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In situ preparation of polypropylene/1-butene alloys using a $MgCl_2$-supported Ziegler–Natta catalyst

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Abstract

Sequential polymerizations were carried out using a high-activity $MgCl_2$/Ziegler–Natta catalyst to evaluate whether the in situ preparation of polypropylene/1-butene alloys was possible inside the reaction vessel and analyze the effects of 1-butene on the final material properties. Propylene/1-butene alloy resins were synthesized in a sequential two-stage process. In the first stage, liquid pool propylene polymerizations were carried out in batch. In the second stage, 1-butene was polymerized inside the polypropylene matrix in gas-phase in semibatch mode. According to the obtained results, it is possible to incorporate 1-butene upon the polypropylene matrix inside the reactor at very low pressures, without affecting the properties of the continuous polypropylene matrix significantly.

Keywords: Sequential polymerizations; Propylene; 1-Butene; Ziegler–Natta catalysts

1. Introduction

Liquid-phase polypropylene processes are frequently performed in continuous stirred tank reactors and tubular loop reactors. In both processes, the use of liquid monomer allows for maximization of the polymerization rates due to the high monomer concentration in the reaction medium. These processes are normally used to synthesize homopolymers and random copolymers. Heterophasic polypropylene copolymers cannot be produced in liquid-phase processes due to the solubility of the rubber phase in the liquid monomer. For this reason, heterophasic copolymers are normally produced in hybrid processes, where the homopolymer matrix is produced in liquid-phase or in slurry and the copolymer material is produced in gas-phase [1].

Recently, Machado et al. [2,3] developed a family of random polyprolylene/1-butene copolymer

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grades for gas-phase and bulk processes intended for packaging and film applications. It was shown for the first time that it is possible to produce propylene/1-butene random copolymers in semi-batch gas-phase processes with a Ziegler–Natta catalyst system [2]. In the particular case of the polymer material obtained from bulk process, the copolymerizations were performed in batch mode. It was also shown that 1-butene can be significantly incorporated into the polymer chain over the whole range of copolymer compositions [3]. In both gas-phase and bulk processes, it was observed that 1-butene can be successfully incorporated into polypropylene chains at high polymerization rates, resulting in random polymer materials with lower melting temperatures, and that the microstructure of the resulting chains can be controlled by adjusting the propylene pressure.

The final properties of polypropylene-based materials can also be modified through preparation of alloys with different polymeric materials, allowing for increase of the range of possible applications. For instance, polypropylene/ethylene alloys that simultaneously contain crystalline and elastomeric phases present improved impact properties. Production of similar structured materials is desirable because they present advantages, such as high resistance at low temperatures, good mechanical properties and excellent resistance to heat aging [4].

Polymerizations performed with $MgCl_2$-supported Ziegler–Natta catalysts allow for formation of highly porous polymer particles. The porous nature of the catalyst (polymer) particle makes incorporation of different monomers much easier, which may be advantageous for preparation of polypropylene-based polymer alloys. In the case of polypropylene/ethylene alloys, it is possible to prepare samples that contain up to 70% of the elastomeric phase.

There are few studies in the open literature concerning the synthesis of polypropylene alloys obtained via sequential polymerization [5–16]. These works focus upon the synthesis of polypropylene/ethylene-based materials, where both polyethylene and/or poly(ethylene-co-propylene) can be used to form a heterophasic material with improved impact properties. To the best of our knowledge, the work developed by Cecchin et al. [17] is the only one that presents experimental data for propylene/1-butene alloys produced in sequential polymerizations. In this case, the liquid 1-butene was continuously fed into the reactor in order to obtain a polypropylene/(1-butene-co-propylene) sample containing high fractions of 1-butene. However, 1-butene was used in this case only to provide information about the mechanism of polypropylene growth over $MgCl_2/TiCl_4$ catalyst system. According to Cecchin et al. [17], the micromorphology of the resulting heterophasic copolymer shows crystalline poly(1-butene) lamellae surrounding the polypropylene subglobules and forming a cobweb-like morphology.

In order to evaluate whether it is possible to produce polypropylene/1-butene alloys in situ and verify the effects of 1-butene on the final material properties, sequential polymerizations were carried out in this work using a high-activity $MgCl_2$/Ziegler–Natta catalyst. As the incorporation of 1-butene may exert a profound impact on the properties of the polymer material [2,3], 1-butene incorporation was kept at low levels on purpose. It is shown for the first time that it is possible to incorporate 1-butene into the polymer structure when the polymerization is performed in gas-phase at very low pressures, which may be very advantageous for production of new polymer grades in existing industrial polymerization plants. In addition, it is shown that the properties of the polypropylene matrix remain essentially unaffected by 1-butene incorporation at the analyzed conditions.

2. Chemicals, experimental procedure and analyses

Propylene with minimum purity of 99.5%, 1-butene with minimum of purity of 99.0% and hydrogen with minimum purity of 99.9% were purchased from AGA S/A (Rio de Janeiro, Brazil). Heptane, obtained from VETEC (Rio de Janeiro, Brazil) was used for preparation of the cocatalyst solution and of the catalyst system slurry after pre-treatment on 3 Å molecular sieves (purchased from Spectrum Chemical, USA). The triethylaluminum (TEA) cocatalyst was provided by Akzo Nobel (Brazil). Cyclohexyl-methyl-dimethoxysilane (DMMCHS) was used as external electron donor. Nitrogen purchased from AGA S/A (Brasil), with minimum purity of 99.0%, was used to keep the reaction environment free of oxygen. All gases were purified by forced flow through successive beds of copper catalysts and 3 Å molecular sieves. Unless otherwise stated, chemicals were used as received, without additional purification. A standard commercial $MgCl_2$-supported $TiCl_4$ catalyst with catalyst titanium content of 2.0 wt% containing diisobutyl phthalate (DIBP) as internal donor, was used to perform the polymerizations.

Sequential polymerizations were carried out in a 1000 mL moveable PARR 4531 reactor equipped with a PARR 4842 temperature controller (Parr Instruments, Moline, Illinois, USA). The system was kept under isothermal conditions and constant agitation of 500 rpm. Gas feed lines were equipped with Kobold MAS-4010 mass flow meters (Kobold Instruments Inc. – Germany). The reaction temperature and the gas feed flowrates were monitored in line with a microcomputer equipped with an AD/DA data acquisition system PCI-1710 (Advantech Brazil, São Paulo). The software ADPol 2.0 was used for data acquisition [18]. In the experimental runs, the catalyst/DMMCHS weight ratio ($\mathscr{R}_{CAT/ED}$) was varied within the range of 1.8–2.3. In the first stage, liquid pool propylene polymerizations were carried out in batch mode at 70 °C. In the second stage, 1-butene was polymerized into the polypropylene matrix in semibatch mode in gas-phase at 60 and 70 °C at 1 atm. (Previous studies had already shown that incorporation of 1-butene at high reaction rates in the liquid-phase was possible and that polymer properties were very sensitive to incorporation of 1-butene [2,3].)

The weight-average molecular weight and the MWD of the polymers were measured on a Waters Alliance GPCV 2000. The system was equipped with a refractometer, a viscometer and Waters Styragel HT2 and HT6E gel columns. Analyses were performed at 150 °C using trichlorobenzene as solvent. Surface morphology of polymer particles was determined through SEM. The images were recorded with a S800 Hitachi microscope (Hitachi, Tokyo, Japan) operating at accelerating voltages of 15 keV. Copolymer composition was determined by liquid ^{13}C NMR in a Bruker DRX 400 spectrometer (Bruker Instruments, France), operating at 100.6 MHz and equipped with probes of 5 mm. The ^{13}C NMR copolymer spectra were obtained at 90 °C. Typical accumulations included 70° flip angle and 4.44 s recycle time. Samples were dissolved in tetrachloroethylene and benzene-d_6 (2/1 v/v). The melting temperature was determined by DSC measurements in a Pyris 1 calorimeter (Perkin Elmer, USA) at heating rates of 5 °C/min.

3. Results and discussion

Reactions were performed to verify the influence of the 1-butene on the properties of the propylene/1-butene alloys produced by sequential polymerization. The basic polymerization recipe is presented in Table 1.

In the first stage of the process, the high-pressure liquid pool propylene polymerizations were carried out in batch mode at a constant high pressure. In liquid pool polymerizations, the evaluation of the reaction rate data is generally difficult because the liquid monomer keeps the reaction pressure constant throughout the polymerization, so that in-line evaluation of the reaction rate is much more difficult (on-line calorimetry or repetition of reaction experiments for different batch times are required). For this reason, reaction rate profiles were not obtained. In the second stage, 1-butene was polymerized into the polypropylene matrix in semibatch mode in gas-phase. The gaseous 1-butene was fed into the reactor at a constant low pressure to avoid formation of the liquid-phase. Fig. 1 presents some reaction rate profiles of 1-butene polymerization during the second reaction stage, using the polypropylene particles formed after the first reaction stage.

It can be observed in Fig. 1 that the kinetic profiles are strongly influenced by the reaction temperature, especially during the first moments of the second-stage polymerization. As the reaction temperature increases, the polymerization rates also increase. As a consequence, the 1-butene content of the final polymer material increases with the polymerization temperature, as measured through NMR analyses and shown in Table 2. However, it is important to observe that the reaction rates decrease very fast, after a period of increasing catalyst activity.

This type of catalyst behavior is very different from the ones observed previously for both gas-phase and liquid pool random polymerizations, when 1-butene/propylene reactions could be per-

Table 1
Sequential polymerization conditions[a]

Run	Temperature (°C)		$\mathscr{R}_{CAT/ED}$ (w/w)	H_2 (mol%)
	Stage I	Stage II		
01	70	–	1.87	0.38
02	70	70	1.80	0.34
03	70	70	1.83	0.00
04	70	60	1.84	0.00
05	70	60	1.84	0.38
06	70	60	1.75	0.38

[a] Reaction time: 15 min. Propylene in the batch reactions: 200 g.

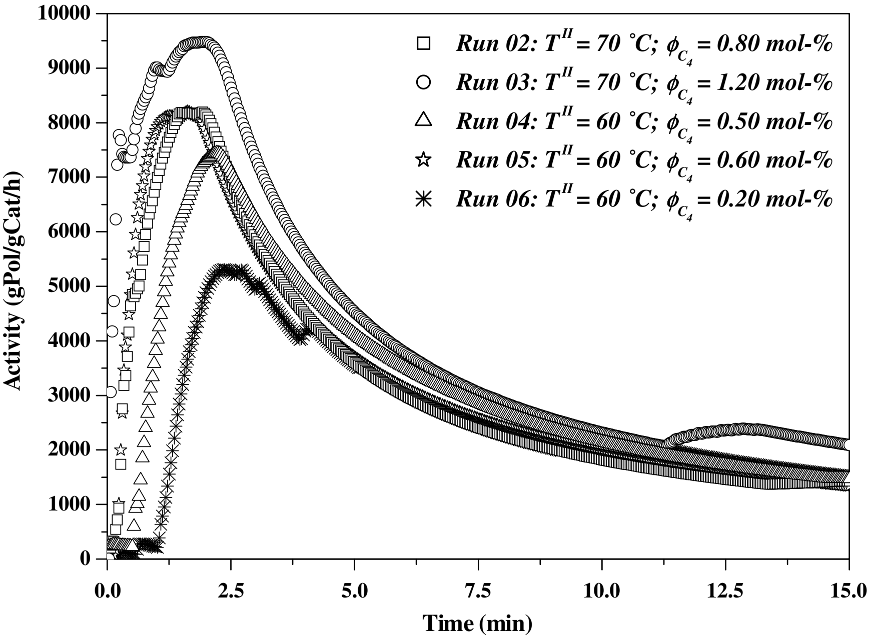

Fig. 1. Kinetic profiles obtained from the semibatch gas-phase polymerization of 1-butene.

Table 2
Polymer composition and crystallinity[a]

Run	$\mathscr{P}$ (g_{POL}/g_{CAT})	ϕ_{C_4} (mol%)	T_m (°C)	Crystallinity (%)
01	5693.95	0.00	162.45	49.66
02	5343.51	0.80	163.69	50.82
03	6323.19	1.20	162.80	45.69
04	5968.99	0.50	163.38	50.80
05	4662.00	0.60	163.14	48.30
06	6519.97	0.20	164.52	53.21

[a] Based on the heat of fusion of polypropylene 100% crystalline [27]: $\Delta H_f^* = 165\ \mathrm{J\,g^{-1}}$.

formed at very high rates for a broad range of 1-butene compositions. However, this is in accordance with experimental observations of propylene/ethylene polymerizations, when it was observed that the increasing accumulation of the heterophasic material contributes with the apparent catalyst deactivation due to mass transfer effects [19].

One might wonder whether the initial increase of catalyst activities might have been caused by 1-butene dissolution into the polypropylene matrix, but this does not seem to be the most important effect. First, the measured flow rates are higher at higher temperatures, while the solubility of the gaseous monomer into the polymer matrix decreases with the increase of temperature. Second, the 1-butene compositions obtained by NMR analyses confirm the overall mass balances of the system. However, it is possible that the combination of high polymerization rates and much poorer heat transfer conditions during the gas-phase polymerization stage might have caused local temperature increase and catalyst deactivation. This hypothesis is not supported, though, by previous random gas-phase polymerizations performed with propylene/1-butene mixtures, as very high polymerization rates were attained even at very low pressures [2].

The reaction rates seem to stabilize around 1000 g of polymer per gram of catalyst per hour at the analyzed low-pressure conditions (one should not overemphasize the low catalyst activities, given the low pressures of 1 atm and the low 1-butene concentrations in the gas-phase). Besides, reaction rates are strongly affected by hydrogen and cocatalyst concentrations. These results clearly indicate that 1-butene incorporation is indeed possible in the gas-phase, although optimization of reactor operation conditions is certainly required.

Polymer composition was determined by ^{13}C NMR through quantitative analysis of the characteristic peaks of the group CH_2 based on the dyads PP, BP and BB, which are placed at 46.00–46.95 ppm, at 43.02–43.51 and at 40.11 ppm, respectively, where P denotes propylene and B denotes 1-butene monomer units [20,21]. The peaks used for characterization of the polymer alloys were the ones described by Machado et al. [2,3] and the reader should refer to the published material for more detailed information. Fig. 2 shows the characteristic NMR spectrum of the polymeric material used for the microstructure characterization and computation of copolymer composition. The 1-butene content of the polymer alloys was determined from the dyad distributions by using standard relationships [20,21].

$$B = [BB] + 0.5[BP] \tag{1}$$

$$P = [PP] + 0.5[BP] \tag{2}$$

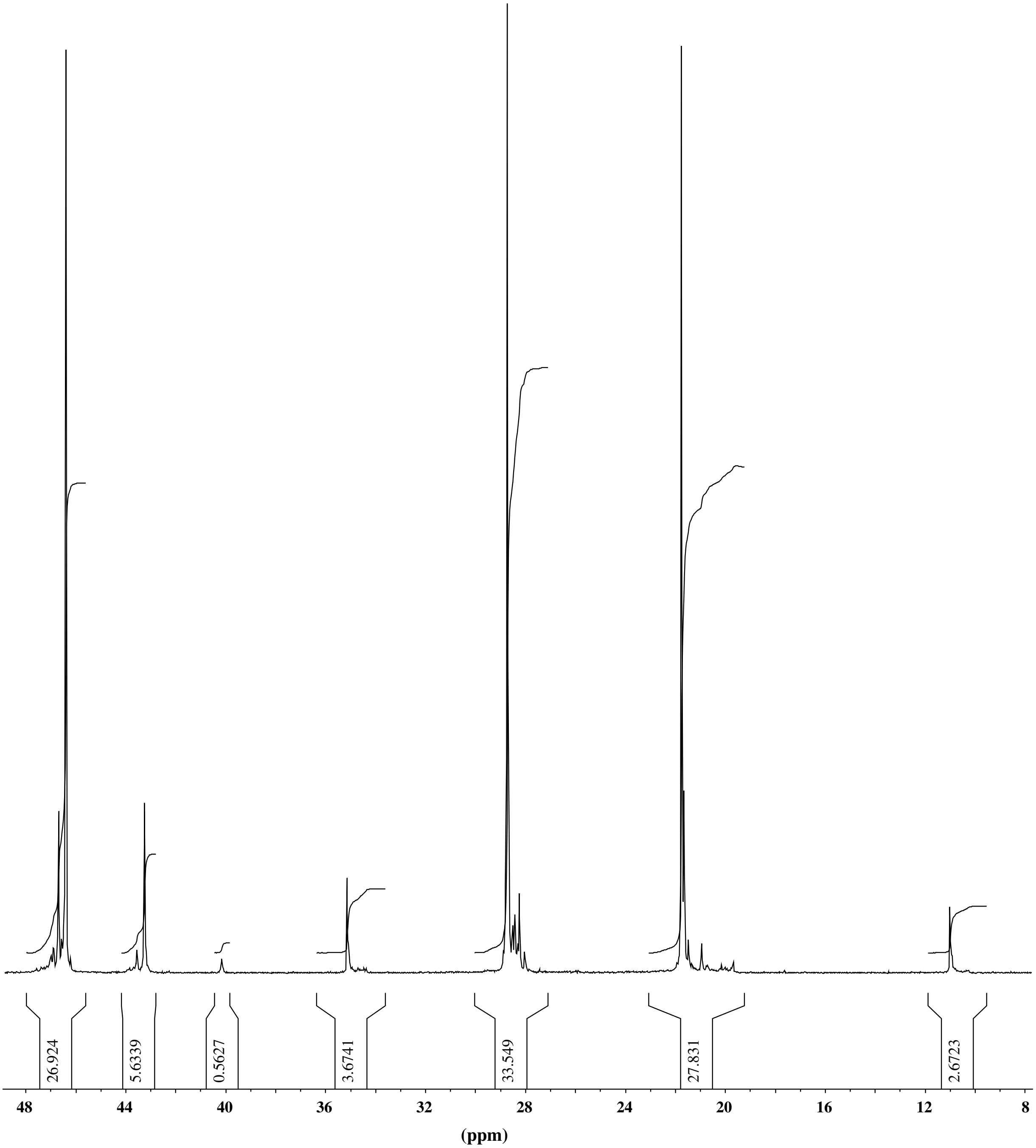

Fig. 2. ^{13}C NMR spectra of the polymeric material.

$$\phi_{C_4} = \frac{B}{B+P} = \frac{[BB] + 0.5[BP]}{[BB] + [PP] + [BP]} \quad (3)$$

Table 2 shows the 1-butene incorporation (ϕ_{C_4}). It can be observed that it is indeed possible to incorporate 1-butene in the polypropylene matrixes for polymerizations carried out at low 1-butene pressure. It is very important to note that the polymerizations were not designed for production of large amounts of rubber, but for observation of 1-butene incorporation. For this reason, the second polymerization stage was performed at short times (15 min) and low pressures. However, it seems reasonable to consider that the 1-butene incorporation may increase very significantly at higher pressures and longer runs.

Table 2 also shows the material crystallinity and melting temperature (T_m) of obtained polymer samples. Significant changes of the crystallinity and T_m of the materials cannot be observed, except perhaps for experiment 03, where the 1-butene incorporation is higher than 1%. This may be regarded as an important result, because the previous studies [2,3] indicate very significant changes of the crystallinity and melting temperature of the polymer material after incorporation of small amounts of 1-butene. It is particularly important to observe that T_m is systematically higher for polymer samples that contain 1-butene, although one might expect the opposite effect for random copolymers. Obtained results seem to confirm indirectly that 1-butene forms a different phase and is not evenly distributed into the polypropylene matrix (and polymer chains). Therefore, the properties of the continuous polymer matrix are not significantly affected by the second polymerization stage. This is also confirmed by NMR spectra, as propylene/1-butene dyads were not detected. In addition the incorporation of 1-butene as a comonomer is thought to improve the morphology of the particles and to help reduce fines formation.

Table 3 shows the average molecular weights and the polydispersities of the final polymer materials. It can be observed that the average molecular weights are not affected significantly by hydrogen concentration and 1-butene contents in the analyzed range. However it should be pointed out that in these sequential polymerizations, it seems that 1-butene tends to form polymer chains of larger molecular weights, which behavior is different from the one observed previously for random copolymers [2,3], where it was observed that the average molecular weight of polymeric material decrease as the concentration of the 1-butene in the copolymer increase. It should be emphasized that, as the incorporation of 1-butene was kept at low levels (0.80–1.20 mol%), the effect of 1-butene content on the average molecular weight was not observed at the analyzed conditions. This reinforces the fact that hydrogen feed should be used for optimization of the process performance.

Table 3
Weight-average molecular weight and polydispersity index

Run	M_n (g/mol)	M_w (g/mol)	PDI	I_2 (g/10 min)	I_5 (g/10 min)	I_5/I_2
01	73,781	538,293	7.30	0.56	2.45	4.38
02	141,440	566,295	4.00	0.40	2.14	5.36
03	77,707	549,454	7.07	0.69	3.30	4.78
04	77,926	538,471	6.91	0.50	1.74	3.48
05	80,395	570,449	7.10	0.75	3.45	4.60
06	76,936	463,605	6.03	0.88	4.28	4.87

Table 3 also shows the melt flow index (MFI) values obtained in accordance with ASTM D1238 (I_2, 190 °C, 2.16 kg) and ASTM D 1239 (I_5, 190 °C, 5 kg). MFI measurements are widely used as an additional indicator of the average molecular weights and the molecular weight distributions of polymers and constitute important performance indexes for the polyolefin business. In some situations, it is very interesting to determine the MFI at low (I_2) and high shear rate (I_5). The I_5/I_2 ratio can be used to give useful information about the shape of the molecular weight distribution of polymeric material through the definition of a characteristic value range for I_5/I_2 for each particular material. According to Table 3, I_5/I_2 assumes values in the range of 3.5–4.9 for polydispersities ranging from 6 to 7. It is also very important to notice that the MFI values are within the range of commercial interest for this kind of polymeric materials. From a practical point of view, it may be said that the incorporation of 1-butene does not affect the MFI of the final polymer samples. This can also be regarded as an important observation, because the incorporation of small amounts of polyethylene can cause a very significant effect on the MFI of polypropylene grades [22].

Analysis of surface morphology of polymer particles was performed through SEM. Fig. 3 shows the surface morphology of typical polymer particles (N.B. This image was chosen from a number of different analyses and is quite representative of the particle population as a whole). Polymer particles with good morphology can be obtained after

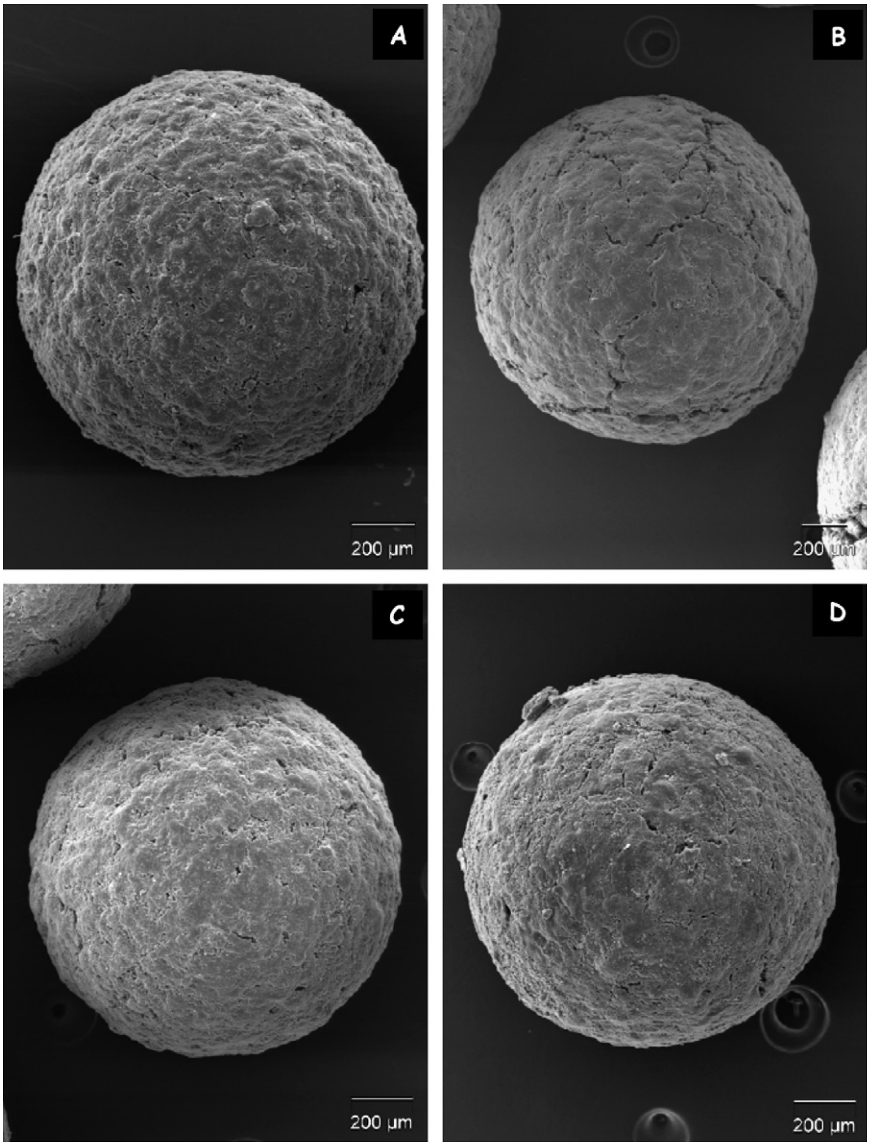

Fig. 3. Polymer particles morphology. (A) run 01; (B) run 06; (C) run 02 and (D) run 03.

sequential polymerization process in the whole range of analyzed experimental conditions. It is desired that polymer particles present regular shape because the absence of fines prevents reactor fouling problems and undesirable fluidization effects. It is important to emphasize that incorporation of small amounts of 1-butene do not lead to formation of sticky polymer particles. In addition, it was not observed the formation of fines in the reactor after polymerization.

Deconvolution of molecular weight distributions (MWDs) has been widely used to give insights about the polymerization kinetics and provide information about the catalyst behavior. The MWDs can generally be described as the summation of the Schulz–Flory distributions [23,24], as

$$W_i = \sum_{j=1}^{NS} \alpha_j w_{i,j} \quad (4)$$

where NS is the number of active sites, α_j is the mass fraction of polymer produced by the individual catalyst active site j and $w_{i,j}$ is the weight Schulz–Flory distributions [24] given as

$$w_{i,j} = i(1 - q_j)^2 q_j^{i-1} \quad (5)$$

The propagation probability (q) depends on the polymerization mechanism is normally represented as

$$q = \frac{K_{\mathrm{P}}M}{K_{\mathrm{P}}M + \sum_k K_{\mathrm{T}_k} X_k} \qquad (6)$$

where M and X are monomer and chain transfer agent concentrations, while K_{P} and K_{T} are the kinetic constants for propagation and transfer to the chain transfer agents.

In some cases it is more convenient to express the weight Schulz–Flory distributions as a function of the cumulative weight fraction (ξ) of the polymer material, given as

$$\xi_{i,j} = (1 - q_j)^2 \sum_{i=1}^{n} i q_j^{i-1} = 1 - q_j^i - i(1 - q_j)q_j^i \qquad (7)$$

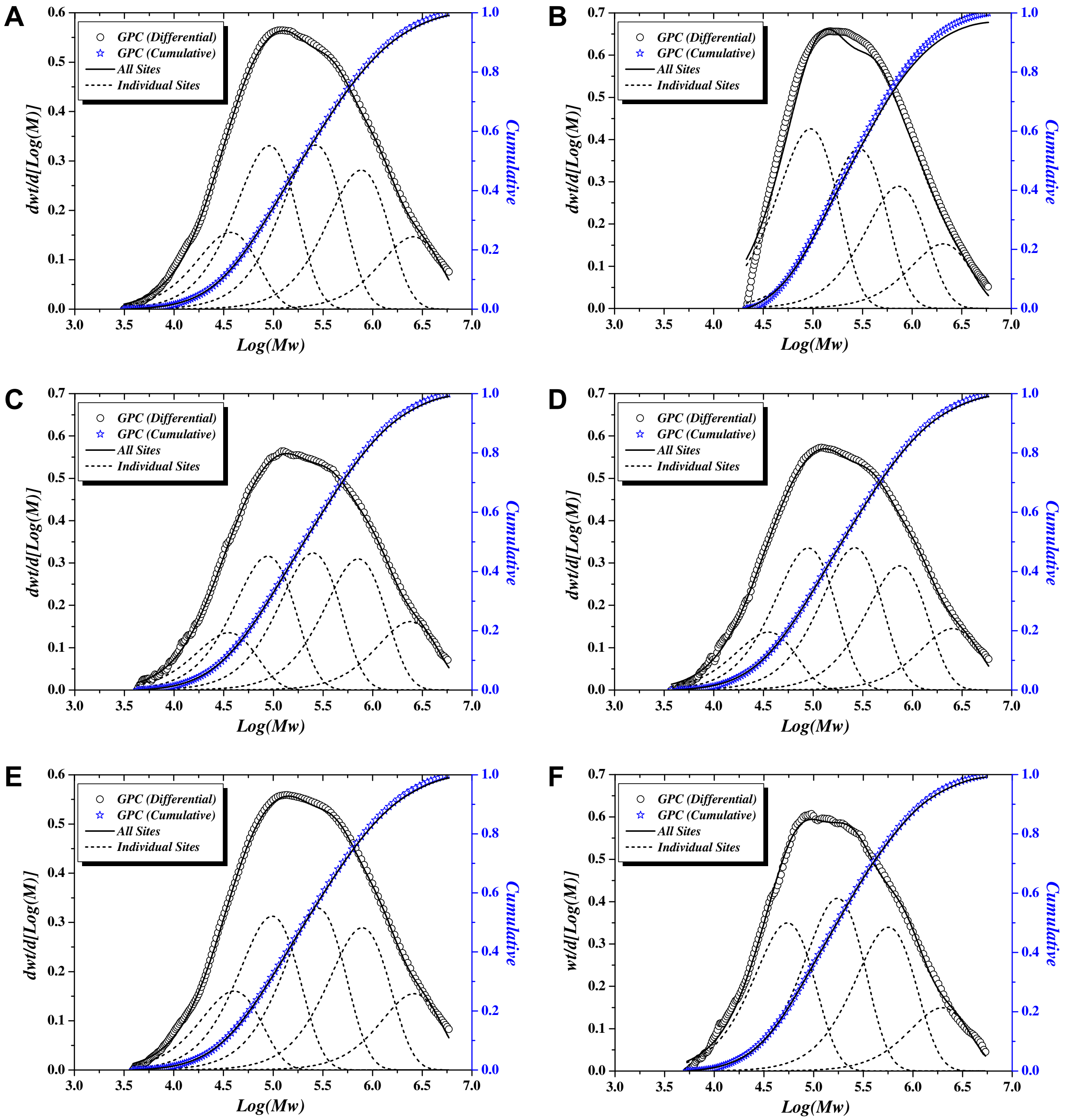

Fig. 4. Deconvolution of MWD into Schulz–Flory distributions. (A) run 01; (B) run 02; (C) run 03; (D) run 04; (E) run 05 and (F) run 06.

Table 4
Weight-average molecular weight and mass fraction of polymer determined through deconvolution of GPC data

Site	Experiment											
	01		02		03		04		05		06	
	α	M_w (g/mol)	α	M_w (g/mol)	α	M_w (g/mol)	α	M_w (g/mol)	α	M_w (g/mol)	α	M_w (g/mol)
I	0.118	2,575,497	0.123	2,061,252	0.130	2,379,187	0.116	2,540,801	0.124	2,618,419	0.120	1,979,621
II	0.125	36,933	–	–	0.109	35,685	0.110	35,638	0.129	40,458	–	–
III	0.226	763,490	0.232	731,189	0.248	713,942	0.235	748,034	0.232	787,188	0.272	568,723
IV	0.265	90,972	0.341	94,628	0.254	87,945	0.269	89,520	0.251	97,687	0.281	54,548
V	0.266	266,914	0.304	291,978	0.260	250,741	0.270	262,635	0.264	281,278	0.327	173,886

Therefore, the summation of the Schulz–Flory distributions used to evaluate the MWDs of polymer materials can be expressed as:

$$\Omega_i = \sum_{j=1}^{NS} \alpha_j \xi_{i,j} = \sum_{j=1}^{NS} \alpha_j [1 - q_j^i - i(1 - q_j) q_j^i] \qquad (8)$$

The set of equations composed by the 2NS – 1 unknown variables to be determined (the dimensions of q and α are NS and NS – 1, respectively) was solved numerically, using a direct search COMPLEX algorithm [25]. The standard numerical procedure DBCPOL, obtained from the IMSL™ library [26], was used for implementation of the computer code.

Fig. 4 illustrates both the MWDs and the cumulative weight fractions obtained from GPC analysis, deconvoluted into Schulz–Flory distributions. It can be observed that as many as five Schulz–Flory distributions may be required to describe the GPC data of the polymer samples. According to Fig. 3A–F and to Table 4, the deconvoluted MWDs are very similar for each individual active site. As can be observed for the experiments R02 and R06, only four sites are required to describe the MWD. According to Table 4, results obtained from deconvolution of MWDs show that the catalyst site of type II does not contribute to the formation of polymer chains. In the particular case of experiment R02, the polydispersity index, I_5/I_2, and the shape of the MWD curve were significantly affected.

This is also of practical importance, as no significant increase of the low-molecular weight fraction of the polymer sample can be observed in the presence of 1-butene. Therefore, the deconvolution analyses seem to confirm that poly(1-butene) of high molecular weight is produced by the catalyst, despite the very low pressures, the very low 1-butene concentrations and the polymerization in the gas-phase.

4. Conclusion

According to the obtained results, it is possible to incorporate 1-butene upon the polypropylene matrix in polymerizations performed in the gas-phase and at low pressures of 1-butene. The obtained results also indicate that the properties of the continuous polymer phase are not significantly affected by the increasing 1-butene content of the polymer samples (crystallinity, melting temperature, melt flow index, particle morphology) during the sequential polymerization. These results indicate that a family of polypropylene/1-butene in-reactor alloys can probably be developed for applications as high-performance structured materials.

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