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Separation of Poly(propylene) Samples According to Tacticity Using a Hypercarb Column

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Summary: Samples of polypropylene having different stereoregularities, *i.e.*, differing in the isotactic or syndiotactic stereosequence distribution, were separated by means of high-temperature gradient adsorption liquid chromatography. The porous graphite was used as stationary phase in the column packing (Hypercarb®). Predominantly isotactic samples eluted in 1-decanol, while predominantly syndiotactic samples eluted in a binary gradient composed of 1-decanol and 1,2,4-trichlorobenzene. Their elution volumes increased with the average content of the syndiotactic units (*racemo* dyads mole fraction as determined with the NMR spectroscopy) in the samples. Thus these chromatographic separations represent a new method for the analysis and characterization of stereoregular polyolefins. It requires substantially less time and solvents than the commonly used methods.

Keywords: liquid chromatography; poly(propylene); tacticity

Introduction

The polypropylene *tacticity*, *i.e.*, the stereochemical relative configuration of the methyl groups along the macromolecular chain, strongly influences the physical properties of the resulting polymeric material: highly *isotactic* polypropylene (iPP) is a semicrystalline material, with advantageous mechanical, physical and chemical properties. Combining these characteristics with the cheapness of the monomer made this material one of the most produced synthetic polymers world-wide.[1] On the other hand, highly *syndiotactic* polypropylene (sPP) still remains a niche product. Poorly isotactic (syndiotactic) polypropylene, usually referred as *atactic* PP, is an amorphous and soft material with increasing commercial interest as asphalt modifiers/compatibilizer. *Stereoblock* homopolymers of propylene, where the ratio between isotactic and syndiotactic block content and length, and the stereoregularity of the stereoblocks are varied in dependence of their synthetic parameters, could have a great potential interest in the field of nanostructured materials and as phase compatibilizers in iPP/sPP polymer blends, notoriously immiscible each other.

Due to the strong impact of the PP stereoregularity on the main material properties that are relevant for the usual industrial applications, many groups attempted to fully characterize the very complex mixtures of polymers produced by typical ZN catalyst systems according to the stereoregularity.[2] These catalyst systems behave in α-olefin polymerization as multicenter catalysts with a more or less broad distribution of classes of active sites,[3] varying from those site-controlled, highly isotactic-selective, to those chain end-controlled, poorly syndiotactic-selective. As a result, polymers synthesized with these catalyst systems are blends of PP having widely different stereoregularities.

The simplest way to characterize the different PP stereochemical components

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has been to fractionate the given polymer sample using a series of organic solvents with increasing boiling points (*i.e.*, according to crystallinity and/or solubility). As a result, it is possible to collect a series of soluble and insoluble polymer fractions[4–8] for each polymer sample, which can then be characterized by NMR,[9] FTIR,[10] SEC,[11] DSC[12,13] or other methods.

TREF and CRYSTAF techniques separate polymers according to their crystallinity and were successfully applied to PP materials.[14–18] CRYSTAF separated a PP mixture into its highly crystalline, lower crystalline and amorphous components,[19] but irrespective to their iso- or syndiotactic nature. A mixture of syndiotactic PP, isotactic PP and linear polyethylene has been separated by CRYSTAF as well.[20] The CRYSTAF analysis takes, however, 10–15 hours for each sample.

There have been several reports on the separation of stereoregular polymers by interaction chromatography. Inagaki and co-workers were the first to report on the separation of poly(methyl methacrylate) (PMMA) according to tacticity by thin layer chromatography,[21,22] Sato et al.[23] have applied for this purpose liquid chromatography. Liquid chromatography at critical conditions was applied by Berek et al. to separate PMMA[24–26] and poly(ethyl methacrylate) (PEMA)[27,28] according to tacticity. Isotactic and syndiotactic PMMA as well as PEMA were separated by liquid chromatography under limiting conditions of desorption.[29] The selectivity of the method, however, did not allowed to efficiently separate samples with continuous, broad distribution of stereoregularity.[29] Separations of stereoisomers have also been realized by temperature gradient interaction chromatography.[30,31] Moreover, it was demonstrated that coupling HPLC-^{1}H-NMR on-line enables to determine tacticity of PEMA[28] or PMMA[32] after separation of the polymer samples in a chromatographic columns.

Recently, conditions for chromatographic separation of blends composed from isotactic, atactic and syndiotactic PP were identified.[33,34] Using Hypercarb columns adopting porous graphite as the stationary phase and 1-decanol as the mobile phase, atactic PP and syndiotactic PP were fully adsorbed, while isotactic PP eluted in SEC mode. After addition of 1,2,4-trichlorobenzene into the mobile phase, atactic PP and syndiotactic PP eluted from the column. It was shown by Sato et al.[23] and Berek et al.[24,29] that the separation of polymers according to tacticity may be problematic due to aggregation of stereoregular samples[23,24] or due to small sensitivity of a LC method.[29] Such effects were not observed in system Hypercarb/1-decanol/1,2,4-trichlorobenzene.[33,34] It implicates that this system could be suitable for separation of stereoregular propylene polymers, which contain isotactic and/or syndiotactic sequences in the polymer chains in various concentrations. The corresponding HPLC measurements were realized and the results are described in this paper.

Experimental Part

Instrument

A high-temperature chromatograph PL-GPC 210 (Polymer Labs, Church Stretton, England) equipped with an evaporative light scattering detector (model PL-ELS 1000, Polymer Labs, Church Stretton, England) has been used for all measurements. The following parameters have been used at the ELSD: gas flow rate 1.5 L/min, nebulizer temperature 160 °C, evaporator temperature 260 °C. A quaternary gradient pump (model Agilent 1200 Series) was used for all measurements. Flow rate was 0.5 mL/min.

A column Hypercarb, 100 × 4.6mm i.d. with a particle diameter of 5 μm, a surface area of 120 m^2/g, a pore size of 250 Å (Thermo Scientific, Dreieich, Germany) has been placed in a column oven and thermostated at 160 °C.

The polymer samples have been dissolved in 1-decanol at 160 °C at a concentration of about 1–2 mg/mL. The time of

dissolution for the samples varied between 30–100 minutes. 13 μL of each sample solution has been injected in the LC.

Solvents

1-decanol and 1,2,4-trichlorobenzene (TCB, VWR, Darmstadt, Germany) have been used as the mobile phases and to perform a linear gradient 1-decanol/1,2,4-trichlorobenzene. The composition of the mobile phase has been changed in 10 minutes from 0 to 100% TCB, then 100% TCB has been pumped 10 minutes. A linear gradient from 100 to 0% TCB followed in 2 minutes. Finally, the column was purged 25 minutes with pure 1-decanol.

Polymer Samples

All the samples of iPP, sPP with different stereoregularities and (supposed) mainly iPP-*stereoblock*-sPP with different stereoblock content and length have been synthesized at the University of Naples.[35–37] The stereoregularity of the samples depends on the choice of the catalyst system**:** Samples 1-6 are iPP obtained with a typical C_2-symmetric *ansa*-metallocene (*rac*-Me_2Si(2-Me-benz[*e*]-1-indenyl)$_2ZrCl_2$ (catalyst **1**).[35] Samples 7–11 are sPP obtained with a typical C_s-symmetric *ansa*-metallocene catalyst (Ph_2C(cyclopentadienyl)(9-fluorenyl)$ZrCl_2$ (catalyst **2)**[36] Samples 12 iX-sY (being iX ''soluble at X °C'' and sY ''insoluble at Y °C'') are polymer fractions of a single PP sample synthesized with $MgCl_2$/dibutylphtalate/$TiCl_4$/ triethylaluminium/2,6-lutidine catalyst system (catalyst **3**).[37] These polymer fractions were obtained extracting the polymer sample in n-octane by means of a Zambelli-modified Soxhlet extractor termostated from 15 to 65 °C choosing a temperature step of 10 °C: the seven obtained polymer fractions are expected to contain a progressively higher amount of iPP in the fractions obtained at the higher T intervals. The samples were characterised in Naples by the group of prof. V. Busico and their properties are summarised in Table 1.

Table 1.
Characterization data of the polymer samples.*

Sample #	M_n (kg/mol)	M_w (kg/mol)	PDI	[*m*] (mol %)
1	2.9	3.6	1.2	82.3
2	3.2	5.6	1.8	88.8
3	2.9	5.0	1.7	90.6
4	9.7	27.1	2.8	92.4
5	23.8	64.0	2.7	95.3
6	52.3	135.8	2.6	97.0

Sample #	M_n (kg/mol)	M_w (kg/mol)	PDI	[*r*] (mol %)
7	3.7	7.3	2.0	82.2
8	30.2	73.7	2.4	89.5
9	127.0	237.6	1.9	94.3
10	85.8	188.8	2.2	94.8
11	70.4	208.6	3.0	95.8

Sample #	M_n (kg/mol)	M_w (kg/mol)	PDI	iPP (mol %)
12 i15-s25	22.8	53.9	2.4	31.5
12 i25-s35	19.1	55.4	2.9	17.4
12 i35-s45	30.8	75.6	2.5	34.7
12 i45-s55	23.3	60.1	2.6	43.1
12 i55-s65	23.9	66.0	2.8	36.5

*M_n = the number average molar mass; M_w = the weight average molar mass; PDI = M_w/M_n; [*m*] – mole fraction of *meso* diads; [r] – mole fraction of *racemo* diads; [iPP] – mole fraction of isotactic PP.

Microstructural Characterization

Quantitative ^{13}C NMR spectra were recorded with a Bruker Avance DRX400 spectrometer operating at 100 MHz, on 10-20 mg/mL polymer solutions in tetrachloroethane-1,2-*d*2 at 90 °C. Conditions: 5 mm probe; 76° pulse; acquisition time, 2.4 s; pulse delay, 2.6 s; 32K transients. Peak integration was carried out by means of full simulation, with the Shape2004 software package.[38] The mole fractions of *meso* diads (for iPP samples, [*m*]), *racemo* dyads (for sPP samples, [*r*]) and the mole fraction of iPP in the sample (for iPP-*stereoblock*-sPP samples, estimated as the abundance of isotactic-selective sites by means of statistical analysis of the polymer microstructure[38] with a 2 sites stochastic model, see below), were evaluated as explained in ref.[37]; the confidence intervals were estimated using the Monte Carlo simulation routine of the Confstat suite,[39] accepting all the solutions with a value of the χ^2_r function up to 1.2 times that

at the absolute minimum of the *enantiomorphic-sites* chain propagation model (catalyst **1**),[2] of the *chain migratory* model (catalyst **2**)[2] or of the *enantiomorphic-sites + chain end* model (catalyst system **3**).[2]

GPC Characterization

GPC curves for polypropylene samples were recorded at 135 °C with a Waters Alliance GPCV2000 system with refractometric and viscometric detection, on polymer solutions in 1,2-dichlorobenzene (added with 0.25 mg/mL of 4-methyl-2,6-di-*tert*-butylphenol as a stabilizer). A set of 4 columns (3 mixed-bed Styragel HT 6E and 1 Styragel HT 2, provided by Waters) was used. Universal calibration was carried out with 12 samples of monodisperse polystyrene (M_w between 1.3 and 3700 kg/mol). Calculation of MWD was carried out with the ShapeGPC program using the traces from refractometric detection.[40]

Results and Discussion

The column packed with porous graphite, Hypercarb, and flushed with gradient 1-decanol-TCB, enables, as it was demonstrated previously,[33] separation of isotactic PP from syndiotactic PP. It was shown that the difference in the elution volumes of both substances is larger, than the difference caused by differences in molar masses between the isotactic PP and syndiotactic PP samples.[33]

The polymer samples were dissolved in 1-decanol and injected into the column. Some samples eluted in one peak, while other eluted in two (Figure 1a, 2a). As value characterizing the retention behaviour of the polymer samples the elution volume at the peak maximum is considered. The first component, having an elution volume between 1 and 3.5 mL, eluted in 1-decanol (Figure 1b, 2b) and consists in PP with a predominance of *meso* dyads (*i.e.*, highly

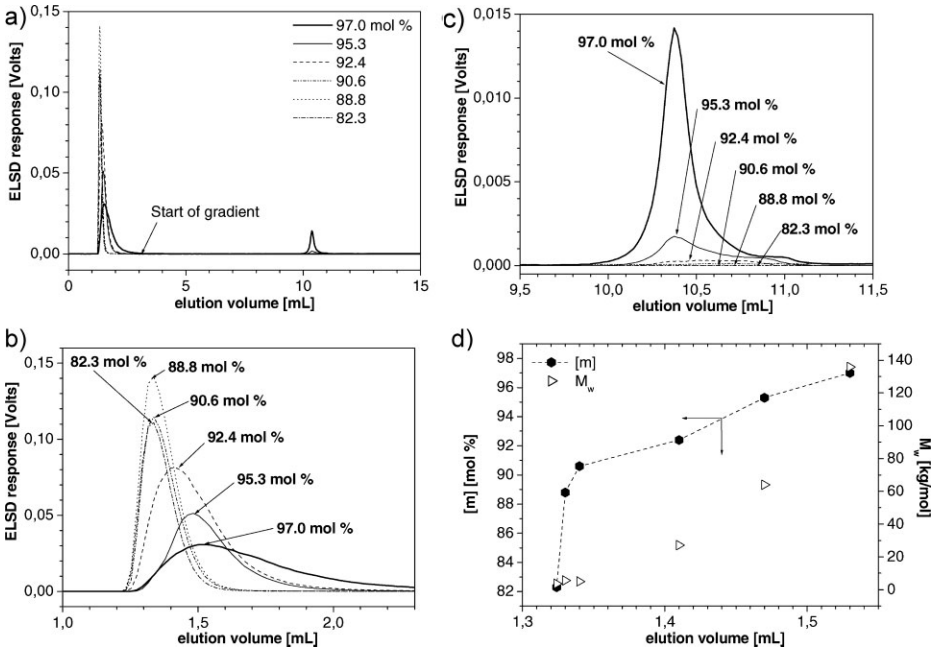

Figure 1.
a) Overlay of chromatograms corresponding to the iPP homopolymers (Samples # 1-6 in Table 1). b) Part of the chromatograms corresponding to components eluted in 1-decanol. c) Part of the chromatograms corresponding to components eluted in the gradient 1-decanol/TCB. d) Dependence between the elution volume and the average concentration of *meso* diads [*m*] as well as the weight average molar mass of the samples.

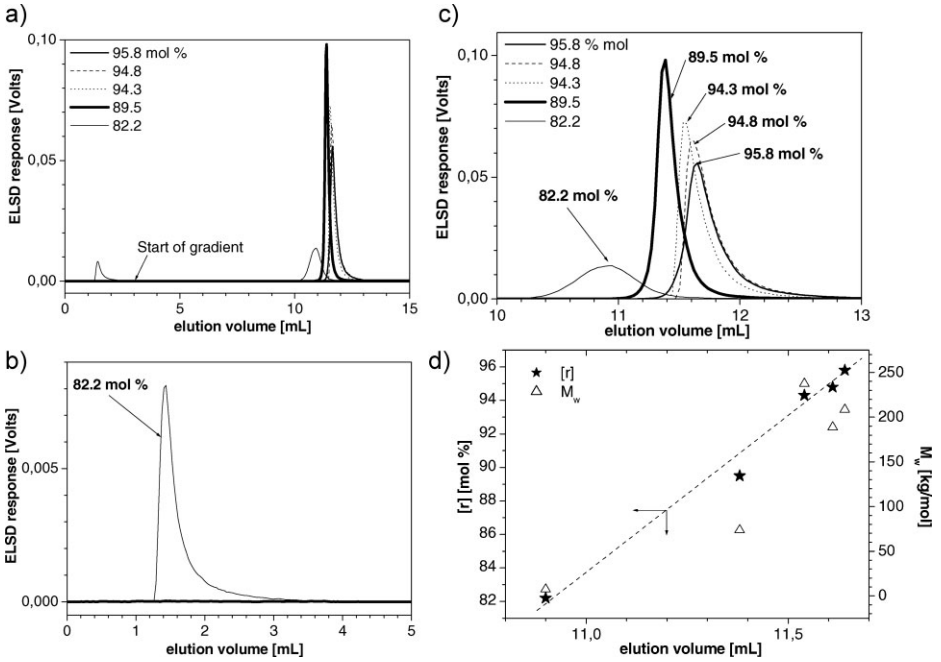

Figure 2.

a) Overlay of chromatograms corresponding to the sPP homopolymers (Samples # 7-11 in Table 1). b) Part of the chromatograms corresponding to components eluted in 1-decanol. c) Part of the chromatograms corresponding to components eluted in the gradient 1-decanol/TCB. d) Dependence between the elution volume and the average concentration of *racemo* diads ([*r*]) as well as the weight average molar mass of the samples.

stereoregular iPP) and this iPP represents the major component for the eluted iPP samples #1-6 (Figure 1a), but it is present also in one sPP sample (#7) as a contaminant (Figure 1b). In the case of the iPP samples series, this polymer component shows a fair correlation between the elution volume and the content of the meso diads ([*m*]) as evaluated from ^{13}C NMR (Figure. 1d). An inverted correlation with the average molar mass of the samples is observed (Figure 1d). As an example, sample #1 with $M_w = 3.6$ kg/mol would elute in SEC mode after the sample 6 with $M_w = 135$ kg/mol, but the opposite elution order is observed. It indicates that not SEC mechanism, but adsorption determines the elution behaviour of these samples.

The second component, having an elution volume between 10 and 13 mL, was adsorbed strongly and eluted only after the addition of TCB into the mobile phase, *i.e.*, in the gradient (Figure 1c, 2c). This component consists in PP having a predominance of *racemo* dyads. This component is found to be the major one in the chromatograms of the sPP samples series (Figure 2a). I This syndiotactic-like component is present in small concentrations in the iPP samples #4-6 also, in amounts growing with [*m*] (Figure 1c). Probably, the origin of this minor polymer fraction could be attributed to the presence of the *meso*-C_s, non-stereoselective form of the catalyst **1**, always present in trace amounts in C_2-symmetric *ansa*-metallocene catalyst stocks.

The progression of the elution volumes correlates fairly linearly with the ^{13}C NMR average stereoregularity of the sPP samples ([*r*]), as illustrated in Figure 2d. The mole fractions of the samples reflect difference in their tacticity. This is only difference between the samples; from chemical point of view, all samples are pure PP. However, the samples are not perfectly homoge-

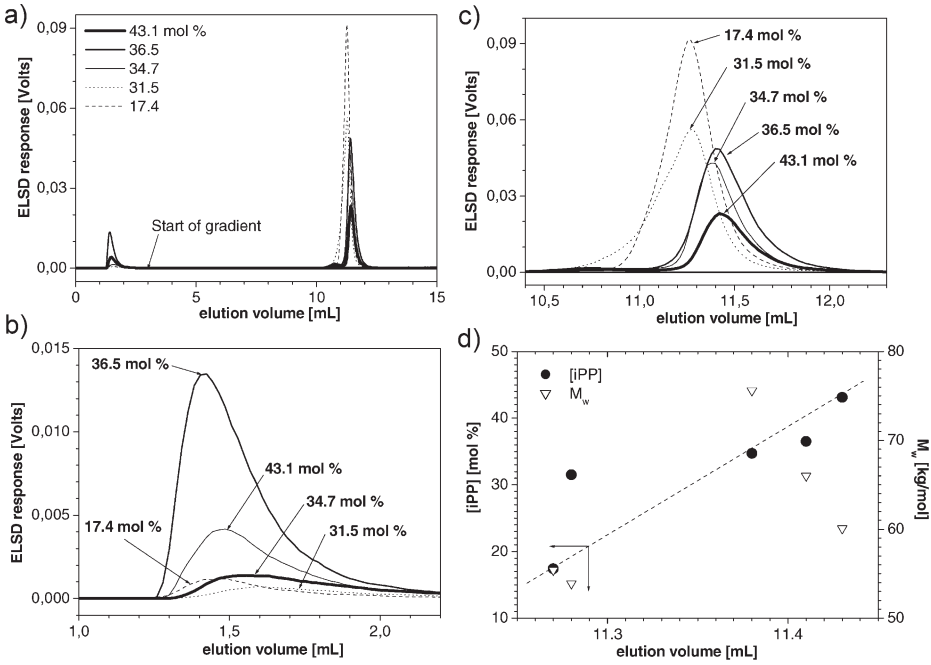

Figure 3.
a) Overlay of chromatograms corresponding to the PP samples # 12iX-sY (Table 1). b) Part of the chromatograms corresponding to components eluted in 1-decanol. c) Part of the chromatograms corresponding to components eluted in the gradient 1-decanol/TCB. d) Dependence between the elution volume and both the average iPP stereoblock content and the weight average molar mass of the samples.

neous, i.e., each sample with a known average value of tacticity (Table 1) has a distribution in the tacticity. As a result, the peaks of samples with various values of the average tacticity may overlape. Taking into account results described previously,[33] it is supposed that the molar mass has small effect on the described separation. Really, a correlation between the elution behaviour and the average molar mass is missing (Figure 2d). Linear correlations were found in Hypercarb/1-decanol/TCB system also for propene/1-alkene and ethylene/1-alkene copolymers, in this case the correlations between the elution volume and the average chemical compositon of the copolymers were identified.[41]

While the majority of the samples #1-11 contained one stereochemical component only in high concentration, the #12 iX-sY samples are mixtures of poorly stereoregular iPP, sPP and possibly iPP-*stereoblock*-sPP having different iPP (sPP) stereoblock relative abundance and/or length.[37] These polymer blends were separated into two peaks (Figure 3a) that are supposed not to differ substantially in their molar mass distribution, because the original samples eluted in SEC as monomodal peaks (samples #12 i35-s45 to i55-s65) or as tailed, but single peaks (samples #12 i15-s25 and i25-s35). The first peak eluted in 1-decanol (Figure 3b), that must consist in isotactic PP. On the other side, the syndiotactic-like part of the samples show a correlation between the elution volumes and the average sPP content (Figure 3d). Only one sample (#12 i15-s25), the broader one both in SEC and HPLC mode, significantly deviates from the straight line.

The average values [mol% iPP] shown in Figure 3b are, however, too low for to be compatible with the elution of PP in 1-decanol and the average values [mol % iPP] shown in Figure 3c are increasing with the elution volume, but they should decrease,

Table 2.
Elution behaviour of polypropylene samples.

Sample #	sPP [mol%]	elution volume [mL]	iPP peak area [%]	elution volume [mL]	P_r	sPP peak(s) area [%]
12 i15-s25	68.5	1.59	1.76	11.28	0.872	98.24
12 i25-s35	82.6	1.47	1.71	11.27	0.912	98.29
12 i35-s45	65.3	1.57	6.39	11.37 (2 peaks)	0.912	93.61
12 i45-s55	56.9	1.49	14.45	11.42 (2 peaks)	0.914	85.55
12 i55-s65	63.5	1.42	20.29	11.40	0.920	79.71

similarly as in Figure 2d, because sPP is responsible for the adsorption. We conclude that the average content of iPP determined by NMR for several #12 iX-sY samples is different from the actual content of iPP in the first (Figure 3b) and the second peak (Figure 3c), because both components are present in larger concentrations (Table 2).

Considering that the stereoregularity of the sPP contained in all these samples, expressed as a function of P_r (probability of *r* dyad formation for a chain end-controlled stochastic propagation model [2]), doesn't vary significantly with the extraction elution temperature interval, an educated guess could be that the length of the sPP stereoblocks is the driving force for this separation: in fact it is likely that the polymer fractions obtained at higher temperature intervals contain shorter sPP stereoblocks, till the progressive disappearance of this stereochemical component in the highly stereoregular iPP fractions.[37]

The ELS-detector used for this investigation is a concentration detector: its response is proportional to the concentration of the polymer in the mobile phase. The response, however, may be a function of the sample (stereo)chemical composition, molar mass and the nature of the mobile phase (some components eluted in the gradient, *i.e.*, in mixture 1-decanol + TCB).[42,43] Aiming at obtaining reliable quantitative values about the amount of each component in the samples, a proper calibration of the detector will be needed.

We summarize that if the samples contain only one stereochemical and syndiotactic component (*i.e.*, only one peak after the gradient appeared on the chromatogram), then there is a linear dependence between the average *r* dyad mole fraction in the sample and the elution volume, as it was found for the above discussed sPP samples (Figure 2d). On the contrary, if a polymer sample contains two or more main components differing in tacticity and/or stereoregularity (*i.e.*, two or more peaks appeared on the chromatogram), then the average content of the *r* dyads obtained from NMR does not correspond to the actual content of the r dyads, which are present in the separated fractions. The actual tacticity of macromolecules eluted in one peak may be estimated from the calibration of the HPLC separation using well characterized standards or determined by coupling HPLC-NMR on-line, like it was demonstrated in studies of various stereolegular PEMA or PMMA samples by Kitayama et al.[28] and Hiller et al.[32]

Conclusion

Samples of polypropylene with different tacticities and stereoregularities were separated using the gradient adsorption liquid chromatography. Samples characterized by the dominance of isotactic stereosequences eluted from column Hypercarb flushed with 1-decanol, while samples characterized by the dominance of syndiotactic stereosequences were adsorbed. They eluted from the column only applying a gradient of 1-decanol/1,2,4-trichlorobenzene. Their elution volumes linearly correlated with the average stereoregularity of the samples, as determined by NMR.

Samples constituted by a mixture of iPP, sPP and iPP-*stereoblock*-sPP with different iPP (so, sPP) stereoblock abundance and length in the macromolecules were separated in two main components: ''pure'' iPP and very plausibly iPP-*stereoblock*-sPP in combination with ''pure'' sPP (if present). A proper calibration of the response of the ELS detector as a function of the polymer concentration, stereoregularity and average molecular weight are needed for obtaining reliable quantitative data about concentration of each component. The development of a preparative high-temperature HPLC – NMR off-line or on-line coupling is strongly desirable in order to analyse the stereochemical fractions and on such basis to obtain a full, quantitative stochastic description of the kinetic processes that originate these so complex and interesting polymer fractions. Nevertheless, we can affirm that, up to now, no other analytical technique has been able to give so crucial information on the stereochemical composition of such polymer mixtures. Last but not least, the described HPLC analysis requires considerably less solvent and time than the commonly used experimental methods applied to obtain information about the distribution of tacticity in the polyolefin samples.

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