Controlled Degradation by Melt Processing with Oxygen or Peroxide of Ethylene/Propylene Copolymers

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ABSTRACT: Ethylene/propylene copolymers with the same composition but different sequence of monomer distribution were submitted to thermal degradation in an inert atmosphere, in the presence of oxygen and/or free radical initiators. The analysis of the reaction products, consisting of lower molecular weight macromolecules with double bonds and oxygenated functional groups, was performed by viscosimetric, FTIR, NMR, and differential scanning calorimetry (DSC) analysis. The presence of linear ethylene blocks of different length with distinct melting temperatures was detected by the self-annealing methods based on DSC. The results are used to evaluate the effect of the copolymer macromolecules' microstructure and the processing conditions on the degradation extent and the molecular structure of the degradation products. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 372–381, 2004

Key words: ethylene/propylene copolymers; degradation; melt processing; free radical

INTRODUCTION

In the present work, two different ethylene/propylene copolymers (EPM1 and EPM2) with similar high ethylene content were analyzed and characterized from the point of view of the molecular structure and with specific reference to the comonomer sequence distribution in order to understand how the microstructure can affect the thermal response of the macromolecule.

Accordingly, ethylene polymers and copolymers containing different degrees and distributions of branching and functional groups, such as double bonds, aromatic groups, and ester groups, show a distinct behavior when submitted to melt processing in mechanical mixers either in the presence or in the absence of peroxides.[1]

To this purpose EPM1 and EPM2 were successively submitted to thermal degradation in an inert atmosphere in the presence of oxygen and/or free radical initiators.

The reaction products generally consisted of shorter macromolecules with unsaturations and oxygen-containing substituents.[2]

Detailed analysis of these products was performed by FTIR, NMR, differential scanning calorimetry (DSC), and DSC annealing and viscosity determination. The information about the correlation between the starting ethylene/propylene copolymer sequence distribution and the characteristics of the degradation products were rationalized on the basis of free radical assisted mechanisms.

EXPERIMENTAL

Materials

Solvents were obtained from Aldrich Chemical Co., J. T. Baker, and Carlo Erba and were used without purification. Commercial ethylene/propylene copolymers were used as received. The polymers' physical characteristics are reported in Table I.

A solution of 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxanone 41% in odorless mineral spirits (Trigonox 301) obtained from Akzo Nobel was used without purification.

Degradation experiments

20 g of the virgin polymer was processed in a Brabender plastograph mixer (Model No. OHG47055, 30 cc) under nitrogen or air atmosphere at a temperature set to 180, 200, 220, and 250°C with a rotor speed of 50 rpm. In the case of free radical initiated degradations, 0.10–0.20 mol % of Trigonox 301 was also added into the mixer after the complete melting of the polymer and stabilization of the torque (about 3 min after the introduction of the polymer). For all runs the torque

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TABLE I
Ethylene/Propylene Copolymers Characteristics

Sample	Ethylene wt %	Viscosity Mooney (ML (1+4), 100°C)	$\bar{M}w$	$\bar{M}w/\bar{M}n$
EPM1	70–74	40–48	138,000	2,5
EPM2	71–74	36	115,000	2,0

behavior was recorded. After 25 min, the mixing was stopped and the recovered materials were molded in a Campana PM20/200 hydraulic press at 150°C and 2 atm. Films with about 0.2 mm thickness were obtained.

Characterization methods

Infrared spectroscopy (FTIR)

The infrared spectra of the films obtained by compression molding or casting from dilute toluene solutions on KBr windows were performed with a Perkin-Elmer 1330 FTIR spectrometer.

For the determination of the ethylene content of EPM1 and EPM2 before processing the ratio between A1, the absorbance value at 4390 cm^{-1} associated with the combinational band of the methyl C-H stretching and bending modes, and A2, the absorbance value at 4255 cm^{-1} associated with the methylene band, were calculated.[3] The ethylene wt % amount was then evaluated by interpolation of a calibration curve obtained from ethylene/propylene copolymers of known composition.

^{13}C-NMR spectroscopy

^{13}C-NMR spectra of the materials were run on 0.5 wt % solution in 1,1,2,2-tetrachloroethane-d$_2$ (TCE-d$_2$) with the solvent resonance at 74 ppm as internal standard. The spectra were acquired on a Varian Gemini-200-MHz spectrometer at a temperature of 90 ± 0.1°C with a 45° impulse angle, an acquisition time of 0.6 s, a delay time of 0.4 s, and decoupling during acquisition. To acquire acceptable signal-to-noise ratios, about 50,000 scans were necessary.

DSC

Differential scanning calorimetry measurements were performed by a Perkin-Elmer DSC7 calorimeter equipped with a CCA7 cooling device. Mercury (m.p. = -38.4°C) and indium (m.p. = 156.2°C, ΔH = 28.47 J/g) standards for low-temperature scans were used for instrument calibration. Heating and cooling thermograms were carried out at a scan rate of 10°C/min.

In the successive self-nucleation/annealing (SSA) DSC method the sample was first melted at a temper-
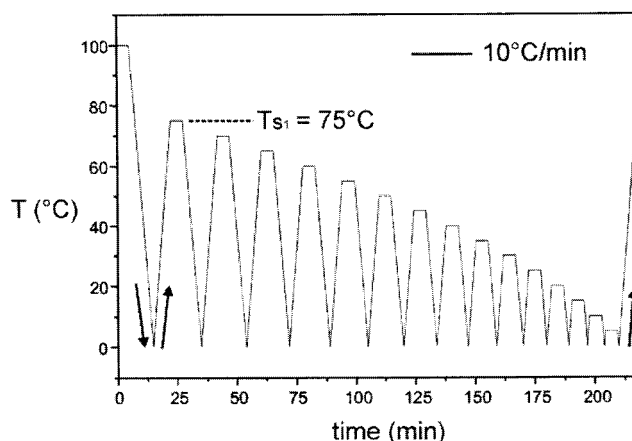

Figure 1 Schematic representation of SSA thermal treatment.

ature of 100°C and cooled at 10°C/min to 0°C to create a new thermal history. Successively, the sample was subjected to a thermal conditioning based on sequential application of self-nucleation and annealing steps.[4] Finally, at the end of the thermal treatment, the melting behavior was determined at 10°C/min rate. All the SSA performed scans are reported in Figure 1.

Viscosity measurements

Viscosity was determined for polymer solutions in decahydronaftalene in a capillary Ubbelhode viscometer at 135°C. For each sample three solutions at different concentrations were prepared by dissolving 0.01–0.02 g of the polymer in 10 mL of the solvent. Intrinsic viscosities were obtained from both the equations of both Huggins[5] and Kraemer.[5,6] The weight-average molecular masses (Mw$_\eta$) of all the samples were evaluated from the intrinsic viscosities by applying a modified Mark–Houwink expression[7] for ethylene/propylene copolymers using literature values[7] for the equation parameters.

RESULTS AND DISCUSSION

The thermal response of the two different ethylene/propylene copolymers was investigated: (a) inder in-

TABLE II
Thermal Degradation Conditions of EPM2 and EPM1

Degradation conditions	Temperature (°C)	Additive
Inert	180	N$_2$
	200	N$_2$
	220	N$_2$
	250	N$_2$
Oxidative	180	Air
Free radically initiated:	180	0.10 mol %
Trigonox 301	180	0.15 mol %
	180	0.20 mol %
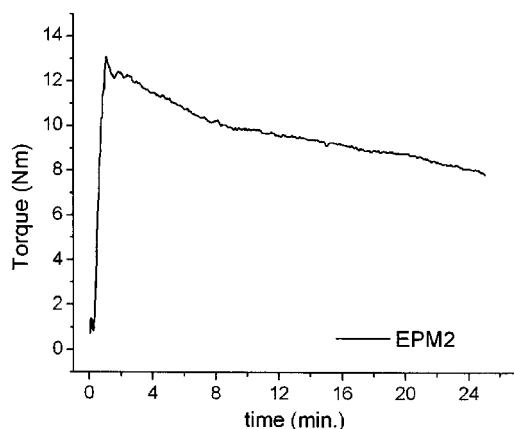
Figure 2 Torque of EPM2 as a function of the processing time at 180°C under nitrogen atmosphere.

TABLE IV
Viscosity Values and Weight-Average Molecular Masses of the Ethylene/Propylene Copolymers before and after Thermal Processing in Nitrogen Atmosphere at High Temperature

Sample (thermal treatment)	$[\eta]inh^a$ (L/g)	$[\eta]rid^b$ (L/g)	Mw_η^c
EPM1 (none)[d]	0.21	0.21	135,100–136,300
EPM2 (none)[e]	0.20	0.20	123,200–125,300
EPM1 (250°C N_2)	0.16	0.16	95,300–95,100
EPM2 (250°C N_2)	0.14	0.14	77,700–73,400

[a] Using the Kraemer equation.
[b] Using the Huggins equation.
[c] Calculated on the basis of the equation reported in literature.[8]
[d] Considering the content of ethylene = 72 wt % from IR data.
[e] Considering the content of ethylene = 74 wt % from IR data.

ert conditions, under nitrogen atmosphere; (b) under oxidative conditions, under air atmosphere; and (c) in the presence of small amounts of a free radical initiator.

All degradation processes were performed in a Brabender-type Plastograph mixer and the rheological behavior of the polymeric material during the treatment was monitored by means of the torque.

The degradation conditions adopted are summarized in Table II.

The polymer products recovered after processing were analyzed by melting behavior measurements, infrared and ^{13}C nuclear magnetic resonance spectroscopies, viscosity measurements, and differential scanning calorimetry.

Thermal degradation under inert conditions

As reported in Table II, the copolymers were subjected to four different processing temperatures to evaluate the effect of this parameter on the polymer degradation feed.

Thermal behavior

The torque response (Fig. 2) recorded during the processing is a direct evidence of the polymer degradation due to the correlation among the torque, the power consumed during the mixing process to maintain a constant speed of the rotors of the mixer, and the viscosity and the molecular weight of the melted polymer.

$\Delta Tq/Tq_f$ was introduced to evaluate a sort of normalized degradation that can directly connect the variation of the torque during the processing with the degradation extent.

The final torque values (Tq_f) are lower than the initial values, both for copolymers and for all the processing temperatures (Table III). In particular, $\Delta Tq/Tq_f$ indicates that the normalized degradation is higher for EPM2, but the differences decrease with temperature.

Viscosity measurements

The viscosity pristine copolymers and the samples produced by treatment at 250°C were determined by the equations of Huggins[5] and Kraemer.[5,6] The viscosimetric molecular weights (Mw_η) were calculated using a modified Mark–Houwink expression reported in the literature[8] for ethylene/propylene copolymers (Table IV).

The viscosity values reported in Table IV show the decrease in molecular weight after thermal processing

TABLE III
EPM1 and EPM2 Torque Values after Thermal Processing at Various Temperatures

Temperature (°C)	Tq_f		ΔTq		$\Delta Tq/Tq_f$	
	EPM1	EPM2	EPM1	EPM2	EPM1	EPM2
180	12.4	7.9	1.6	5.3	0.1	0.6
200	9.2	6.5	4.4	4.8	0.5	0.7
220	9.2	6.2	2.5	2.2	0.3	0.3
250	6.3	4.9	2.0	2.0	0.3	0.4

Figure 3 Infrared spectra of EPM1.

Figure 4 Final heating scans after SSA treatment of un-processed EPM1 and EPM2.
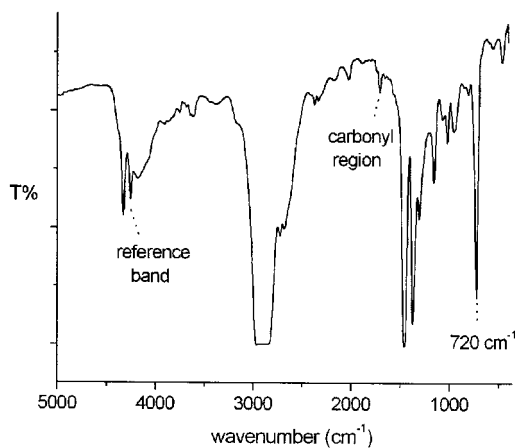
at 250°C. Comparing the viscosimetric molecular weight of both copolymers before and after processing, EPM2 showed higher degradation than EPM1.

Infrared spectroscopy

The effect of the thermal processing on the macromolecular structure of the examined copolymers was also studied by infrared spectroscopy.

Macromolecular chain scission promoted by thermal degradation or the introduction of polar functionalities on the polymer backbone by oxidizing processing conditions can be actually monitored analyzing, respectively, the absorption at 722 cm^{-1} attributed to the bending $\gamma_{(CH2)\geq5}$ and the absorptions in the range between 1710 and 1750 cm^{-1} in the carbonyl region assigned to the stretching vibration $\nu_{(C=O)}$ of carboxylic acid, carboxylic ester, aldehyde, and ketone functionalities (Fig. 3).[9]

To quantify the effect of degradation conditions on the macromolecular structure, the integrated contributions of these absorptions were normalized respect to a reference band located in the range between 4500 and 3950 cm^{-1} attributed to overlapping combination bands of stretching and bending methylenic and methyl fundamentals. For this purpose two parameters, R_1 and R_2, are defined by Eqs. 1 and 2, respectively,

$$R_1 = \frac{A_{720}}{A_{ref}} \qquad (1)$$

$$R_2 = \frac{A_{carbonyl}}{A_{ref}}, \qquad (2)$$

where A_{ref} is the integrated area of the reference band and $A_{carbonyl}$ represents the integrated contribution of the carbonyl region.

In Table V the parameters evaluated for EPM2 and EPM1 before and after thermal degradation under inert conditions at 250°C are reported.

As reported in Table V, R_1 values calculated for both pristine copolymers indicate that EPM1 is composed of a lower amount of long ethylene sequences than EPM2. These values decrease much more for EPM1 after thermal processing, suggesting an higher influence of the degradation conditions on the macromolecular chain structure.

TABLE V
R Parameters before and after Thermal Processing at 250°C in Nitrogen Atmosphere of EPM1 and EPM2

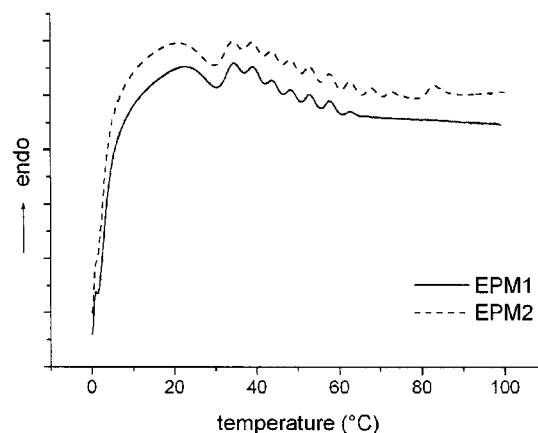| Sample		R_1	R_2
EPM1	Unprocessed	0.52	—
	Processed	0.47	0.02
EPM2	Unprocessed	0.57	—
	Processed	0.55	0.02

Figure 5 Final heating scans after SSA treatment of EPM1 and EPM2 submitted to thermal processing in nitrogen atmosphere.

TABLE VI
Peak Heights and Integrated Areas after SSA Treatment of EPM1 and EPM2

Peak	EPM2	EPM2 (250°C N₂)	EPM2 (180°C air)	EPM1	EPM1 (250°C N₂)	EPM1 (180°C air)
T1 (°C)	34.5	34.5	34.8	34.9	34.5	35.0
% integrated area	*22.0*	*19.5*	*16.9*	*28.0*	*27.1*	*24.6*
T2 (°C)	39.5	38.9	38.9	39.9	39.4	39.6
% integrated area	*25.1*	*20.1*	*21.7*	*33.3*	*28.6*	*24.4*
T3 (°C)	43.8	43.6	43.7	45.0	43.9	44.1
% integrated area	*16.5*	*15.8*	*15.6*	*19.7*	*16.6*	*17.9*
T4 (°C)	48.4	48.3	48.3	49.0	48.3	48.6
% integrated area	*10.5*	*11.5*	*11.9*	*6.5*	*10.0*	*12.2*
T5 (°C)	53.1	53.0	53.0	53.3	53.0	53.0
% integrated area	*7.2*	*9.3*	*10.2*	*5.3*	*9.0*	*11.5*
T6 (°C)	57.7	57.7	58.0	57.9	57.7	57.7
% integrated area	*5.8*	*6.7*	*6.9*	*5.6*	*6.7*	*6.7*
T7 (°C)	62.6	62.6	63.0	63.1	62.6	62.6
% integrated area	*4.2*	*4.7*	*4.6*	*1.6*	*2.0*	*1.9*
T8 (°C)	67.8	67.6	68.1	—	—	—
% integrated area	*2.4*	*2.8*	*2.9*			
T9 (°C)	73.0	72.9	73.1	—	—	—
% integrated area	*1.9*	*2.5*	*2.2*			
T10 (°C)	83.4	83.0	83.6	—	—	—
% integrated area	*3.7*	*7.1*	*7.1*			

This phenomenon is probably due to the EPM2 macromolecular structure whose long ethylene sequences confer the copolymer a particular thermal stability.[10]

On the other hand, R_2 values, indicating the intensity of the carbonyl band, do not show for either copolymer any changes after thermal processing. These results, in agreement with those of other authors,[11] prove that there are almost no oxidative reactions during the processing because of the absence of oxygen within the mixer.

DSC

The standard DSC analysis showed that the two pristine copolymers are characterized by similar thermal properties: the T_g is at about -45°C and there is a melting transition in the range between -10 and 50°C for both samples; the associated enthalpies are 36.5 and 33.4 J/g for EPM1 and EPM2, respectively.

The samples were also analyzed by SSA-DSC[4] (Fig. 1).

The self-nucleation temperature Ts_1, as determined separately by DSC standard analysis, was set at 75°C

for all samples. However, to better compare the thermograms resulting from the SSA-DSC runs, all isothermal steps were set at the same temperatures. Therefore, the final DSC curves reported in Figure 4 for the starting materials and in Figure 5 after thermal processing at 250°C reflect the differences in the microcrystallinity of the various samples.

The thermogram related to the unprocessed EPM2 is characterized by 10 melting peaks in the temperature range from 35 to 83°C; in the case of EPM1 we observed 7 peaks from 35 to 63°C. The presence of crystallized fractions at higher temperature for the EPM2 sample indicates that this copolymer is characterized by longer linear ethylene sequences, according

TABLE VIII
Viscosity Values and Weight-Average Molecular Masses of the Ethylene/Propylene Copolymers before and after Thermal Processing in Air Atmosphere

Sample (thermal treatment)	[η]inh[a] (L/g)	[η]rid[b] (L/g)	Mw[c]ₙ
EPM1 (none)[d]	0.21	0.21	135,100–136,300
EPM2 (none)[e]	0.20	0.20	123,200–125,300
EPM1 (180°C air)	0.13	0.13	68,800–68,600
EPM2 (180°C air)	0.08	0.08	43,700–43,750

[a] Using the Kraemer equation.
[b] Using Huggins equation.
[c] Calculated on the basis of the equation reported in the literature.[8]
[d] Considering the content of ethylene = 72 wt % from IR data.
[e] Considering the content of ethylene = 74 wt % from IR data.

TABLE VII
EPM1 and EPM2 Torque Values after Thermal Processing in Air Atmosphere

Temperature (°C)	Tq_f EPM1	Tq_f EPM2	ΔTq EPM1	ΔTq EPM2	ΔTq/Tq_f EPM1	ΔTq/Tq_f EPM2
180	5.2	2.5	9.3	10.6	1.8	4.2

TABLE IX
R **Parameters before and after Thermal Processing in Air Atmosphere of EPM1 and EPM2**

Sample		R_1	R_2
EPM1	Unprocessed	0.52	—
	Processed	0.46	0.04
EPM2	Unprocessed	0.57	—
	Processed	0.56	0.03

to the results obtained by infrared analysis. After the thermal treatment under inert condition similar thermograms were collected for both samples with the same methodology, thus indicating that the structural changes that occurred during the melt processing did not disrupt dramatically their ability to crystallize.

Nevertheless, by integrating and normalizing the area of the peaks (Table VI) it is evident that the enthalpy associated with the peaks at lower temperature decreases, besides the increase observed for the enthalpy associated with the peaks at higher temperature (starting from the peak at about 48°C for both copolymers).

We can consider that the small amount of copolymer that is able to crystallize is characterized by a different kind of ethylene sequence: the shorter ethylene sequences, which are presumably associated with the lower temperature melting peaks, are characterized by a lot of defects (branching) and could be considered more reactive toward degradation processes; on the other hand, the longer ethylene sequences could be considered more stable and so their melting peaks are not affected by the thermal treatment.

Thermal degradation in air

The analysis, as indicated in Table I, was performed without flowing nitrogen into the chamber of the mixer, but under stronger mixing conditions due to the presence of air.

Thermal behavior

The torque values reported in Tables VII and III suggest that both copolymers are much more affected by oxidative conditions with respect to the thermal processing performed in a nitrogen atmosphere. In particular, as indicated by the $\Delta Tq/Tq_f$ ratio, EPM2 seems to be more sensitive by oxidative degradation conditions with respect to EPM1.

Viscosity measurements

These results were confirmed by viscosity measurements (Table VIII): the thermal treatment in the presence of air produces samples characterized by the lowest molecular weight and seems to be more effective for the EPM2 sample.

Infrared spectroscopy

The presence of air within the mixer does not seem to affect the scission behavior of the two copolymers with respect to the results presented after thermal processing under inert conditions as evidenced by the calculated R_1 parameters. On the other hand, the R_2 values after processing indicate growth of the car-
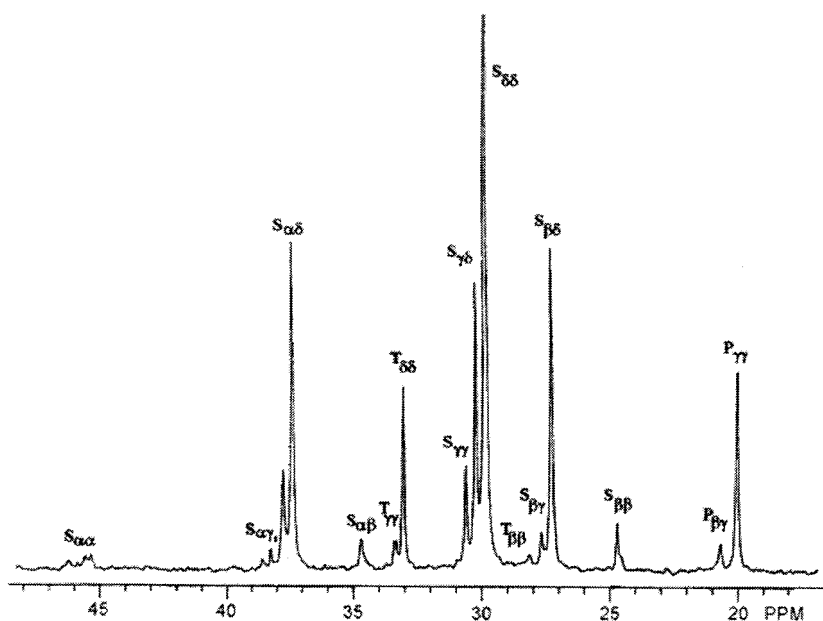

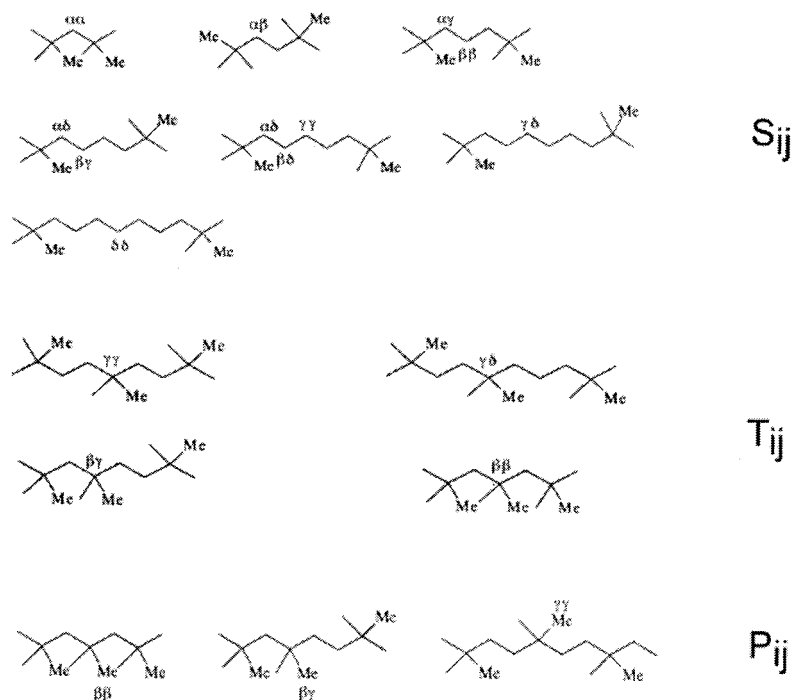**Figure 6** ^{13}C NMR spectra of EPM1 and peak assignments.

Figure 7 Methylenic sequences (S_{ij}), methyl contributions (P_{ij}), and trisubstituted carbon atom attributions (T_{ij}) according to Paul and Grant nomenclature.

bonyl band, suggesting the introduction on the polymer backbone of polar functionalities (Table IX).

¹³C-NMR spectroscopy

The ¹³C-NMR spectrum of EPM1 is reported in Figure 6.

The nomenclature assigning the peaks for various carbons of the ethylene/propylene copolymer follows the method suggested by Wilkes et al.[12] A methylene carbon (-CH₂-) is attributed to the letter S and a pair of

Greek letters that indicate its distance in both directions from the nearest tertiary carbons. A methyl carbon is identified by the letter P, and a tertiary carbon is labeled by the letter T. The carbon nomenclature and the peak assignments are shown in Figures 6 and 7.

In addition, the reactivity ratio products ($r_E \cdot r_P$) were evaluated according the procedure proposed by Wilkes et al.[12] (Table X) to confirm the different sequence distribution of the two ethylene/propylene copolymers.

TABLE X
¹³C Spectral Assignments, Integral Regions, and Reactivity Ratios of EPM2 and EPM1 and of EPM1 after Thermal Processing in Air

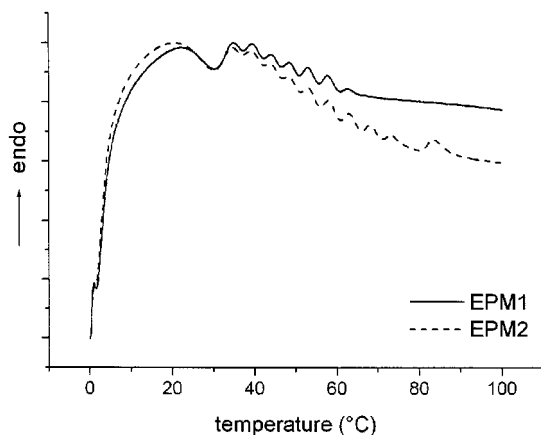| Contributions	δ (ppm)	EPM2 area %	EPM1 area %	EPM1 (180°C air) area %
$S_{\alpha\alpha}$ (PPPP+PPPE+EPPE)	46.3–45.6	1.7	1.7	1.1
$S_{\alpha\gamma}$	37.9–37.8	4.4	5.2	9.7
$S_{\alpha\delta}$	37.5–37.4	12.6	12.0	12.9
$S_{\alpha\beta}$	34.9	1.9	2.2	1.9
$T_{\gamma\gamma}$	33.8	1.5	1.7	1.8
$T_{\delta\delta}$	33.1	5.8	5.9	5.9
$T_{\beta\gamma}$	30.7	—	—	—
$S_{\gamma\gamma'}$, $S_{\gamma\delta'}$, $S_{\delta\delta}$	30.6–29.8	49.5	45.2	46.0
$T_{\beta\beta}$	28.7	—	1.3	—
$S_{\beta\gamma'}$, $S_{\beta\delta}$	27.9–27.4	13.4	13.1	15.1
$S_{\beta\beta}$	24.7–24.4	1.7	2.4	2.2
$P_{\beta\gamma}$ (PPPE^P_E, EPPE^P_E)	20.7–20.5	0.8	1.7	1.3
$P_{\gamma\gamma}$	19.8	6.7	7.7	7.8
Reactivity ratios	—	0.68	0.54	—

Figure 8 Final heating scan after SSA treatment of EPM1 and EPM2 submitted to thermal processing in air atmosphere.

The analysis of the ^{13}C-NMR contributions showed that EPM2 is composed of a larger number of long ethylene sequences to respect to EPM1 according to the results obtained by infrared spectroscopy. In addition, the higher value of the reactivity ratio product calculated for EPM2 confirms that its polymer structure is blockier than that of EPM1.

The integrated and normalized signals of EPM2 after thermal treatment in air (Table X) evidenced an enrichment of the amount of the medium and long ethylene sequences (see in Table X the increasing of the $S_{\alpha\gamma}$, $S_{\alpha\delta}$ and $S_{\beta\gamma}$, $S_{\beta\delta}$ signals). Indeed, long ethylene sequence does not seem to be affected by degradation conditions with respect to the short ones.

SSA-DSC

The integrated and normalized area of the peaks after the thermal processing in air shows a decrease of the enthalpy associated with the peaks at lower temperature (Table VI, Fig. 8). Actually, as reported for the thermal degradation under inert conditions, the longer ethylene sequences could be considered more stable with respect to the shorter ones, characterized by a lot of defects, and therefore more reactive toward degradation processes.
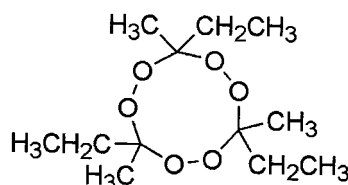

Figure 9 Chemical structure of Trigonox 301.

TABLE XI
Viscosity Values and Weight-Average Molecular Masses of the Ethylene/Propylene Copolymers before and after Thermal Processing in the Presence of 0.15 mol % of Trigonox 301

Sample (thermal treatment)	$[\eta]inh^a$ (L/g)	$[\eta]rid^b$ (L/g)	Mw_η^c
EPM1 (none)^d	0.21	0.21	135,100–136,300
EPM2 (none)^e	0.20	0.20	123,200–125,300
EPM1 (180°C perox)^f	0.13	0.13	74,200–75,400
EPM2 (180°C perox)^f	0.09	0.09	72,700–72,200

^{a} Using the Kraemer equation.
^{b} Using the Huggins equation.
^{c} Calculated on the basis of the equation reported in the literature.[8]
^{d} Considering the content of ethylene = 72 wt % from IR data.
^{e} Considering the content of ethylene = 74 wt % from IR data.
^{f} Using Trigonox 301 (0.15 mol %).

Influence of a peroxide on degradation

Trigonox 301 (Fig. 9) shows at 180°C a half-time ($t_{1/2}$) of 30 s in chlorobenzene. The compound was reported as a very efficient peroxide for the production of controlled rheology polypropylene in extrusion processes.[13]

Thermal behavior and viscosity measurements

The viscosity measurements performed on the polymer samples treated with 0.15 mol % of peroxide confirmed the occurrence of the degradation process (Table XI).

However, this behavior is affected by the amount of Trigonox 301; indeed, as illustrated by the $\Delta Tq/Tq_f$ ratio in Table XII for EPM2, increasing this last degradation effect is reduced, probably in connection with recombination reactions favored by an increased concentration of macroradicals.

Infrared spectroscopy

The values of R_2 parameters listed in Table XIII for peroxide degradation processing in a nitrogen atmosphere were similar to that reported for thermal pro-

TABLE XII
EPM1 and EPM2 Torque Values after Thermal Processing in the Presence of Peroxide

Trigonox 301 (mol %)	Tq_f		ΔTq		$\Delta Tq/Tq_f$	
	EPM1	EPM2	EPM1	EPM2	EPM1	EPM2
0.10	8.5	9.1	4.0	4.6	0.5	0.5
0.15	4.2	6.6	10.9	6.5	2.6	0.9
0.20	4.2	11.9	10.4	2.0	2.5	0.2

cessing in air (Table IX) probably due to the presence of oxygen generated by the peroxide decomposition within the mixer.

On the other hand, EPM2 evidenced a more pronounced chain modification with respect to EPM1, probably because of the higher sensitivity of the long ethylene sequences of EPM2 to processing conditions at high peroxide concentration.
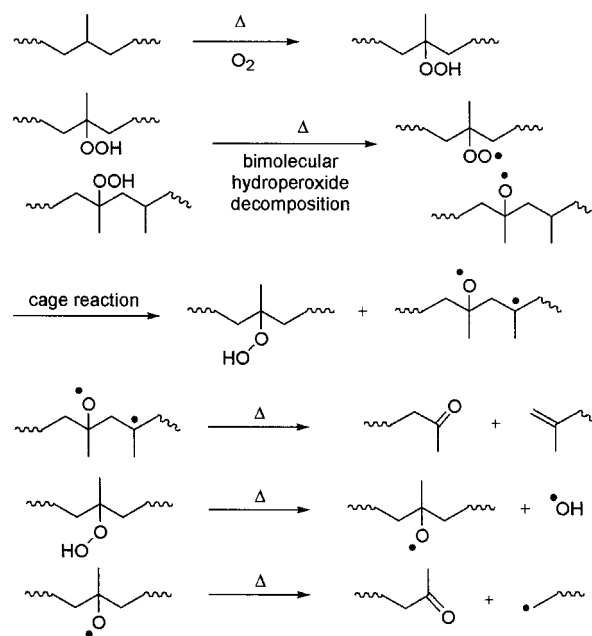
CONCLUSION

The analysis of the samples obtained through modulated degradation processing in the melt of two ethylene/propylene random copolymers containing similar amounts of propylene units but different distribution of the monomeric sequences indicated that the modification of the structure, the content of the functional groups, and the extent of chain breaking reactions depend on the experimental conditions (in an inert or oxidative atmosphere or in the presence of a peroxide) and on the microstructure of the starting polymers.

In particular, the treatment of the two copolymers in the presence of an oxidative atmosphere or in the presence of peroxide gave at the same time a decrease in the chain length and formation of a significant amount of functional groups grafted onto the polymer backbone. The degradation in the presence of oxygen seems to be more effective for both copolymers than in an inert atmosphere. The presence of oxygen could actually favor the degradation reactions through the hydroperoxide reactive formation onto the polyolefin backbone even if the effect is different for propylene isolated units with respect to propylene short blocks (Scheme 1).

In addition, the presence of longer ethylene sequences in the macromolecular chain grants a greater persistency of crystallinity after degradation in the presence of air as deduced from DSC results. This behavior confirms the larger thermoxidation stability of EPM2 samples with a blockier structure with respect to EPM1 samples composed of a larger number of short ethylene/propylene sequences and then characterized by a greater number of defects that make the copolymer more reactive toward degradation processes.

Scheme 1

These data confirm in particular that polymers with different microstructure and similar composition could be characterized by different thermal behavior during processing in the melt.

Degradation processes performed in the presence of Trigonox 301 as peroxide showed results that were similar to those obtained using oxidative conditions due to the production of oxygen during mixing. On the contrary, at high peroxide concentration crosslinking reactions occur especially for EPM2 due to the presence of longer ethylene sequences.

TABLE XIII
R Parameters before and after Thermal Processing in the Presence of 0.15 mol % of Trigonox 301

Sample		R_1	R_2
EPM1	Unprocessed	0.52	—
	Processed	0.51	0.06
EPM2	Unprocessed	0.57	—
	Processed	0.52	0.03

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