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Structural transformations of anisotactic polypropylene submitted to low-frequency plasma treatment

Summary — Anisotactic PP was prepared over the *rac*-Et $(Ind)_2ZrCl_2$—MAO catalyst system and PP films were treated with a low-frequency (50 Hz) glow discharge plasma. The treatment resulted in whole-volume structural modifications whose extent was related to the initial α-/γ-phase ratio in original PP. At γ-phase contents $\leq 60\%$, nearly all the γ- became the α-phase, the m. p. of the PP treated rose (from 130°C to 164°C, Table 2), isotactic pentad fraction rose (^{13}C NMR spectra, Table 5), stereoregularity increased (IR spectra, Table 4), and MW and MWD rose (Table 6). The PP treated thus acquired the properties of a PP prepared over heterogeneous Ziegler—Natta catalysts. As the γ-phase content was raised to 72%, only 10% of the γ- turned into the α-phase. At γ-phase contents $\geq 80\%$, the PP remained unaffected. The VUV component of the low frequency discharge plasma is believed to be responsible for the modifications observed. The VUV is believed to be too weak to modify PP containing high γ-phase proportions.

Key words: polypropylene, low-frequency glow discharge plasma, structural modifications, α- and γ-phases

Plasma treatment has been shown to enable not only the surface properties of polypropylene (PP) but also the polymer volume as a whole to be modified [1, 2]. The PP samples to be investigated were prepared over a heterogeneous catalytic δ-$TiCl_3$-$AlEt_2Cl$ system in the presence of hydrogen and over a homogeneous *rac*-Et$(Ind)_2ZrCl_2$—methylalumoxane (MAO) system (I). The molecular weight (*MW*) and melting temperature (T_m) of each sample investigated were found to increase upon plasma treatment. The structural modification was especially great for the PP synthesized with the metallocene system I. In this case *MW* increased approximately ten fold and the melting temperature rose from 130 to 164°C. Plasma was found to induce transformation of the γ- into the α-phase. This transformation is likely to have resulted in increased melting temperature.

The changes caused in the PP structure by a high-frequency discharge (433 MHz) plasma have been reported elsewhere [3]. The resulting structural transformations of PP included: (i) the transition from the amorphous into the smectic phase and (ii) from the smectic into the α-phase.

This paper sets out to describe new results of the study on the influence of low-frequency glow discharge on the morphology and crystallization mechanism of anisotactic polypropylene (PP-s).

EXPERIMENTAL

Anisotactic polypropylene was synthesized in the liquid monomer at 50—60°C with the catalytic system I. Such a PP-s is well known to be less stereo- and regioregular and to have a lower molecular weight than the PP obtained over traditional Ziegler—Natta catalysts. Anisotactic polypropylene has also a distinct propensity to crystallize as a thermostable γ-modification which upon heating is not transformed into the α-modification [4].

We used metallocene catalyst samples endowed with different catalytic activities (Table 1).

For plasma experiments, PP-s films 100 μm thick were prepared by molding a PP powder at 180°C and then slowly cooling it under pressure.

The absence of orientation was confirmed by the X-ray data recorded for the PP-s films in mutually perpendicular planes by the photo method with a URS-2.0

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Table 1. Activity of *rac*-Et(Ind)$_2$ZrCl$_2$ catalysts

Catalyst	PP	Catalyst activity kg PP/ (mol Zr · h)
1	PP-s	2000
1	II-s[a)]	—
2	PP-50	3600
2	PP-60	4700
3	PP-1	74 000

[a)] II-s — boiling heptane-soluble PP-s fraction; content in polymer, 90%.

X-ray apparatus equipped with a Ni filter (Cu-K$_\alpha$ radiation).

The procedure of plasma treatment of the PP films was as described in [5]. The glow discharge current was kept equal to 100 mA; current frequency, 50 Hz; exposure time, 60 s. Air and nitrogen were used as plasma working gases. The gas pressure in the reaction chamber was kept at 13.3 Pa. All the experiments were carried out by placing the PP samples in the cathodic gradient.

Thermophysical characteristics of PP-s were determined by DSC with a Perkin-Elmer DSC-7 differential scanning calorimeter over the temperature interval from -150 to +220°C, heating rate 20°C/min; after complete melting and cooling at a rate of 200°C/min (quenching) a second scan was run. The temperature scale was calibrated against indium (melting point of In is 429.6 K). Sample weights were varied from 10 to 50 mg.

X-ray diffraction studies of PP-s were carried out with a DRON-2 X-ray diffractometer (Cu-K$_\alpha$ radiation; Ni filter; scanning speed, 1°(2θ)/min). The crystallinity degree (C) and the fractions of the α- and γ- modifications were calculated according to [6, 7].

The ratios D_{998}/D_{973} and D_{841}/D_{973}, *i.e.*, the stereoregularity parameters of PP, were determined from the IR spectra recorded with Beckman 4260 and UR-20 spectrophotometers. The intensities of the regularity bands at 973, 998 and 841 cm^{-1} correspond to isotactic sequences with $n \geq 5$, 11 and 13 monomer units (the maximum ratios D_{998}/D_{973} and D_{841}/D_{973} are equal to 1 and 0.96, respectively) [8]. The crystallinity degree was evaluated from D_{841}/D_{973} [9].

NMR spectra were recorded with a Bruker AM-270 spectrometer operated at 67.89 MHz in the PFT (Pulsed Fourier Transform) mode at 103°C. In each measurement, CPD (composite pulse decoupling) was used to remove ^{13}C—^{1}H couplings, the pulse angle was 90°, the pulse repetition time was 24 s, and 4500 free induction decays were stored in 32 000 data points using a spectral window of 4950 Hz. The NMR samples were prepared by dissolving 100—150 mg polymer in 2 mL C$_2$D$_2$Cl$_4$ (used also as a lock solvent) in a 10-mm outer diameter tube, and hexamethyldisiloxane (1%) was added as an internal chemical shift reference.

Gel chromatograms of PP-s samples were taken with a Waters chromatograph in *o*-dichlorobenzene at 140°C; the average molecular weight was calculated according to the universal calibration curve ascertained by using PS standards.

RESULTS AND DISCUSSION

Figure 1 presents the DSC curves of the PP-s samples before and after plasma treatment. These thermograms show the thermophysical parameters of the polymers to have considerably changed (Table 2).

The melting endotherm of the original PP-s in the high temperature region at the first scan reveals two apparent peaks, at 131°C and 157.5°C, which correspond to the melting temperatures of the α- and γ- modifications of PP, respectively [7]. A shoulder at 55—65°C is likely to be due to low-melting defective crystallites of the γ-modification (Fig. 1a, curve 1). Quenching is seen to result in some structural modifications: the melting peaks in the region of lower temperatures (126 and

Table 2. The influence of low-frequency glow discharge plasma on thermophysical property data of anisotactic PP

Sample	T_m, °C		ΔH, J/g		T_g, °C	
	1 scan	2 scan	1 scan	2 scan	1 scan	2 scan
PP-s	53.0/131.0/157.0	125.9/155.0	83.2	90.1	-15	-7
PP-s (N$_2$ plasma)	162.6	159.3	123.2	97.4	0	-1
II-s	58.0/129.8	125.9	106.8	77.4	6	-10
II-s (N$_2$ plasma)	165.4	161.9	138.6	99.5	9	4
PP-60	62.0/131.9	83.5/128.5	95.7	65.7	-6	-6
PP-60 (air plasma)	133.7	125.2	—	—	-7	-7
PP-60[a)]	136.0	133.0	69.1	57.5		
PP-60[a)] (air plasma)	136.0	136.0	68.3	59.8		
PP-50[a)]	138	134	—	58.6		
PP-50[a)] (air plasma)	139	136	77	60.5		
PP-1[a)]	131.4	130	81.9	67		
PP-1[a)] (air plasma)	128.9	129/163.4	—	66.8		

[a)] With a DSM-2M system over 100°C to 200°C at identical 16°C/min heating and cooling rates.

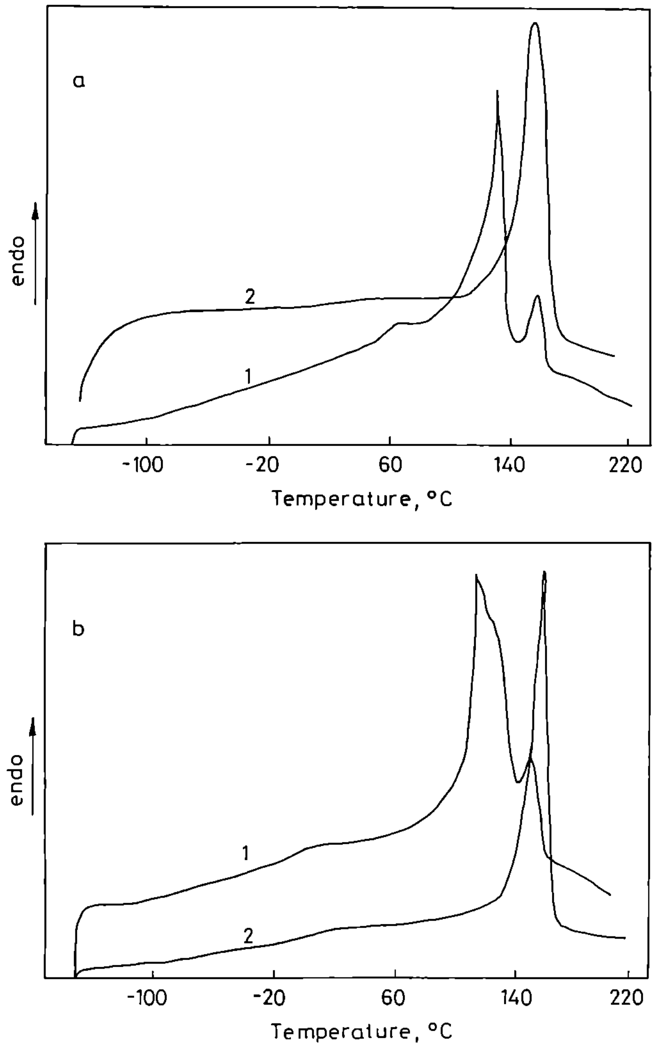

Fig. 1. DSC curves of original (1) and nitrogen plasma-treated (2) PP-s samples: a — first scan; b — second scan

155°C) become shifted and the low-temperature shoulder (55—65°C) disappears (Fig. 1b, curve 1).

The plasma treatment affected the structure of PP-s cardinally. The low-temperature shoulder as well as the peak characterizing the γ-modification of anisotactic PP disappeared already in the endotherm of the first scan. At the same time, the high-temperature peak (162.2°C) corresponding to the melting temperature of the α-modification of PP increased drastically (Fig. 1a, curve 2). The endotherms in the region of negative temperatures revealed changes in the amorphous phase of the polymers. The plasma treatment resulted in the glass transition temperature (T_g) of PP-s increased from -15 to 0°C at the first scan and from -7 to -1°C at the second scan (after quenching). The rise in Tg reflects a reduced segmental mobility in the amorphous phase. It is likely to result in an increased degree of crystallinity of the polymer [10].

Such a transition increased the enthalpy of melting by nearly 50% (Table 2). Quenching reduced, but slightly, the melting temperature and the enthalpy; however, the structural changes resulting from the plasma treatment remained unaffected.

Comparison of the X-ray diffractograms and the DSC data of the original with the treated PP-s shows the changes in the thermophysical parameters to be due to the transition of the γ- into the α-modification of PP. As a result, the PP-s treated consists of the α-modification only. Thus, the plasma treatment is seen to induce the transformation of the γ- into the α-modification; and the degree of crystallinity is seen to have increased in the treated polymer (Table 3).

Table 3. X-ray diffraction results for PP

Sample	C, %	Fraction of α-modification	Fraction of γ-modification	$C_α$$^{a)}$, %	$C_γ$$^{a)}$, %
PP-s	64	0.58	0.42	37.1	26.9
PP-s (air plasma)	70	1.00	0.00	70.0	0.0
II-s	62	0.40	0.60	24.8	37.2
II-s (air plasma)	71	0.91	0.09	64.6	6.4
PP-50	34	0.13	0.87	4.4	29.6
PP-50 (air plasma)	30	0.15	0.85	4.5	25.5
PP-60	30	0.14	0.86	4.2	25.8
PP-60 (air plasma)	29	0.15	0.85	4.4	24.6
PP-1	53.5	0.28	0.72	14.98	38.52
PP-1 (air plasma)	50	0.38	0.62	19	31

$^{a)}$ $C_α$ and $C_γ$ — degree of crystallinity of α- and γ-modifications.

Table 4. Effect of plasma treatment on stereoregularity parameters and crystallinity degree of anisotactic PP evaluated from IR data

Sample	D_{998}/D_{973}	D_{841}/D_{973}	D_{841}/D_{1170}	C, %
PP-s	0.88	0.76	0.76	63
PP-s (air plasma)	0.98	0.92	0.82	68
PP-s (N_2 plasma)	1.00	0.79	0.75	63
II-s	0.78	0.63	0.73	62
II-s (air plasma)	0.95	0.96	0.86	72
II-s (N_2 plasma)	0.95	0.86	0.86	72
PP-60	0.89	0.74	0.77	63
PP-60 (air plasma)	0.89	0.73	0.76	63

IR data also demonstrate the increased crystallinity of the polymer as well as the rise in chain stereoregularity (Table 4).

Simultaneously, the microstructure of PP has changed (Table 5). The ^{13}C NMR spectrum of original PP-s is a typical spectrum of a polypropylene prepared with metallocene catalysts in terms of tacticity (fraction of isotactic pentads [mmmm] is equal to 0.828), regioregularities (2, 1 invertions, 0.88%; erythro inversion, 0.56%; threo inversion, 0.32%) and chain end groups (*n*-propyl and *n*-butyl as chain end groups). After plasma treatment, PP-s is more stereo- and regioregular: the fraction of isotactic pentads [mmmm] has increased from 0.828

Table 5. Steric sequence distributions of PP-s samples before and after plasma treatment

Pentad	mmmm	mmmr	rmmr	mmrr	mrmm + rmrr	rmrm	rrrr	rrrm	mrrm
Chemical shift, ppm	19.69	19.42	19.18	18.89	18.66	18.51	18.12	17.99	17.66
PP-s[a] pentad fraction	0.828	0.087	—	0.060	—	—	trace	—	0.025
PP-s (nitrogen) pentad fraction	0.896	0.035	0.003	0.022	0.009	0.005	0.012	0.009	0.009

[a] 2,1 — inversions, 0.88% (erythro inversion, 0.56%; threo inversion, 0.32%).

to 0.895 and the content of 2, 1 inversions has decreased from 0.88% to 0.

The thermophysical behavior of PP II-s is analogous. This is the PP-s fraction soluble in boiling heptane; it represents the less stereo- and regio-regular portion of the polymer product. Therefore, the endotherm of the original II-s (Fig. 2a, curve 1) contains no high-temperature peak corresponding to crystallites melting at T_m = 157°C. However, the X-ray data show the content of the α-phase in this sample to be equal to 40%. Probably, in this case the α-phase consists of defective crystallites which melt at a lower temperature. The absence of the high-temperature peak in the endotherm curve and at the same time the presence of reflections of the α-phase on the X-ray diffractogram has also been observed by B. Rieger *et al.* [4] in the investigation on the morphology of fractions of anisotactic PP. In PP II-s, the plasma produced by low-frequency glow discharge also gives rise to the transition of low-melting (T_m = 129.8°C) into high-melting crystallites (T_m = 165.4°C) (Fig. 2a, curve 2). The content of the α-phase increased after plasma treatment from 40 to 91% (Table 3).

The glass transition data indicate that there are also changes in the amorphous region of this polymer. (T_g increased upon plasma treatment from 6 to 9°C at the first scan, and from -10 to 4°C at the second scan). The T_m and ΔH data permit to suppose that the structure of the modified PP II-s is more resistant to amorphization.

The thermophysical behavior of PP-1 allows to infer that, upon plasma treatment, the high-melting fraction of crystallites (163.4°C) co-exists with the main fraction of crystallites melting at T_m = 129°C (Fig. 3). However, this effect is observed only after the second scan. The X-ray data show these changes to be accompanied by an increase in the content of the α-phase by 10% (Table 3).

The plasma treatment has not resulted in any visible structural transformation in PP-50 and PP-60. The melting temperatures of these polymers remained practically unaffected. However, these investigations were limi-

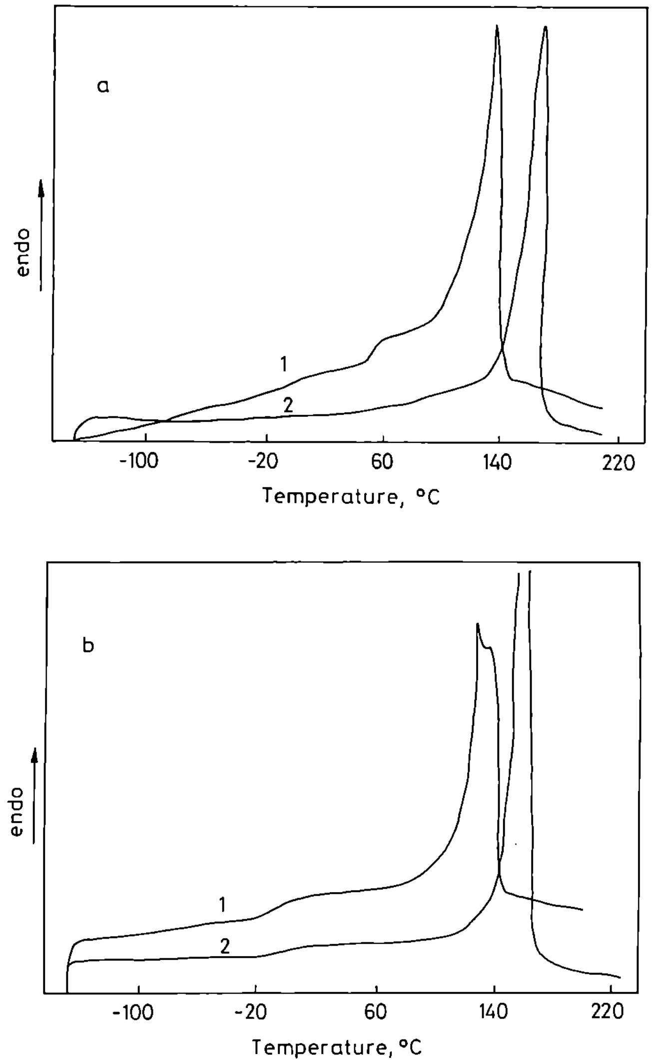

Fig. 2. DSC curves of original (1) and nitrogen plasma-treated (2) II-s samples: a — first scan; b — second scan

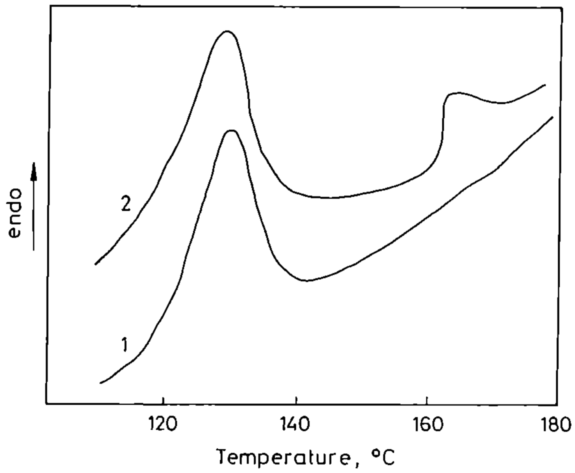

Fig. 3. DSC curves of original (1) and air plasma-treated (2) PP-1 samples

ted to a temperature interval of 100—200°C. Table 2 shows the ΔH quantities obtained at a different temperature interval to differ considerably. Therefore, to draw a final conclusion, experiments at temperatures lower than 100°C are desirable.

Table 6. Effect of plasma treatment on MW and MWD of anisotactic PP

Sample	$\overline{M}_n \cdot 10^{-3}$	$\overline{M}_w \cdot 10^{-3}$	$\overline{M}_w/\overline{M}_n$
PP-s	17	60	3.5
PP-s (air plasma)	90	575	6.4
II-s	17	55	3.2
II-s (air plasma)	67	410	6.1
PP-50	14	31	2.2
PP-50 (air plasma)	13	29	2.2
PP-60	12	25	2.1
PP-60 (air plasma)	12	25	2.1
PP-1	16	31	1.9
PP-1 (air plasma)	16	30	1.9

Table 6 presents molecular weights and *MWD* for all samples of PP before and after plasma treatment. The plasma treatment is seen to result in a great increase in molecular weight and broadening of the molecular-weight distribution for PP-s and II-s and in practically no changes in PP-60 and PP-1.

From the results obtained one can see the varying effects of low-frequency glow discharge on the structure and *MW* of anisotactic polypropylene synthesized with different samples of the same catalyst. The plasma is particularly effective when the content of the γ-modification is $\leq$ 60% (PP-s and II-s samples). In PP-1 containing originally as much as 72% of the γ-phase, only 10% of the γ-phase was transformed into the α-phase. At γ-phase contents $\geq$ 80% (PP-50, PP-60), the plasma treatment produced no structural transformation.

Earlier we hawe shown the VUV component of the low-frequency glow discharge plasma (λ = 120—250 µm) to be responsible for structural conversion of PP [1]. The morphological transformations of PP have been suggested to be explicable by absorption of the plasma VUV radiation by the polymer film [3]. Probably the energy of VUV radiation is not high enough to produce structural transformations in a PP with a high content of the γ-modification.

CONCLUSIONS

In the case of effective plasma action, the γ-modification has been nearly entirely transformed into the α-modification. The transformation resulted in the increase of the melting temperature from 130 to 164°C. Simultaneously, the fraction of isotactic pentads determined from the ^{13}C NMR spectra and the stereoregularity parameters determined from IR-spectra have risen. A great increase in molecular weight and broadening of molecular-weight distribution have also been observed to occur. As a result, anisotactic PP has become similar to a PP obtained with heterogeneous Ziegler—Natta catalysts.

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