Propylene Oligomers: Extraction Methods and Characterization by FTIR, HPLC, and SEC

H. EL MANSOURI,¹ N. YAGOUBI,¹ D. SCHOLLER,² A. FEIGENBAUM,² D. FERRIER¹

¹ Centre d'études pharmaceutiques, Laboratoire de chimie analytique, rue J. B. Clément, 92290 Chatenay - Malabry (France)

² Institut National de Recherche Agronomique (INRA), CPCB - Moulin de la Housse - BP 1039, 51687 Reims Cédex 2-France

Received 21 October 1997; accepted 26 March 1998

ABSTRACT: Propylene oligomers were isolated from polymer matrix by dissolution precipitation and Soxhlet methods and characterized by Fourier transform infrared spectrometry, ultraviolet, high-performance liquid chromatography, and gel permeation chromatography. Both extracts showed that these hydrocarbon chemicals have a maximal absorption at 210 nm and are eluted from a C8 column with a strong mobile phase (tetrahydrofuran). However, their average molecular weights are different depending upon the quality of extraction: the fraction obtained by the dissolution-precipitation method is homogeneous in molecular weight, whereas the one obtained by Soxhlet extraction has a higher polydispersity index $(\overline{M_n}/\overline{M_w})$. The specific migration test of propylene oligomers in a food simulant (isooctane) shows total diffusion within 60 min. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 371–375, 1999

Key words: propylene oligomers; polypropylene; dissolution precipitation; Soxhlet; gel permeation chromatography

INTRODUCTION

Processing of polypropylene under high temperature (200-300°C) and exposure to ultraviolet (UV) may induce oxidation following radical reaction mechanisms. These may involve chain scission, branching, or crosslinking of the macromolecular chains.¹ To prevent degradation and to extend service life, polypropylene is protected by additives.² Migration of oligomers and of additives when polypropylene is used as food packaging may represent a source of food contamination. Therefore, accurate and sensitive analytical methods were developed for identification and quantification of additives used in food packaging.^{3–9} As far as oligomers are concerned, two issues are to be raised. The first concerns their extraction from polypropylene and their analysis by chromatographic methods without interference from additives.⁶⁻⁷ The second is to explain the degradation mechanisms of polypropylene¹⁰⁻¹³ and to determine the propylene oligomers structure by techniques such as ¹Hnuclear magnetic resonance (NMR), C¹³-NMR,¹⁴ and mass spectrometry.¹⁵ The present study was developed with the main purpose of determining the kinetic migration of oligomers such as isooctane in food simulants. We used two chromatographic characterization techniques: (1) the extraction of the potential oligomeric migrants from polymeric matrices at different temperatures and their reversed-phase high-performance liquid chromatography (HPLC) analysis without interference from additives; and (2) the molecular

Correspondence to: H. El Mansouri.

Journal of Applied Polymer Science, Vol. 71, 371-375 (1999)

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/030371-05

weight determination of these oligomers by size exclusion chromatography (SEC). Data from these techniques were used to explain their behaviors toward packaged food products in polypropylene packaging.

EXPERIMENTAL

Chemicals

The antioxidants (Irganox 1010 and Irgafos 168) were provided by Ciba-Geigy (Reuil Malmaison, France), and the 1,3,2,4-di-*p*-methyl benzylidene sorbitol (DBS) by Chemical Melicken. Polypropylene was supplied by Solvay, Belgium. The HPLC-grade solvents acetonitrile, methanol, toluene, and methylene chloride were obtained from Prolabo (Fontenay-sous Bois, France), and tetrahydrofuran (THF) from OSI (Elancourt, France).

Soxhlet Extraction

Polypropylene (5 g) was cut into smaller pieces $(0.2 \times 1 \text{ cm})$ and placed in a 34-by-170-mm Schleicher & Schuell cartridge, provided by Prolabo. The Soxhlet extraction was performed for 25 h under reflux at 40°C, with 250 mL methylene chloride. The extraction solvent was evaporated under reduced pressure. The residue obtained was dissolved in 2 mL THF.

Extraction by Dissolution Precipitation

Polypropylene (5 g) was cut in smaller pieces (0.2 \times 1 cm) and dissolved in refluxing in toluene (100 mL). After dissolution, 250 mL of methanol was added. The precipitate was filtered under vacuum on a sintered glass filter fitted with a 0.45- μ m porosity, 47-mm diameter, GF/C Whatman filter obtained from Prolabo. The mixture of solvents was evaporated to dryness. The residue was then dissolved in 2 mL THF for analysis by SEC and HPLC.

Size Exclusion Chromatography

The chromatograph consisted of a pump (Hewlett Packard series 1050; Hewlett Packard, Les Ulis, France); a Rheodyne 7125 sampling valve with $20-\mu$ l loop, coupled with two Waters analytical styragel columns [300×7.8 mm inner diameter (I.D.), HR 0.5 (50 Å) and HR 1 (100 Å)] (Waters, St. Quentin-en-yvelines, France); a Hewlett Packard HP 1047 RI detector; and a Spectra Physics

Table IGradient Elution in HPLC

Time (min)	Solvent A (%)	Solvent B (%)	
0	100	0	
7	100	0	
35	0	100	

Chromjet integrator which connected to Spectra Physics GPC software (Spectra Physics, Les Ulis, France). Saturated hydrocarbons, provided by Waters, were used as standards to determine the number- $(\overline{M_n})$ and weight- $(\overline{M_w})$ average molar masses of propylene oligomers. The eluent was THF at a flow rate of 1 ml/min.

High-performance Liquid Chromatography

The liquid chromatograph consisted of a Jasco 880 PU pump (Prolabo) and a Rheodyne 7125 sampling valve with a 20- μ l loop, coupled with a Waters 990 photodiode array detector which connected to a computer (NEC Power Mate 2 APC) provided by Waters. The separation used 250-by-4-mm I.D., 5- μ m LiChrospher RP-select B C8 column (Merck, Nogent sur Marne, France).

The gradient elution was a mixture of two solvents: A, THF : acetonitrile : methanol : water, 40 : 10 : 10 : 40 vol/vol; and B, THF : acetonitrile : methanol 40 : 30 : 30 vol/vol. The gradient was varied during 35 min as shown in Table I. The flow rate was 1 mL/min.

HPLC was used for identification of low molecular-weight species present in the dissolutionprecipitation and Soxhlet extracts.

Fourier Transform Infrared Spectrometry (FTIR)

Spectra were collected in the IR transmission sampling mode with a Jasco spectrometer from Prolabo. Potassium bromide, 100 mg, was mixed with an aliquot (50 μ l) of propylene oligomers obtained from Soxhlet and dissolution-precipitation extracts. After solvent evaporation, the mixtures were pressed into disks.

RESULTS AND DISCUSSION

Polypropylene samples were extracted by boiling toluene, and the major part of the polymeric materials was precipitated by addition of methanol. Alternatively, polypropylene samples were also Soxhlet-extracted by methylene chloride. The cor-



Figure 1 RP-HPLC chromatogram of dissolutionprecipitation extract. Identified additives: (1) DBS, (2) 2,4,di-*tert*-butyl phenol, (3) Irganox 1010, (4) Irgafos 168.

responding reverse-phase HPLC chromatograms showed the presence of the additives DBS, Irgafos 168, Irganox 1010, and other products which were not identified (Fig. 1). The reverse-phase HPLC chromatogram of Soxhlet extract, not shown here, exhibited the same additives. The non-observation of polypropylene oligomers by reverse-phase HPLC under UV light could be the result of peak overlapping or of a compound not eluted by the quaternary gradient (THF, acetonitrile, methanol, water).

The latter possibility was confirmed by the use of a stronger mobile phase, namely THF. The polypropylene oligomers desorbed from the C8 column with THF (Fig. 2). They were identified by the lack of absorption above 210 nm (which is characteristic of the antioxidants studied). They were recovered in quantities suitable for investigation by FTIR and SEC, as indicated in Scheme 1.

The FTIR spectra of the collected HPLC fractions exhibited the characteristic absorption bands of propylene, such as asymmetric vibration of CH_2 (2957 cm⁻¹), stretching symmetric vibration of CH_3 (2924 cm⁻¹), deformation vibration of CH_2 (1460 cm⁻¹), and symmetric deformation vibration of CH_3 (1370 cm⁻¹). Considering these results, we confirmed that the oligomers provided by dissolution-precipitation procedure from polypropylene were aliphatic hydrocarbons. Analysis by SEC (Fig. 3, 3.a) provided a molecular weight distribution which was characterized by the elution volume at the top of the chromatographic peak, near 11 mL. The average molecular weights calculated are summarized in Table II. The oligomers that we extracted by the Soxhlet method and characterized by similar techniques gave the same UV and FTIR spectra. In contrast, the chromatographic peak obtained by SEC (Fig.



Figure 2 Elution of adsorbed oligomers on the C8 column by THF: (1) oligomers.



Figure 3 SEC chromatogram of propylene oligomers: (3.a) oligomers isolated from dissolution-precipitation extract; (3.b) oligomers isolated from Soxhlet extract.

3, 3.b) showed a distinct shoulder and a shorter elution than the previous one (oligomers by dissolution precipitation). Therefore, this comparison clearly indicates that differences in the oligomers isolated from polypropylene were due to the extraction technique. Indeed, the fraction extracted by the dissolution-precipitation method was homogeneous in molecular weight, whereas the one obtained by Soxhlet extraction was relatively polydisperse because its molecular weight distribution appeared bimodal. Lattimer¹⁶ reported that a series of residual propylene oligomers is present in polypropylene but most of these products are saturated hydrocarbons and have a molecular weight equal to 42n + 2, (where n is the degree of polymerization). Ishihara and

Table IIMolecular Distributionof Propylene Oligomers

Extraction Methods	$\overline{M_n}$	$\overline{M_w}$	Polydispersity Index
Dissolution precipitation Soxhlet	997 1,491	1,057 1,627 1,234	$1.05 \\ 1.09 \\ 1.07$

colleagues¹⁷ described two major chemical structures in polypropylene oligomeric fraction:

CH3-(-C H-CH2)_n-H
$$(42n + 16)$$

CH3
CH3-(-C H-CH2-)_{n-1}-CH2-CH3 $(42n + 2)$
CH3

In our case, the $\overline{M_n}$ obtained for propylene oligomers and the monomer mass showed that the mean degrees of polymerization were approximately 28 and 36 for oligomers extracted by Soxhlet and around 24 for oligomers extracted by the dissolution-precipitation method. This difference can be attributed to the thermal degradation of high-mass molecular oligomers or their precipitation by methanol.

According to the relatively low molecular weight of these oligomers and their lowest polarity, their migration in food and simulants is likely to occur. Thus we have determined their specific migration in isooctane, in order to compare it with the profiles of additive migrations obtained in another work.¹⁸ The curve representative of de-



Figure 4 Area of propylene oligomers migrating in isooctane versus square root of time.

sorbed oligomers area, from the C8 column, versus square root of time is shown in Figure 4. They achieved equilibrium of the migration at 60 min, whereas the Irganox 1010 ($M_w = 1178$) presented an equilibrium of migration at 72 h. This result proves that the low polarity governs the contaminants' migration in the isooctane more than the molecular weight.

CONCLUSION

The oligomers were presumably previously present within the plastic material. The quality of polypropylene oligomers is different according to the extraction method: the degrees of polymerization are approximately 28 and 36 for the oligomers extracted by Soxhlet and around 24 for oligomers extracted by the dissolution-precipitation method. This difference can be attributed to the thermal degradation of high-mass molecular oligomers or their precipitation by methanol. Indeed, they achieved the plateau of the migration, in isooctane, more rapidly than did the additives. This proves that the low polarity governs the contaminants' migration in the isooctane more than the molecular weight.

REFERENCES

- Mercier, J. P.; Marechal, E. Chimie des Polymeres: Syntheses, Reactions, Degradations; Presses Polytechniques et Universitaires: Lausanne, 1993; p. 393.
- Botrel, J. Les Polymeres: Chimie et Reglementations des Emballages; Masson: Paris, 1980; p. 123.
- Hanely, M. A.; Dark, W. A. J Chromatogr 1980, 18, 655.
- 4. Vargo, J. D.; Olson, K. L. Anal Chem 1985, 57, 672.
- 5. Startin, J. R.; Parker, I.; Sharman, M.; Gilbert, J. J Chromatogr 1987, 388, 509.
- Arpino, P. J.; Dilettato, D.;Nguyen, K.; Bruchet, A. H R C 1990, 13, 5.
- Cotton, N. J.; Bartle, K. D.; Clifford, A. A.; Ashraf, S.; Moulder, R.; Dowle, C. J. H R C 1991, 14, 164.
- Crompton, T. R. Analysis of Polymers: An introduction; Pergamon Press: New York, 1989; p. 243.
- Vimalasiri, P. A. D. T.; Haken, J. K.; Burford, P. P. J Chromatogr 1984, 300, 303.
- Gijsman P.; Hennekens, J. Polym Degrad Stab 1993, 42, 95.
- 11. Lederer, K. Polimeri 1993, 14, 253.
- 12. Pabedinskas, A.; Cluett, W. R.; Blake, S. T. Polym Eng Sci 1994, 34, 598.
- Triacca, V. J.; Gloor, P. E.; Zhu, S.; Hrymak, A. N.; Hamielec, A. E. Polym Eng Sci 1993, 33, 445.
- Nemes, S.; Borbély, J.; Borda, J.; Kelen, T. Polym Bull 1992, 28, 633.
- 15. Lattimer, R. P. J Anal App Pyrolysis 1995, 31, 203.
- 16. Lattimer, R. P. J Anal Appl Pyrolysis 1993, 26, 65.
- 17. Ishihara, N.; Nambu, H.; Sardo, K.; Ikemura, T.; Takesue, T.; Kuroki, T. Fuel 1993, 72, 1115.
- El Mansouri, H.; Yagoubi, N.; Ferrier, D. Food Add Contam, submitted.