e-Polymers **2008**, no. 018

http://www.e-polymers.org
ISSN 1618-7229

Use of the SPME-GC-MS technique to study the thermal degradation of isotactic polypropylene: Effects of temperature and reaction time, and analysis of the reaction mechanism

*Janina H. Bortoluzzi, Rodrigo Cristiano, Hugo A. Gallardo, Eduardo Carasek, Valdir Soldi**

*Chemistry Department, Federal University of Santa Catarina (UFSC), 88040-900, Florianópolis, SC, Brazil; fax: +55 48 3721 6850; e-mail: vsoldi@qmc.ufsc.br

(Received: 19 October, 2007; published: 30 January, 2008)

Abstract: Commercial fibers covered with poly(dimethylsiloxane) were used to pre-concentrate (solid phase microextraction technique) products evolved from the thermal degradation of isotactic polypropylene. Although the analysis by GC-MS indicated the formation of more than one hundred evolved products (ca. forty were identified), only twenty nine formed at 470 °C (the temperature of maximum degradation rate for isotactic polypropylene) were analyzed. The main compounds identified were 2,4-dimethyl-1-heptene, 2-methyl-1-pentene, 2,3-dimethyl hexane, n-pentane and 1,3,5-trimethyl cyclohexane. The analysis at 470 °C, using different degradation times, also indicated that the compounds 2-methyl-1-pentene and 2,4-dimethyl-1-heptene (major products) were formed at 15 and 25 minutes, respectively. The mechanism proposed for the formation of the major compounds was based on radical formation through chain cleavage (allyl and secondary radicals), followed by a chain decomposition process via hydrogen radical addition or cyclization to a thermodynamically stable six-membered ring.

Keywords: isotactic polypropylene, thermal degradation, SPME, poly(dimethylsiloxane) fiber, degradation mechanism

Introduction

Environmental pollution due to synthetic polymers is considered one of the greatest problems nowadays. The total plastics consumption and, consequently, the amount of plastic waste generated have increased considerably in recent years. One alternative used to solve this problem is to recycle the polymer waste using a pyrolysis process for which it is important to know exactly which volatile products are generated. The volatile products and new compounds generated during the pyrolysis process of polymers can be toxic, increasing, as a consequence, the risk of human health problems. Thus, the identification of these compounds is of great importance, along with knowledge of the effects of temperature in the degradation process.

Solid phase microextraction (SPME) is a very useful analytical technique in which the analytes are directly extracted and concentrated on the extraction fibers. It has been applied in environmental and forensic chemistry, and in the pharmaceutical, materials and food industries [1-6]. Although it has been routinely used for the extraction of volatile and semi-volatile organic compounds from samples related to the above mentioned areas, only in recent years has it been used to concentrate volatile products formed during the thermal degradation of polymers [7-11]. For this specific application, advantages such as rapid analysis, improvement of detection limits and total elimination of the use of organic solvents, are of particular interest [1, 2, 4-7].

Recently, we used the SPME technique to analyze the volatile products evolved from the thermal degradation of isotactic polypropylene (iPP) at 470 °C, which is the temperature of maximum degradation rate [7]. The main idea was to compare two different fibers, polydimethylsiloxane and carboxen/polydimethyl siloxane for the product pre-concentration. The results suggest the viability of the use of both fibers in the pre-concentration of volatile products evolved from iPP degradation. Isotactic polypropylene was chosen as a "model polymer" because its thermal degradation behavior has been extensively studied and described in the literature and there is only one stage of mass loss between 300 °C and 500 °C [7, 12-20]. Also, iPP is a commonly recycled polymer and has been used in several technological applications at moderate and high temperatures [12, 13, 16, 18, 21].

Considering that in a previous study the products evolved at 470 °C were analyzed, the aim of this study was to evaluate the effect of temperature and degradation time on the thermal degradation of isotactic polypropylene using the SPME-GC-MS technique. Possibilities are proposed for the reaction mechanisms associated with the formation of the main products evolved.

Results and discussion

Products evolved during the isotactic polypropylene degradation

In Figure 1A the GC-MS chromatogram corresponding to the volatile products obtained in the thermal degradation of iPP at 470 °C, the temperature of maximum degradation rate using a PDMS-covered fiber for pre-concentration, is shown. Although more than one hundred volatile products were detected up to the retention time of 50 minutes, only 41 were identified using the ChemStation B-01-00 database. Twenty nine of the identified compounds (ca. 70%) which showed a high percentage of accuracy in the identification, have a retention time lower than 15 minutes, and for this reason, our analysis focused only on this region (Figure 1B and Table 1). The formation of a high percentage of alkenes (79.3%), was observed, in agreement with the data reported in the literature, which range from 75% to 85% [12, 19]. The percentages of alkanes and dienes were 15.4% and 5.3%, respectively, which are similar to the values determined by the above-cited authors. At up to 15 minutes of retention time C_5-C_{12} compounds were preferentially formed and the main products evolved were 2,4-dimethyl-1-heptene, 2-methyl-1-pentene, 2,3-dimethyl-hexane, n-pentane and 1,3,5-trimethyl-cyclohexane. The behavior, in terms of the relation between normalized peak area and temperature, of the five above-mentioned compounds is shown in Figure 2. As previously reported [7], the 2,4-dimethyl-1-heptene compound formation appears to be favored by the reaction mechanism associated with the random scission of carbon-carbon bonds, followed by an intramolecular hydrogen transfer process (see next section). At the same time, it was observed that the compounds 2-methyl-1-pentene, 2,3-dimethyl-hexane and n-pentane were preferentially formed at temperatures lower than 400°C, decreasing in percentage terms at high temperatures (> 400 °C). The compound 1,3,5-trimethyl-cyclohexane appeared as a volatile product at the five degradation temperatures analyzed, with a percentage of ca. 10% (normalized peak area). Most of the identified compounds were present in percentages lower than 10% (normalized peak area) at some of the studied temperatures.

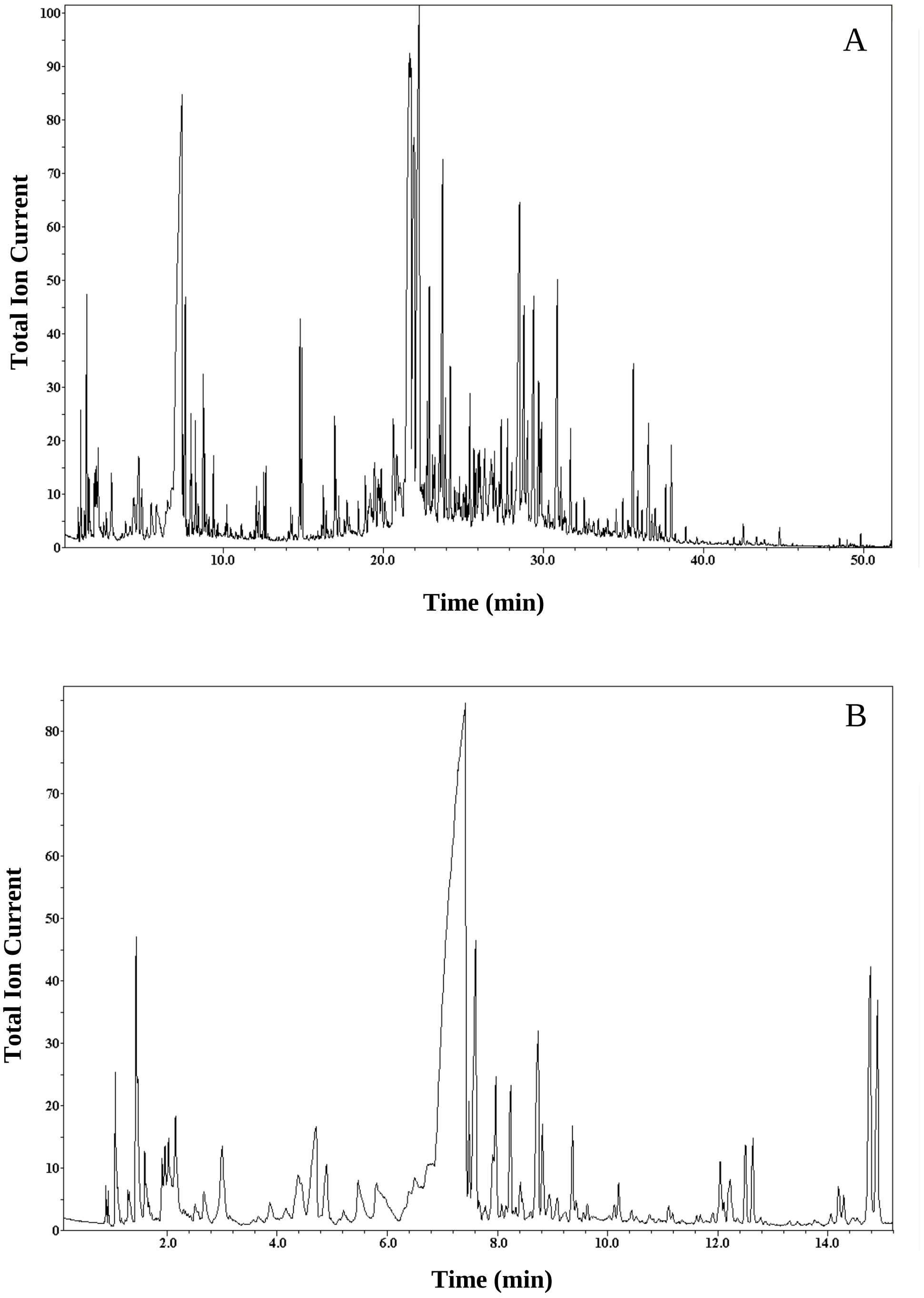


Fig. 1. GC-MS chromatograms for the products evolved from the isotactic polypropylene thermal degradation: (A) total evolved products, (B) magnification of the region 0-15 minutes.

The results shown in Table 1 and Figure 2 confirm that for isotactic polypropylene the maximum degradation occurred at 470 °C as has been previously described in the literature [7]. At this temperature, the twenty nine compounds analyzed in this study were present although most of them in low percentages. Another finding was that some of the compounds appeared only at high temperatures, suggesting that they were formed by the random scission of the polymer chain, probably due to the degradation of some of the compounds formed at low temperatures.

Tab. 1. Retention time and normalized peak areas of the volatile compounds extracted during thermal degradation of isotactic polypropylene at different temperatures.

Peak	Volatile compounds	RT[a] (min)	S[b]	R[c]	Temperatures (°C)				
					370	420	470	520	570
1	2-metil-1-propeno	0.93	917	955	nd	nd	0.46	nd	0.17
2	n-pentane	1.06	935	940	16.35	4.17	3.13	3.00	0.41
3	2-methyl-1-pentene	1.44	930	933	32.34	7.34	7.56	4.71	1.75
4	4-methyl-2-pentene	1.59	940	949	8.85	1.64	2.17	1.01	nd
5	2-methyl-1,3-pentadiene	1.91	846	861	nd	1.36	1.39	1.89	0.74
6	2,4-dimethyl-1-pentene	2.03	895	898	nd	1.84	2.80	1.83	0.08
7	2,4-dimethyl-1,4-pentadiene	2.16	887	894	nd	nd	4.04	2.00	0.58
8	2-methyl-1,5-hexadiene	2.51	872	872	nd	nd	0.94	0.93	nd
9	2-methyl-1-hexene	2.67	829	832	nd	nd	1.54	0.88	nd
10	2,3-dimethyl-1,3-pentadiene	3.00	832	832	nd	1.13	4.08	3.47	1.77
11	3-methyl-1,3,5-hexatriene	3.87	874	890	nd	nd	1.18	1.50	1.26
12	4-methyl-2-heptene	4.38	873	873	nd	nd	2.77	3.13	7.80
13	2,3-dimethyl-hexane	4.90	918	928	22.13	5.06	2.65	3.61	1.77
14	1,2,3-trimethyl-cyclopentene	5,47	875	875	nd	nd	3.33	nd	nd
15	1,1,3,4-tetramethyl-cyclopentane	5,80	821	821	nd	nd	3.08	nd	nd
16	2,4-dimethyl-1-heptene	7.43	937	942	100.00	100.00	100.00	100.00	75.90
17	2,6-dimethyl-2,4-heptadiene	7.49	791	818	nd	nd	2.01	3.17	6.41
18	1,3,5-trimethyl-cyclohexane	7.61	946	951	10.81	9.19	9.78	11.58	8.15
19	p-xylene	7.92	867	867	nd	nd	1.91	6.83	4.29
20	1,2,4,4-tetramethyl-1-cyclopentene	7.98	818	824	6.56	nd	3.51	5.74	1.29
21	1,1-dimethyl-2-ethylidene-cyclopentane	8.08	856	861	nd	4.52	0.66	1.33	1.95
22	2,4,6-trimethyl-3-heptene	8.42	876	892	nd	2.49	1.02	5.89	4.18
23	5,5-dimethyl-1-ethyl-1,3-cyclopentadiene	9.64	779	849	nd	0.95	0.57	2.07	5.30
24	1,2,4-trimethyl-benzene	11.11	951	951	nd	2.29	0.57	2.98	3.49
25	2-methyl-3-methylene-nonane	12.05	801	801	nd	4.18	1.81	6.95	12.41
26	4-methyl-2-decene	12.23	793	797	nd	7.08	1.98	6.98	6.34
27	3,3,5-trimethyl-heptene	12.50	826	840	nd	9.36	1.94	5.11	5.82
28	3,3,6-trimethyl-heptane	12.64	821	837	nd	9.16	1.91	6.98	5.74
29	2,4-dimethyl-3-decene	14.20	833	836	nd	5.50	1.12	5.11	1.92

[a]Retention time for the evolved products of the iPP degradation at 470 °C (T_{MAX}), [b]Similarity, [c]Reverse, nd: not determined

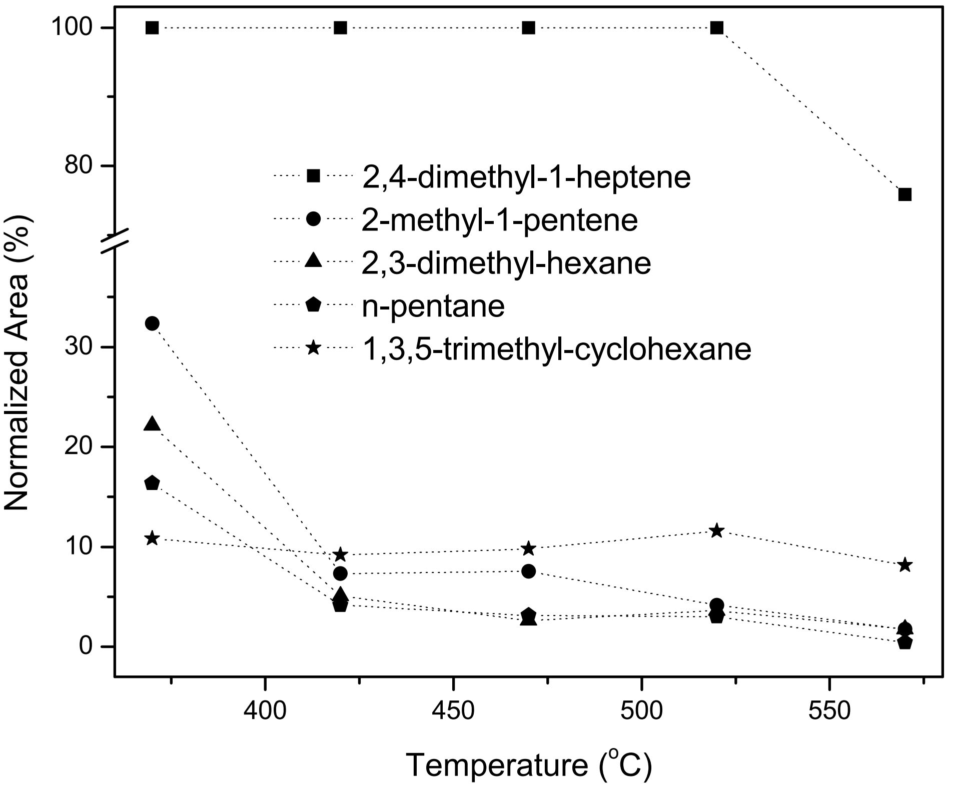


Fig. 2. Normalized peak areas obtained for the major products evolved from the isotactic polypropylene degradation.

Tab. 2. Retention time and normalized peak areas of the volatile compounds extracted during thermal degradation of isotactic polypropylene at 470 ^{0}C at different degradation times.

Peak	Volatile compounds	RT[a] (min)	Degradation Time (min)		
			2-7	12-17	22-27
1	2-methyl-1-propene	0.93	29.96	3.27	nd
2	n-pentane	1.06	12.22	52.49	10.04
3	2-methyl-1-pentene	1.44	33.84	100.00	36.46
4	4-methyl-2-pentene	1.59	nd	12.65	5.66
5	2-methyl-1,3-pentadiene	1.91	nd	5.78	3.10
6	2,4-dimethyl-1-pentene	2.03	nd	17.14	9.50
7	2,4-dimethyl-1,4-pentadiene	2.16	nd	24.90	13.60
8	2-methyl-1,5-hexadiene	2.51	nd	1.99	nd
9	2-methyl-1-hexene	2.67	nd	4.76	3.54
10	2,3-dimethyl-1,3-pentadiene	3.00	nd	10.01	10.43
11	3-methyl-1,3,5-hexatriene	3.87	nd	nd	nd
12	4-methyl-2-heptene	4.38	nd	8.75	11.96
13	2,3-dimethyl-hexane	4.90	9.66	16.52	20.06
14	1,2,3-trimethyl-cyclopentene	5.47	nd	4.53	7.62
15	1,1,3,4-tetramethyl-cyclopentane	5.80	nd	3.21	5.40
16	2,4-dimethyl-1-heptene	7.43	46.18	89.08	100.00
17	2,6-dimethyl-2,4-heptadiene	7.49	nd	5.41	8.14
18	1,3,5-trimethyl-cyclohexane	7.61	nd	nd	nd
19	p-xylene	7.92	nd	nd	nd
20	1,2,4,4-tetramethyl-1-cyclopentene	7.98	nd	nd	nd
21	1,1-dimethyl-2-ethylidene-cyclopentane	8.08	nd	nd	nd
22	2,4,6-trimethyl-3-heptene	8.42	nd	nd	3.41
23	5,5-dimethyl-1-ethyl-1,3-cyclopentadiene	9.64	nd	nd	nd
24	1,2,4-trimethyl-benzene	11.11	nd	nd	nd
25	2-methyl-3-methylene-nonane	12.05	nd	nd	nd
26	4-methyl-2-decene	12.23	nd	nd	nd
27	3,3,5-trimethyl-heptene	12.50	nd	nd	nd
28	3,3,6-trimethyl-heptene	12.64	nd	nd	nd
29	2,4-dimethyl-3-decene	14.20	nd	nd	nd

[a] Retention time for the evolved products of the iPP degradation at 470 °C (T_{MAX}); nd: not determined

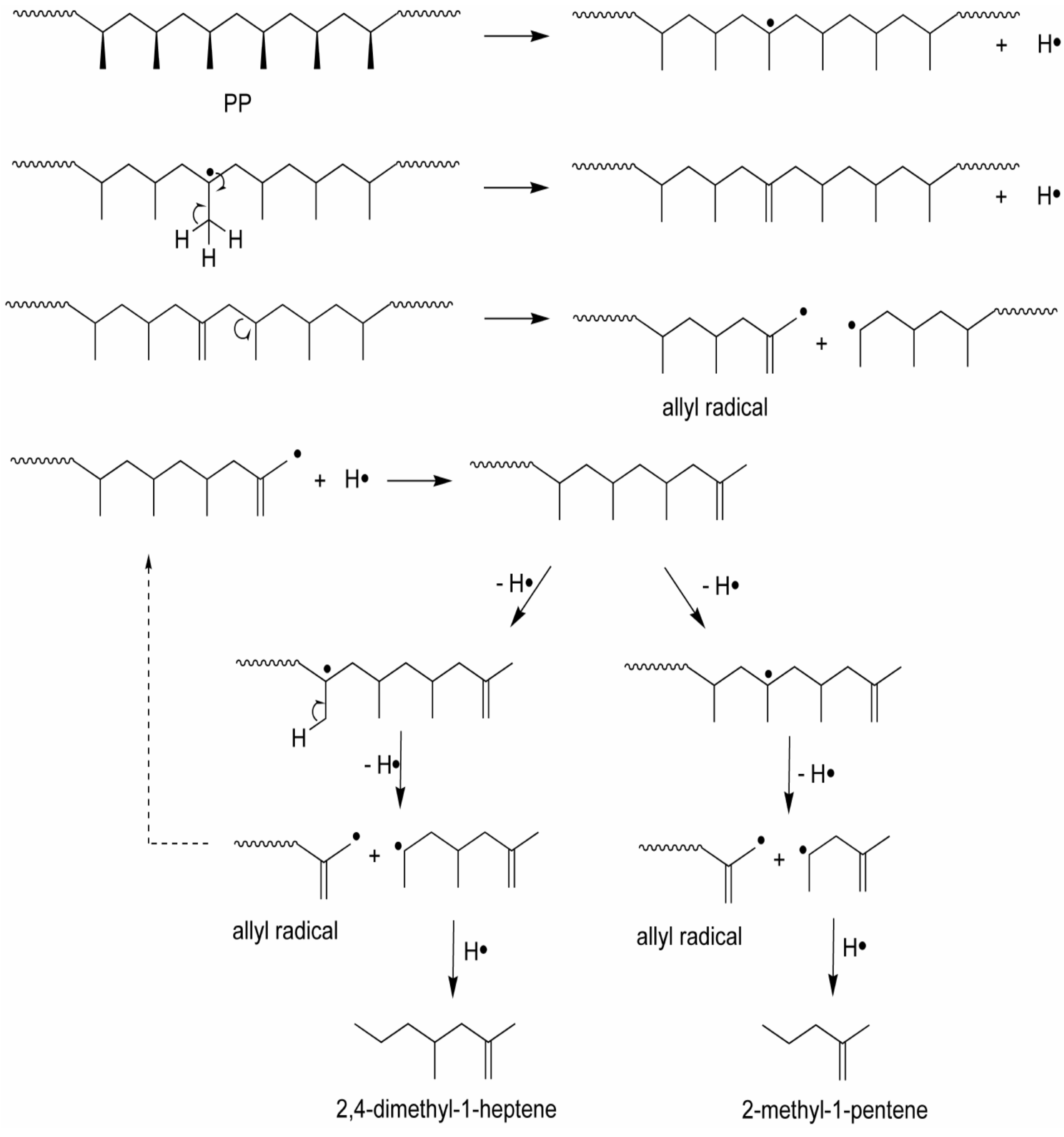
The kinetic parameters for isotactic polypropylene thermal degradation have been analyzed by Chan and Balke considering the thermogravimetric curves obtained under inert atmosphere (argon) [16]. The authors suggested the existence of two main regions associated with low (≤ 10% mass loss) and high (10-100% mass loss) temperatures. The activation energy values determined by the authors for the two regions were ca. 98 and 328 kJ mol^{-1}, respectively, which were attributed to the existence of weak points (low activation energy) and high degrees of random scission (high activation energy) of the main chain. In this study, at 370 °C only seven compounds appeared, increasing to eighteen at 420 °C and to twenty nine at 470 °C, suggesting that above 400 °C the mechanisms of degradation are more complex and associated with the random scission of the chain.

The evolved products were also analyzed at 470 °C (the temperature of maximum degradation rate) at different degradation times (Table 2). Only five products were identified at a first degradation time of 5 minutes: 2-methyl-1-propene, n-pentane, 2-methyl-1-pentene, 2,3-dimethyl-hexane and 2,4-dimethyl-1-heptene. The number of products evolved increased with time, and the experimental procedure (30 minutes) used for the pre-concentration at different temperatures was therefore appropriate.

The compounds 2-methyl-1-pentene and 2,4-dimethyl-1-heptene were the major products evolved between 12-17 and 22-27 minutes, respectively.

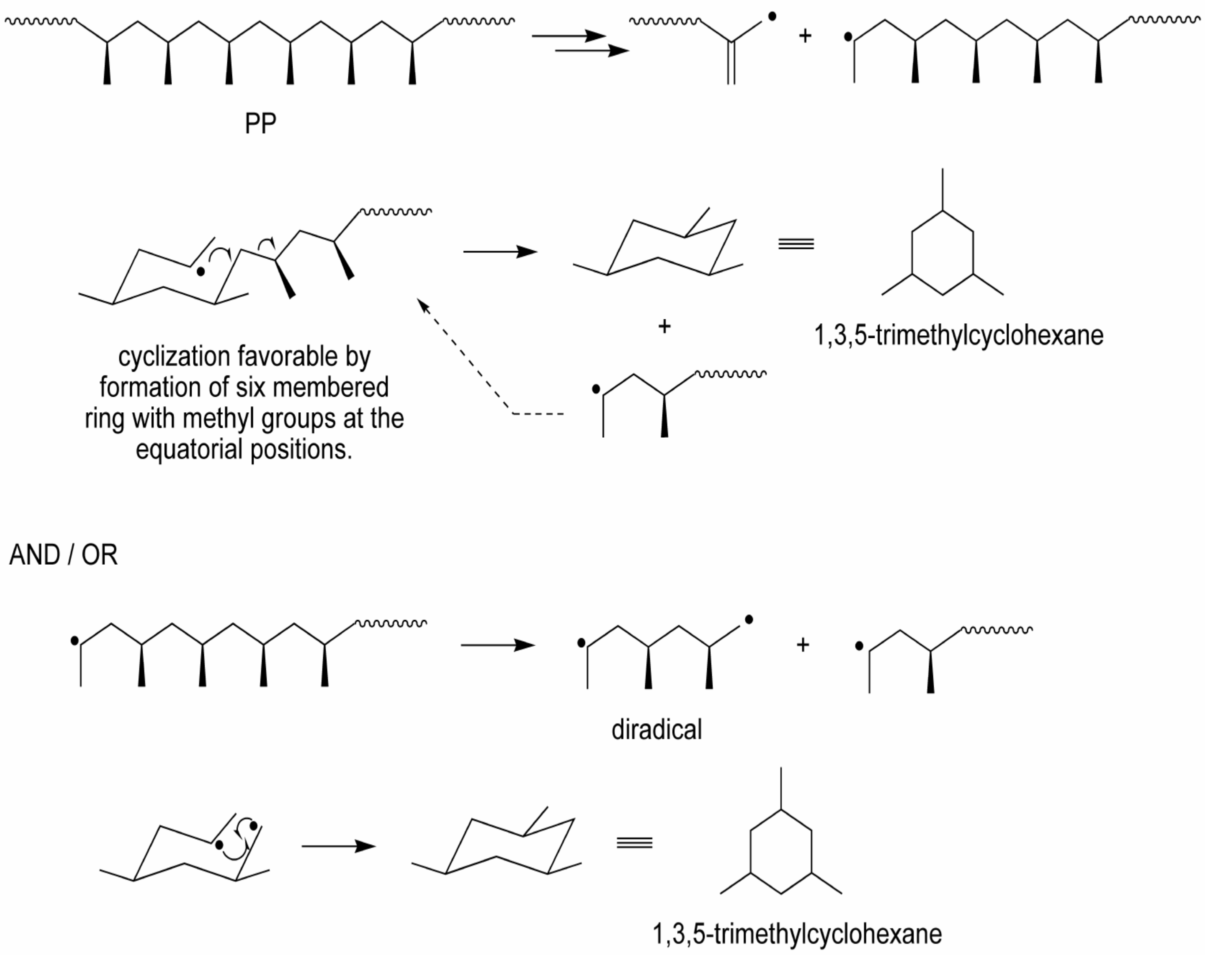
Degradation mechanism

A high number of papers have studied the mechanism associated with polypropylene thermal degradation [12, 17, 22-29]. Despite some conflicting evidence regarding the mechanism, it has generally been described as the formation of alkanes, alkenes and alkadienes as products of polypropylene thermal degradation, by the scission of carbon-carbon bonds, followed by an intramolecular hydrogen transfer process.



Scheme 1. Proposed mechanisms for the formation of 2,4-dimethyl-1-heptene and 2-methyl-1-pentene from isotactic polypropylene degradation.

The formation of alkanes, alkenes or alkadienes has been proposed, as a consequence of a free radical mechanism in which C-C chain scission and the intramolecular transfer can produce primary, secondary or tertiary radicals [17, 23]. Different products are formed during the degradation process depending on the radical type, and it has been suggested that the highest yield products are derived from secondary radicals [22]. Considering that the degradation mechanism is still not totally clear, in this study more in-depth analysis was carried out of the possible mechanism of the formation of the three major compounds: 2,4-dimethyl-1-heptene, 2-methyl-1-pentene and 1,3,5-trimethyl-cyclohexane. Under pyrolytic conditions, at any point of the polymer chain, the C-H bond of the tertiary carbon is broken homolytically generating more stable tertiary radicals (Scheme 1).



Scheme 2. Proposed mechanism for the formation of 1,3,5-trimethyl-cyclohexane from the isotactic polypropylene degradation.

Hydrogen radical elimination from the β carbon to give the terminal C=C double bond may then occur. This makes the polymer chain susceptible to cleavage affording a resonance stabilized allyl radical and a secondary radical as the other part of the chain. The allyl radical may undergo hydrogen radical addition resulting in the neutral polymer containing 2-alkyl-1-propene at one of the ends. The resulting neutral polymer may return to the original allyl radical, or a tertiary radical may be formed through homolytic C-H bond dissociation of some tertiary carbons, which is more likely due to their high occurrence in the polymer. In the same way, this tertiary radical gives another allyl radical and a secondary radical containing 2-alkyl-1-propene at one of the ends. The allyl radical may undergo further hydrogen radical addition and continue the same decomposition process. The other part under go hydrogen radical addition to give neutral molecules such as 2-methyl-1-pentene and 2,4-dimethyl-1-heptene (major products detected) and several other minor homologues with a difference of two carbons in the chain (not discussed).

Rationalization of cyclic product formation may be attributed to the first cleavage that generates an allyl and a secondary radical. The latter may undergo cyclization to the thermodynamically stable six-membered ring according to Scheme 2. The isotactic form of the studied polymer favors six-membered ring formation due to the less hindered approach in the chair conformation with all methyl groups at the equatorial positions. In addition, the secondary radical, generated after cyclization, continues the same decomposition process. This cyclization may occur through the formation of a less stable, but not too unlikely, diradical. Most of the formation of cyclic compounds from the iPP degradation follows a similar mechanism.

Conclusions

Commercial SPME fibers covered with poly(dimethylsiloxane) were used to pre-concentrate products evolved from the thermal degradation of polypropylene. The analysis by GC-MS indicated the formation of more than one hundred evolved products, with ca. forty corresponding to alkenes (79.27%), alkanes (15.38%) and dienes (5.34%) being identified, in full agreement with the literature. The temperature dependence was analyzed in the range 370-570 °C, and indicated the formation of twenty nine evolved products at 470 °C (the temperature of maximum degradation rate for polypropylene), confirming as the main compounds: 2,4-dimethyl-1-heptene, 2-methyl-1-pentene, 2,3-dimethyl-hexane, n-pentane and 1,3,5-trimethyl-cyclo hexane. The analysis at 470 °C using different degradation times indicated, for example, that the compounds 2-methyl-1-pentene and 2,4-dimethyl-1-heptene were the major products evolved between 12-17 and 22-27 minutes, respectively.

The formation of the major compounds may occur through a mechanism based on radical decomposition of the polymer. The first cleavage of iPP generates two radicals: an allyl and a secondary radical. The allyl radical, via a chain process, undergoes hydrogen radical addition followed by further cleavage, generating another allyl radical and the fragment containing the double bond which gives 2-methyl-1-pentene and 2,4-dimethyl-1-heptene by hydrogen radical addition. On the other hand, the secondary radical of the first cleavage undergoes cyclization to a thermodynamically stable six-membered ring affording 1,3,5-trimethyl-cyclohexane and another secondary radical which continues the same decomposition process.

Experimental

Materials

Isotactic polypropylene (average M_w ca. 250,000 g mol^{-1}; average M_n ca. 67,000 g mol^{-1}; density = 0.900 g cm^3 , melting temperature 160-165 °C) was purchased from Aldrich Chemical Company (St. Louis, USA). The isotacticity (94.2%) was determined by ^{13}C-NMR and confirmed by infrared spectroscopy.

SPME procedure

Commercial SPME fibers covered with poly(dimethylsiloxane) (PDMS) (100 μm) were obtained from Supelco (Bellefonte, PA, USA). According to the supplier's instructions, the fibers covered with PDMS were conditioned under nitrogen at 250 °C for 1 hour in the hot port of a gas chromatograph, prior to their use.

For the thermal degradation of isotactic polypropylene (iPP), a tubular oven (Lindberg/Blue) equipped with a quartz tube for the reaction and connected to a solid phase microextraction system, was used [7]. Nitrogen (15 mL min^{-1}) was used as the carrier gas. The oven temperature during the pre-concentration of the degradation products on the fibers was varied from 370 °C to 570 °C. As previously described, the extraction was performed by passing the volatile products from the thermal degradation of iPP around the SPME fiber [7]. After the extraction period (30 min), the fiber was withdrawn from the sample and introduced into the GC-MS injector. The thermal desorption of the degradation products from the PDMS-covered fibers in the heated injector of the gas chromatograph was conducted for 10 minutes. After this period no significant blank values were observed.

In the analysis in which the time period varied, the temperature was maintained at 470 °C. The volatile products from iPP degradation at 470 °C were collected using 190 mL vials.

Mass Spectrometry (GC-MS)

The GC-MS analysis was carried out using a Hewlett Packard gas chromatograph (Mod. 5890) coupled to a mass spectrometer detector and equipped with a split-splitless injector. For the GC separations, a capillary column of fused silica (Agilent HP-5 MS) with 30 m x 0.25 mm ID and a phase thickness of 0.25 µm, was used. The following temperature program was used for the determination of the iPP degradation products: the initial temperature of 35 ^{o}C was held for 3 min and then increased to 120 ^{o}C at 5 ^{o}C min^{-1}. After five minutes the temperature was increased to 200 ^{o}C at 3 ^{o}C min^{-1} and finally to 250 ^{o}C at 10 ^{o}C min^{-1}. The run time was ca. 52 min. The injector and detector temperatures were maintained at 250 ^{o}C and 280 ^{o}C, respectively. The samples were injected in the splitless mode. The carrier gas used was helium at a flow rate of 1 mL min^{-1}. The spectrometer was operated in electron impact (EI) mode with 70 eV detection volts and scan range 41 – 400 m/z. The data were collected and analyzed using the Hewlett Packard ChemStation software (version B-01-00).

Acknowledgements

This work was supported by Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Federal University of Santa Catarina (UFSC).

References

[1] Augusto, F.; Valente, A.L.P. *Trends Anal. Chem.* **2002**, 21, 428.
[2] Grinberg, P.; Campos, R.C.; Mester, Z.; Sturgeon, R.E. *Spectrochim Acta B*, **2003**, 58, 427.
[3] Raikos, N.; Christopoulou, K.; Theodoridis, G.; Tsoukali, H.; Psaroulis, D. *J Chromatogr B*, **2003**, 789, 59.
[4] Vas, G.; Vékey, K. *J. Mass Spectrom.*, 2004, 39, 233.
[5] Miège, C.; Dugay, J. *Analusis*, **1998**, 26, 137.
[6] Charvet, R.; Cun, C.; Leroy, P. *Analusis*, **2000**, 28, 980.
[7] Bortoluzzi, J.H.; Pinheiro, E.A.; Carasek, E.; Soldi, V. *Polym. Degrad. Stab.*, **2005**, 89, 33.

[8] Khabbaz, F.; Albertsson, A.C.; Karlsson, S. *Polym. Degrad. Stab.*, **1999**, 63, 127.
[9] Gallet, G.; Carroccio S.; Rizzarelli, P.; Karlsson, S. *Polymer*, **2004**, 43, 1081.
[10] Gallet, G.; Erlandsson, B.; Albertsson, A.C.; Karlsson, S. *Polym. Degrad. Stab.*, **2002**, 77, 55.
[11] Tehrani, K.A.; Kersiene, M.; Adams, A.; Venskutonis, R.; De Kimpe, N. *J. Agric. Food Chem.*, **2002**, 50, 4062.
[12] Bockhorn, H.; Hornung, A.; Hornung, U.; Schawaller, D. *J..Anal. Appl. Pyrolysis*, **1999**, 48, 93.
[13] Gao, Z.; Kaneko, J.; Amasaki, I.; Nakad, M. *Polym. Degrad. Stab.* **2003**, 80, 269.
[14] Chan, J.H.; Balke, S.T. *Polym. Degrad. Stab*., **1997**, 57, 113.
[15] Chan, J.H.; Balke, S.T. *Polym. Degrad. Stab.*, **1997**, 57, 127.
[16] Chan, J.H.; Balke, S.T. *Polym. Degrad. Stab*., **1997**, 57, 135.
[17] Westerhout, R.W.J.; Waanders, J.; Kuipers, J.A.M.; Swaaij, W.P.M. *Ind. Eng. Chem. Res.*, **1997**, 36, 1955.
[18] Day, M.; Cooney, J.D.; Mackinnon, M. *Polym. Degrad. Stab.*, **1995**, 48, 341.
[19] Amorim, M.T.S.; Comel, C.; Vermande, P. *J. Anal. Appl. Pyrolysis*, **1982**, 4, 73.
[20] Amorim, M.T.S.; Bouster, C.; Veron, J. *J. Anal. Appl. Pyrolysis*, **1982**, 4, 103.
[21] Salvador, M.D.; Amigó, V.; Vidal, M.J.; Ribers, A.; Contat, L. *J. Mater. Process Technol.*, **2003**, 143, 693.
[22] Kiang, J.K.Y.; Uden, P.C.; Chien, J.C.W. *Polym. Degrad. Stab.* **1980***,* 2, 113.
[23] Lattimer, R.P. *J. Anal. Appl. Pyrolysis,* **1995**, 31, 203.
[24] Thornberg, S. M.; Bernstein, R.; Mowery, D. M.; Klamo, S. B.; Hochrein, J. M.; Brown, J. R.; Derzon, D. K.; Clough, R. L. *Macromolecules* **2006**, 39, 5592.
[25] Sasaki, D.; Suzuki, Y.; Toshiki, H.; Yano, S.; Sawaguchi, T. *J. Anal. Appl. Pyrolysis* **2007**, 80, 312.
[26] Kaminsky, W.; Zorriqueta, I-J. N. *J. Anal. Appl. Pyrolysis* **2007**, 79, 368.
[27] Mastral, J.F.; Berrueco, C.; Ceamanos, J. *J. Anal. Appl. Pyrolysis* **2007**, 79, 313.
[28] Mowery, D. M.; Clough, R. L.; Assink, R. A. *Macromolecules* **2007**, 40, 3615.
[29] Williams, P. T.; Slaney, E. *Resources, Conservation and Recycling* **2007**, 51, 754.