, 1975., Vol. 14, Chap. 1., p. 39.
9. I.C. McNEILL, Thermal Degradation, in Comprehensive Polymer Science, G. ALLEN and J.C. BEVINGTON, Eds., Pergamon, Oxford, 1989., Vol. 6, Chap. 15, p. 467.
10. T. SAWAGUCHI, S. NIIKUNI, T. KURAKI and T. IKEMURA, Polym. Prep., 20, 924 (1979)
11. R. FREEMAN, H.D.W. HILL and R. KAPTEIN, J. Magn. Reson., 7, 327 (1972)
12. J.C. RANDALL and E.T. HSIEH, C-13 NMR in Polymer Quantitative Analyses, in NMR and Macromolecules, ACS Symp. Ser. 247, J.C. RANDALL, Ed., American Chemical Society, Washington, D.C., 1984, Chap.9.
13. S.L. PATT and J.N. SHOOLERY, J. Magn. Reson., 46, 535 (1982)
14. A. ZAMBELLI, P. LOCATELLI and E. RIGAMONTI, Macromolecules, 12, 156 (1979)
15. F.C. SCHILLING and A.E. TONELLI, Macromolecules, 13, 270 (1980)
16. H.N. CHENG, Polym. Bull., 14, 347 (1985)
17. H.N. CHENG and D.A. SMITH, Macromolecules, 19, 2065 (1986)
18. H.N. CHENG and G.H. LEE, Macromolecules, 20, 436 (1987)
19. T. ASAKURA, Y. NISHIYAMA and Y.DOI, Macromolecules, 20, 616 (1987)
20. A. GRASSI, A. ZAMBELLI, L. RESCONI, E. ALBIZZATI and R. MAZZOCCHI, Macromolecules, 21, 617 (1988)
21. H.N. CHENG and J.A. EWEN, Makromol. Chem., 190, 1931 (1989)
22. L.P. LINDEMAN and J.Q. ADAMS, Anal. Chem., 43, 1245 (1971)
23. C.J. CARMAN, A.R. TARPLEY, Jr. and J.H. GOLDSTEIN, Macromolecules, 6, 719 (1973)
24. A. ZAMBELLI, P. LOCATELLI, G. BAJO and F.A. BOVEY, Macromolecules, 8, 687 (1975)
25. P.A. COUPERUS, A.D.H. CLAGUE and J.P.C.M. van DONGEN, Org. Magn. Reson., 8, 426 (1976)
26. K.F. ELGERT and W. RITTER, Makromol. Chem., 178, 2857 (1977)
27. A. ZAMBELLI, G. BAJO and E. RIGAMONTI, Makromol. Chem., 179, 1249 (1978)
28. A. ZAMBELLI and G. GATTI, Macromolecules, 11, 485 (1978)
29. A. ZAMBELLI, P. LOCATELLI and G. BAJO, Macromolecules, 12, 154 (1979)
30. M. MÖLLER and H.-J. CANTOW, Macromolecules, 17, 733 (1984)

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