

# Shear-induced crystallization of polypropylene: Influence of molecular weight

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Three series of isotactic polypropylene characterized by different molecular weights and the same isotactic index have been studied during crystallization under static and shearing conditions. The shear is induced by the displacement of a glass fiber in the molten polymer. The monoclinic  $\alpha$ -phase is here formed under shear with a columnar organization at the surface of the glass fiber, and does not appear under static condition. The growth-rate, constant during the shear-induced crystallization experiment, is compared with the result obtained from static crystallization. An important increase of the growth-rate due to the shear flow is observed. This increase depends on the molecular structure. The average molecular weights  $\bar{M}_w$  and  $\bar{M}_z$  seem to be the most important molecular parameters, for which an excellent correlation is obtained. The increase of these parameters  $\bar{M}_w$  and  $\bar{M}_z$  leads to a significant enhancement of the growth-rate, which can be multiplied by a factor of 10 in the present conditions. © 2000 Kluwer Academic Publishers

## 1. Introduction

Flow-induced crystallization of a polymer is able to produce very specific organizations as an effect of the deformation of macromolecular chains. Shish kebabs and row-nucleated arrangements are commonly observed rather than spherulites, characteristic of quiescent crystallization. Various devices were built-in to induce crystallization under shear during laboratory experiments [1–24]: parallel-plates [1, 3, 5, 13–15, 17], coaxial cylinders [2, 4, 7, 8], rotational plate-plate [4, 9], biconical [6], die-extrusion [10–12] and fiber pull-out [13, 14, 16–23]. The latter device widely used during the last period is very efficient to observe by optical microscopy the crystalline growth-rate with a small amount of polymer. Many publications are focused on the analysis of polypropylene crystallization under that condition. Some papers analyze the effect of melt history on interfacial morphology [20–23]. They usually conclude that nucleation is strongly enhanced by the flow and that the effect on the growth-rate is weak. Conversely, in previous works [13–15, 17–19], we have shown for various polypropylenes that the growth-rate is significantly enhanced by the presence of a shear flow. As under static condition, only the monoclinic  $\alpha$ -phase [24–29] is growing under shear, while the  $\beta$ -phase [24–29] is formed after cessation of shear. The enhancement of the growth-rate mainly depends on polypropylene molecular weight and on shear-rate. Three papers deal with this phenomenon [14, 18, 19]. The crystallization after shear of an impact copolymer (polypropylene/ethylene-propylene rubber reactor blend) has first shown the en-

hancement of the crystalline growth-rate with respect to static condition during the relaxation of chain orientation [14].

Afterwards, a study on a series of three polypropylenes exhibits the role of molecular weight on the growth-rate under shear, in spite of a distribution of molecular weight and of isotactic content (95.5% to 97.7%) [18]. A similar analysis has been done more recently on eight polypropylenes with a broader distribution of isotactic content and different molecular weights and distributions [19]. These polymers are produced by the same company but using different catalytic systems. The effect of molecular weight on the growth-rate under shear is more acute, but there is a coupling between tacticity, molecular weight and molecular weight distribution, which leads to a difficult discussion about the respective contribution of these different molecular parameters.

Catalytic systems and polymerization parameters strongly influence the molecular structure of polypropylene, i.e., stereoregularity and molecular weight distribution. In the present paper, we choose to fix the stereoregularity and to modify the average molecular weights as the main molecular parameters and the molecular weight distribution as a further one. This will be done with three series of polypropylene samples. The first one, the mother series, is obtained with one gas-phase catalytic system where only the molecular weight changes. A second series, the first sister series, is obtained by peroxidic degradations [30–32] of a high molecular weight polymer of the mother series.

TABLE I Molecular characteristics of polypropylenes RE

| Polymers              | L0      | L1     | L2     | L3     | L4     | L5     | L6     |
|-----------------------|---------|--------|--------|--------|--------|--------|--------|
| MFI (g/10 min)        | 0.64    | 2.3    | 3.6    | 5.7    | 10.8   | 17.6   | 35     |
| $\bar{M}_n$ (g/mol)   | 28500   | 33300  | 33700  | 30500  | 24900  | 25800  | 21000  |
| $\bar{M}_w$ (g/mol)   | 374500  | 268300 | 235100 | 213900 | 180800 | 159600 | 139400 |
| $\bar{M}_z$ (g/mol)   | 1140300 | 806800 | 678400 | 651900 | 562100 | 486200 | 461700 |
| $\bar{M}_w/\bar{M}_n$ | 13.2    | 8.1    | 7      | 7      | 7.3    | 6.2    | 6.6    |
| $\bar{M}_z/\bar{M}_w$ | 3       | 3      | 2.9    | 3      | 3.1    | 3      | 3.3    |
| Isotactic Index (%)   | 95      | 96     | 95     | 95     | 96     | 96     | 96     |

TABLE II Molecular characteristics of polypropylenes CR

| Polymers              | L1     | L7     | L8     | L9     | L10    | L11    | L12    |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|
| MFI (g/10 min)        | 2.3    | 3.7    | 5.7    | 9.7    | 15.9   | 32     | 49     |
| $\bar{M}_n$ (g/mol)   | 33300  | 41100  | 38500  | 37200  | 27000  | 31600  | 30000  |
| $\bar{M}_w$ (g/mol)   | 268300 | 232000 | 202000 | 169300 | 143700 | 120500 | 109100 |
| $\bar{M}_z$ (g/mol)   | 806800 | 610000 | 500000 | 394000 | 324400 | 256200 | 227000 |
| $\bar{M}_w/\bar{M}_n$ | 8.1    | 5.6    | 5.2    | 4.6    | 5.3    | 3.8    | 3.6    |
| $\bar{M}_z/\bar{M}_w$ | 3      | 2.6    | 2.5    | 2.3    | 2.3    | 2.1    | 2.1    |
| Isotactic Index (%)   | 96     | 95     | 95     | 95     | 96     | 95     | 95     |

It is known that an increase of peroxide amount decreases the molecular weight but also the molecular weight distribution. The third series, the second sister series, is prepared to increase the molecular weight distribution, when the molecular weight changes. It is obtained by mixing, in different proportions, a high and a low molecular weight polymer of the mother series.

The paper is then focused on the effect of molecular weight and molecular weight distribution on the crystalline growth of polypropylene under shear.

## 2. Experimental

The shear-induced crystallization of three different families of polypropylene homopolymers has been studied. The formation and the evolution of the morphologies were followed by optical microscopy during the experiments. Then, the morphologies and the final structure of the resulting material were observed on thin slices cut out of crystallized samples.

### 2.1. Materials

The average molecular weights and the molecular weight distributions of the investigated polymers are deduced from SEC (size exclusion chromatography) measurements with a four-column Waters apparatus, at 135°C, in trichlorobenzene. The MFI (Melt Flow Index) is determined according to the ISO 1133 method under 230°C/2.16 kg conditions. The isotactic index, which corresponds to the percentage of mm triads, is obtained by the NMR <sup>13</sup>C method.

Three series of isotactic polypropylene, supplied by the Solvay Company, have been studied. To fix the isotactic content and the molecular weight distribution, a single polymerization condition is considered here, a gas-phase polymerization used by Solvay. Only the molecular weight is changed by an appropriate adjustment of hydrogen concentration during the process. The polymers obtained are characterized by the same isotactic index of 95–96%, but differ by their molecular weights and polydispersity. The first series is a family

of seven “straight reactor grade” (RE) homopolymers, named L0 to L6 (Table I). These polymer flakes, directly obtained from the reactor, are stabilized and then granulated in the laboratory. Their MFI varies from 0.64 to 35 g/10 min. The average molecular weights decrease from L0 to L6 but there are no significant differences of molecular weight distribution, except for L0, which has a broader one (Table I). Six “controlled rheology type” (CR) polypropylenes, named L7 to L12, form the second series of investigated materials (Table II). They are obtained by a progressive degradation of homopolymer L1 using a peroxide. No change of tacticity has been detected. The average molecular weight  $\bar{M}_w$  decreases from L7 to L12, and consequently the MFI increases from 3.7 to 49 g/10 min. The molecular weight distributions are lower than those of the RE polypropylenes. The last series is a family of homopolymers (B) obtained by blending of L0 and L5 with four different compositions (% w/w): 20/80, 36/64, 50/50 and 80/20 (Table III). The final MFI decreases from 8.5 to 1.4 g/10 min. Blending leads to polymers, mostly in the mid-range of composition, with a broader molecular weight distribution  $\bar{M}_z/\bar{M}_w$  than the starting material. They could be considered as bimodal polymers to be compared with monomodal resins of the same molecular weight (L1 to L4 series).

All these polymers have been chosen in order to evaluate the specific influences of the average molecular

TABLE III Molecular characteristics of polypropylenes B L0/L5

| Polymers              | L0      | L0/L5<br>80/20 | L0/L5<br>50/50 | L0/L5<br>36/64 | L0/L5<br>20/80 | L5     |
|-----------------------|---------|----------------|----------------|----------------|----------------|--------|
| MFI (g/10 min)        | 0.64    | 1.4            | 3.5            | 5.7            | 8.5            | 17.6   |
| $\bar{M}_n$ (g/mol)   | 28500   | 27100          | 32200          | 13000          | 19700          | 25800  |
| $\bar{M}_w$ (g/mol)   | 374500  | 321000         | 254700         | 215900         | 191500         | 159600 |
| $\bar{M}_z$ (g/mol)   | 1140300 | 982300         | 902200         | 769300         | 648400         | 486200 |
| $\bar{M}_w/\bar{M}_n$ | 13.2    | 11.8           | 7.9            | 16.6           | 9.7            | 6.2    |
| $\bar{M}_z/\bar{M}_w$ | 3       | 3.1            | 3.5            | 3.6            | 3.4            | 3      |
| Isotactic Index (%)   | 95      |                |                |                |                | 96     |

weights and the molecular weight distribution on crystallization. Therefore, the effect of the molecular weight and the isotactic index can be separated.

## 2.2. Experimental method

The experimental device used to study isothermal crystallization under static and shear conditions is the fiber pull-out device already described in previous work [13, 14, 16–18] and presented in Fig. 1. It consists of a Mettler FP52 hot stage placed under an optical microscope Reichert Zetopan-Pol with transmitted light, between crossed polarizers. The hot stage is calibrated in temperature with benzoic acid (melting temperature  $T_m = 122.35^\circ\text{C}$ ) and anisic acid ( $T_m = 182.98^\circ\text{C}$ ) under isothermal condition. The calibration and the experiments are carried out under a nitrogen flow, in order to reduce polymer oxidation and to obtain a better thermal control. The temperature accuracy is better than  $0.1^\circ\text{C}$  for the crystallization and heat treatment temperatures. A glass fiber is put between two polypropylene films, forming a composite material, which is placed into the hot stage between two parallel glass plates. The glass fiber has a  $17\ \mu\text{m}$  diameter and a 50–150 mm length. The composite made of the glass fiber and the polymer is heated up to  $210^\circ\text{C}$ , maintained at this temperature during 5 min, and cooled down to the crystallization temperature  $T_c = 126^\circ\text{C}$ , at a constant rate ( $-10^\circ\text{C}/\text{min}$ ). This composite is about 10 mm long, 4 mm wide and 0.3 mm thick. A high thickness is necessary to avoid boundary effects from the glass plates [18]. For static crystallization experiments, considered as a reference, the glass fiber is immobile. For the shearing experiments, the fiber is fixed during the polymer cooling. As soon as the temperature reaches  $126^\circ\text{C}$ , the glass fiber is moved along its axis at a constant speed  $V_f = 350\ \mu\text{m}/\text{s}$ , using an electric motor. This displacement induces a shear flow around the fiber. The maximum displacement (18 mm) is fixed to ensure that the fiber and the polymer observed were in contact from the beginning to the end of the experiment. For longer distances, the fiber region arriving in the observation zone was outside the polymer at the beginning of the experiment, which implies possible artefacts. Consequently, the shearing time is limited and related to the fiber speed. In the present case, its value is 50 s. The

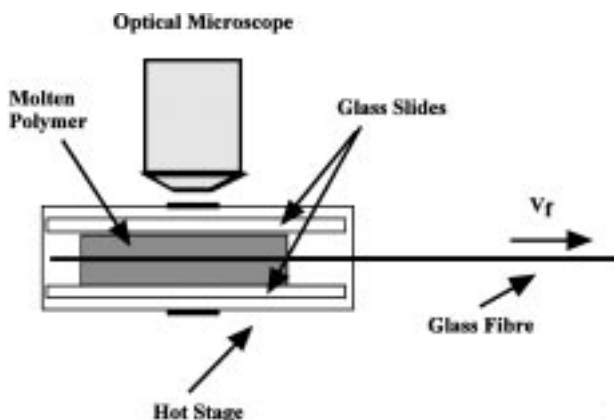


Figure 1 Fibre pull-out device.

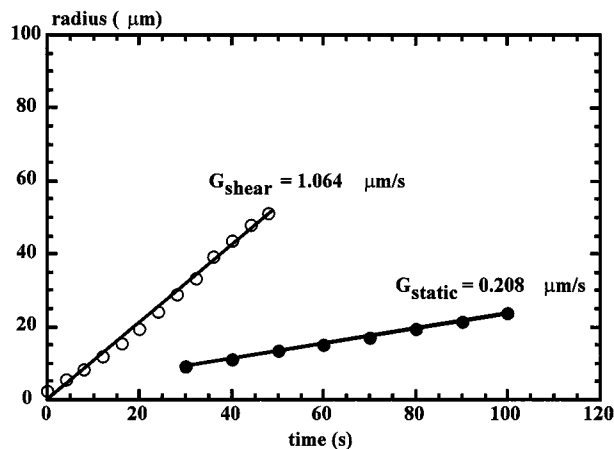


Figure 2 Growth-rate measurements for polymer L1 under static and shear conditions.

morphologies developed during the crystallization experiments are photographed at constant time intervals. The crystalline growth-rate is deduced from the time evolution of the size of the morphologies. It corresponds to the slope of the spherulite radius, or of the cylindrical morphology radius around the fiber, versus time curve. The growth-rate remains constant during crystallization experiments (Fig. 2).

A model has been proposed by Monasse [16, 18] to describe the polymer flow in the vicinity of the glass fiber. The shear-rate  $\dot{\gamma}$  expression is:

$$\dot{\gamma}(r) = \frac{1-n}{n} \frac{1}{r^{1/n}} \left[ \frac{1}{r_f^{(1-1/n)} - r_e^{(1-1/n)}} \right] V_f \quad (1)$$

where  $r_e$  and  $r_f$  are the external and fiber radii, respectively,  $r$  is the location of the considered point in the polymer ( $r_f \leq r \leq r_e$ ) and  $n$  is the exponent in the viscosity power law equation

$$\eta = K \dot{\gamma}^{n-1} \quad (2)$$

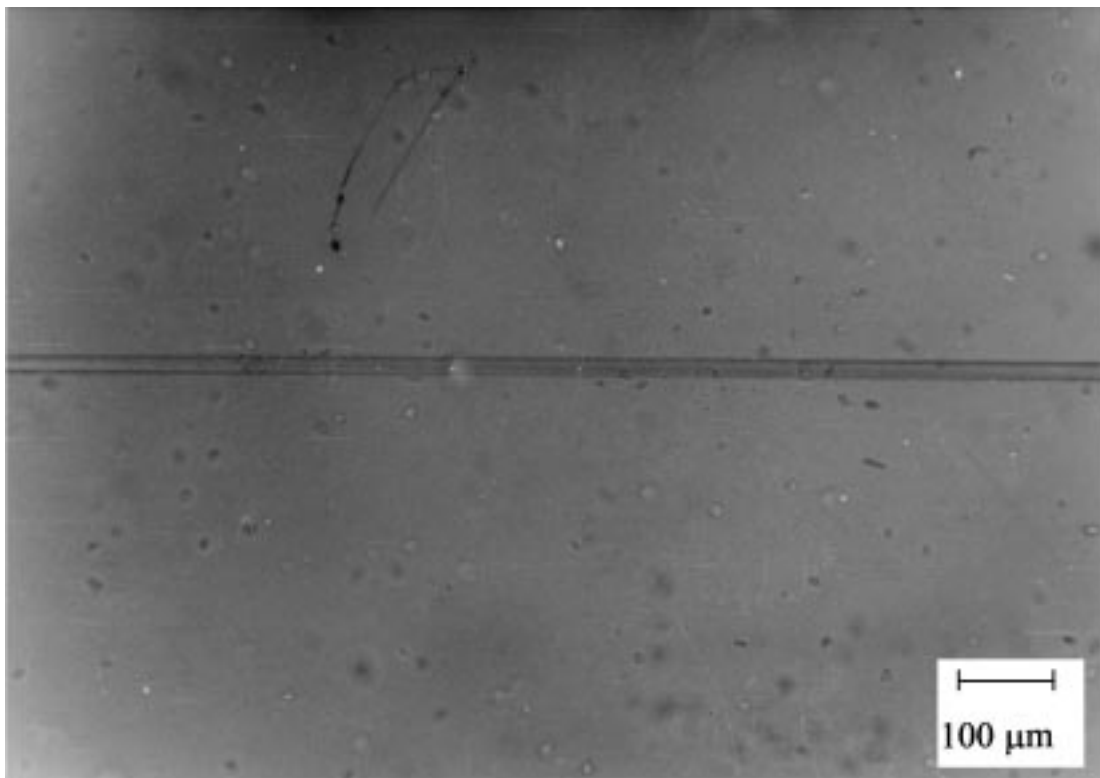
with  $K$  the consistency. This model predicts a strong decrease of the shear-rate versus the radius [16].

Thin slices of samples crystallized under shear were cut in the thickness of the polymer films, perpendicular to the direction of the fiber, using a glass knife (LKB Ultratome 4800A ultramicrotome). Thanks to this method, the morphologies developed around the fiber will be characterized in the third direction.

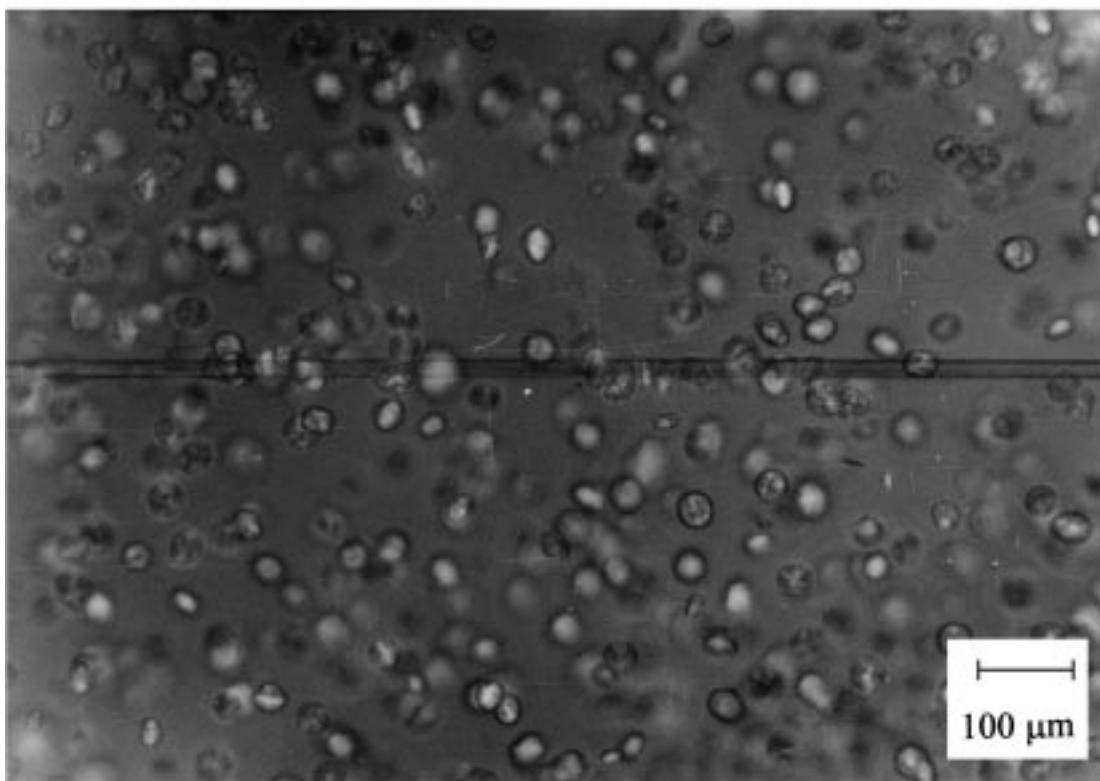
## 3. Results

### 3.1. Static experiments

The morphologies formed during all the static experiments are only  $\alpha$ -phase spherulites for all the studied polymers (Fig. 3a and b). At the chosen crystallization temperature, they are characterized by a low positive birefringence [26], due to the crystalline lamellar organization. The  $\alpha$  monoclinic modification [24–29] is the most common phase in polypropylene, and the thermodynamically most stable under normal-isothermal and static-crystallization conditions.  $\alpha$ -phase spherulites are strongly different from those of the  $\beta$  hexagonal metastable phase, which are characterized by a high



(a)



(b)

Figure 3 Static crystallization of polypropylene L1 at 126°C: (a) after 20 s, (b) after 80 s.

negative birefringence [24–29]. None of them are observed during static experiments. In addition, the uniform distribution of the  $\alpha$ -phase spherulites in the volume, as seen in Fig. 3, shows the non-nucleating effect of the glass fiber. No specific nucleation is observed around the fiber. This behavior is consistent with previous observations [16–19, 33]. Concerning the number of nuclei per unit volume, there is no significant

difference from a polypropylene to another. The nucleation density is around 2000 nuclei/mm<sup>3</sup>. Only for the polymer L0, which has the highest molecular weight, the nuclei density is higher than for the others, which causes difficulties for growth-rate measurements.

During isothermal crystallization under static condition, the growth-rate remains constant, as shown in Fig. 2, for polymer L1. The data obtained for the three

TABLE IV Growth-rates  $G$  ( $\mu\text{m/s}$ ) under static and shear flow conditions, sensitivity  $S$

| RE-PP               | L0    | L1             | L2             | L3             | L4             | L5    | L6   |
|---------------------|-------|----------------|----------------|----------------|----------------|-------|------|
| $G_{\text{static}}$ | 0.21  | 0.205          | 0.2            | 0.215          | 0.21           | 0.215 | 0.24 |
| $G_{\text{shear}}$  | 2.2   | 1.05           | 0.8            | 0.66           | 0.55           | 0.52  | 0.37 |
| $S$                 | 10.5  | 5.1            | 4              | 3.1            | 2.65           | 2.4   | 1.55 |
| CR-PP               | L1    | L7             | L8             | L9             | L10            | L11   | L12  |
| $G_{\text{static}}$ | 0.205 | 0.195          | 0.195          | 0.2            | 0.195          | 0.205 | 0.22 |
| $G_{\text{shear}}$  | 1.05  | 0.73           | 0.59           | 0.49           | 0.4            | 0.37  | 0.37 |
| $S$                 | 5.1   | 3.75           | 3.05           | 2.5            | 2.05           | 1.85  | 1.7  |
| B L0/L5             | L0    | L0/L5<br>80/20 | L0/L5<br>50/50 | L0/L5<br>36/64 | L0/L5<br>20/80 | L5    |      |
| $G_{\text{static}}$ | 0.21  | 0.19           | 0.18           | 0.19           | 0.19           | 0.215 |      |
| $G_{\text{shear}}$  | 2.2   | 1.4            | 0.9            | 0.75           | 0.7            | 0.52  |      |
| $S$                 | 10.5  | 7.5            | 4.7            | 4.1            | 3.35           | 2.4   |      |

series of polypropylene, resulting from three measurements per polymer, are collected in Table IV. The precision of the growth-rate measurements is about 15%. Taking into account this uncertainty, all the RE polypropylenes have almost the same growth-rate, around  $0.2 \mu\text{m/s}$ . The growth-rates of the peroxidized polypropylenes are systematically slightly lower. This could be linked with the presence of impurities due to the peroxide degradation, although these impurities should affect rather nucleation than growth. In spite of experimental error, it seems that the specimens with the lowest molecular weights, L6 and L12, have the highest growth-rates. Concerning the blends of polymers L0 and L5, their growth-rates are close to those of the previous series, but a little lower. A slight minimum is observed for the blend with the 50/50 composition, corresponding to a maximum of the molecular weight distribution  $M_z/\bar{M}_w$ . The peroxidized polymers, which have a narrower molecular weight distribution than the RE polypropylenes, have almost an unmodified growth-rate with respect to the mother polymers. The variation is only about 10%–15% for the blends, which is not really significant, if we take into account the precision of the growth-rate measurements.

In spite of some slight variations, it seems that under static condition, the molecular structure in terms of average molecular weights and molecular weight distribution have no significant influence on the growth-rate of polypropylene.

### 3.2. Shearing experiments

Under shear flow, a  $\alpha$ -phase columnar morphology appears at the surface of the fiber [18, 22, 23], as shown in Fig. 4, for all the considered polymers, forming a crystallized cylindrical envelope around the fiber. Close to this envelope,  $\beta$ -phase spherulites appear, probably formed after cessation of flow. This observation allows us to compare the crystal growth under shear flow with the growth-rate under static condition, since the same crystalline phase grows during these experiments. Close to the fiber, the shear-rate is maximum and induces a strong nucleation at the surface of the glass fiber, due to a high orientation of the macro-

molecular chains [18]. In Fig. 4, the different crystallization behaviors of the RE-PP L0, L1 and L5, the peroxidized polymer L7 and the blend with the proportion 50/50 can be compared under shear flow. At the same shearing time of 20 s, the sizes of the morphologies developed around the fiber by these polymers are different. For example, the increase of the growth-rate with molecular weight is clearly demonstrated by the different sizes of the crystallized envelope of the blend series of polymers L0, B-50/50 and L5 (Fig. 4c–e). The birefringence of the polymer melt varies from a polymer to another, due to the different orientation of the macromolecular chains. Regarding Fig. 4c–e, the birefringence seems to increase with the molecular weight. Far from the fiber, the morphologies observed are  $\alpha$ -monoclinic phase spherulites, as under static condition. The growth-rate of these spherulites is close to the growth-rate measured under static condition. The shear-rate is much lower in these locations and the shear in the melt is not sufficient to induce a crystallization under shear: spherulitic morphologies are then observed and appear later than the entities at the surface of the glass fiber [18].

Under shear, the precision on the growth-rate of the cylindrical envelope is also about 15%. The results are presented in Table IV. The precision of growth-rate measurements is all the better as the molecular weight is high, i.e., as the polymer is sensitive to the shear flow. The experimental procedure must be adapted to the type of sample. On the one hand, for the polymers of lower molecular weights, the crystallized envelope is actually very thin. This leads to measurement difficulties. For these polymers, a first shear was applied at a higher temperature,  $160^\circ\text{C}$ , in order to increase the probability of nucleation at the glass fiber surface and to measure more precisely the further growth. On the other hand, for the polymers of highest molecular weights, the shearing time was shorter, limited by the yield stress of the glass fiber. The viscosity is so high that the glass fiber breaks. In order to decrease this effect, a shorter sample was prepared. Consequently the shearing time for crystallization was reduced. Nevertheless, a minimum sample length of 10 mm is required to avoid some edge effects on crystallization.

For all the polypropylenes, the growth-rate remains constant during the shear experiments, as is shown in Fig. 2. The growth-rate is highly increased compared to that under static condition. For example, it is multiplied by 10 for the most viscous polymer L0. This effect is very large and must strongly enhance the overall kinetics. If we consider an Avrami model with an instantaneous nucleation and a spherulitic growth, the transformed volume fraction  $\alpha$  at time  $t$  is:

$$\alpha(t) = 1 - \exp(-E(t)) \quad (3)$$

with

$$E(t) = \frac{4}{3}\pi N G^3 t^3 \quad (4)$$

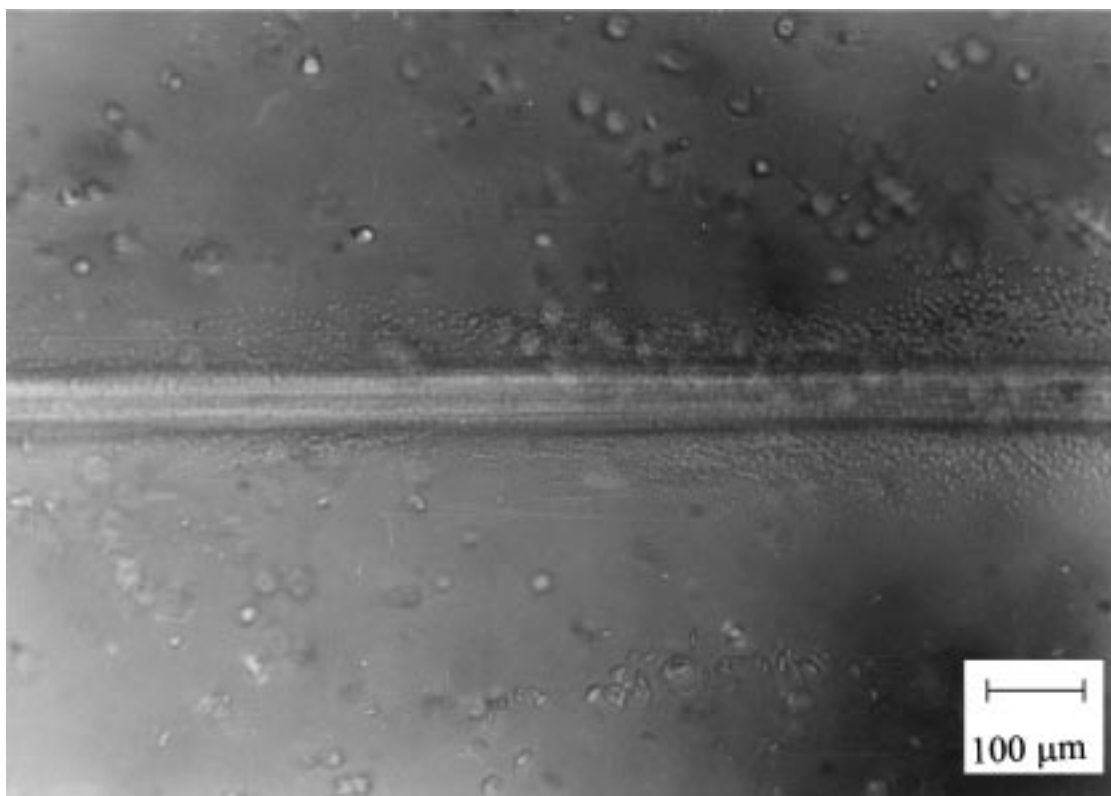
where  $N$  is the number of nuclei per unit volume and  $G$  is the linear growth-rate of the crystals.

An increase of the growth-rate by a factor of 10 increases  $E$  by a factor of 1000. This demonstrates that the

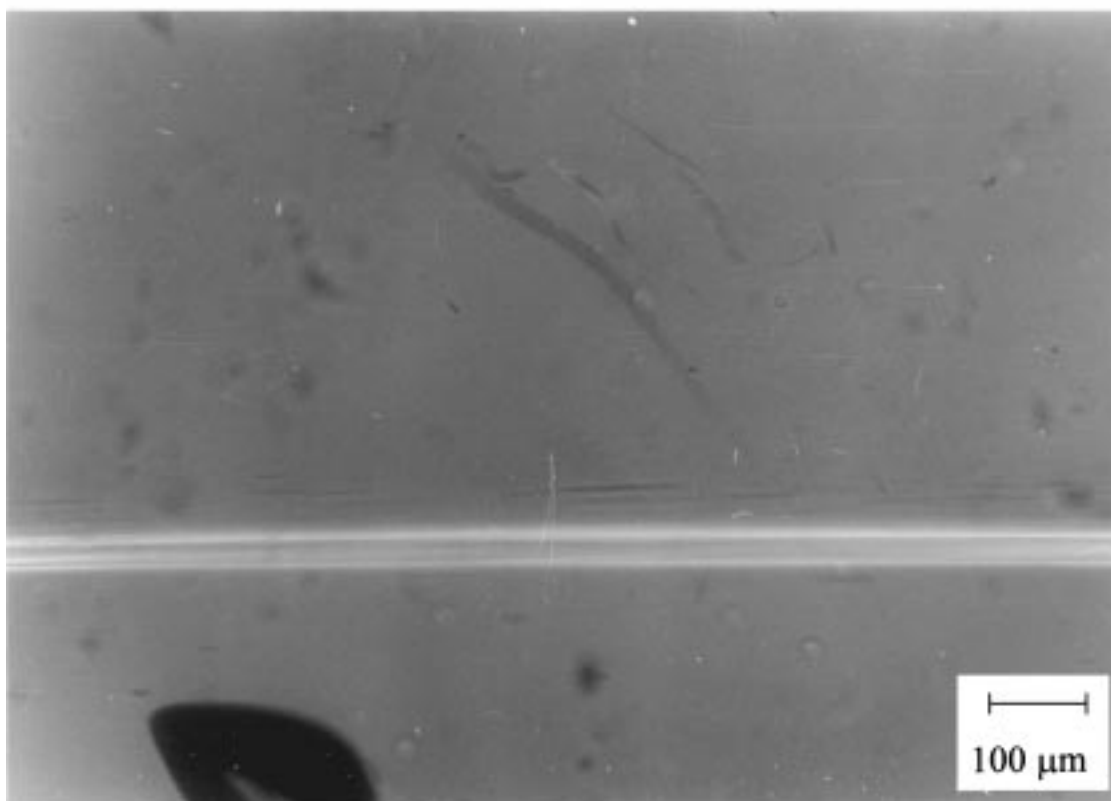
shear flow has a great influence on crystallization kinetics. This fact was already observed on overall kinetics by Haas and Maxwell [1], Lagasse and Maxwell [5], and Liedauer *et al.* [11, 12], but they considered that it was mainly due to a nucleation enhancement without

significant effect on growth-rate. Consequently, very few studies were interested in the influence of the shear flow on the growth-rate [13–15, 17–19].

Concerning the RE polypropylenes, the growth-rate decreases on decreasing the molecular weight, from



(a)



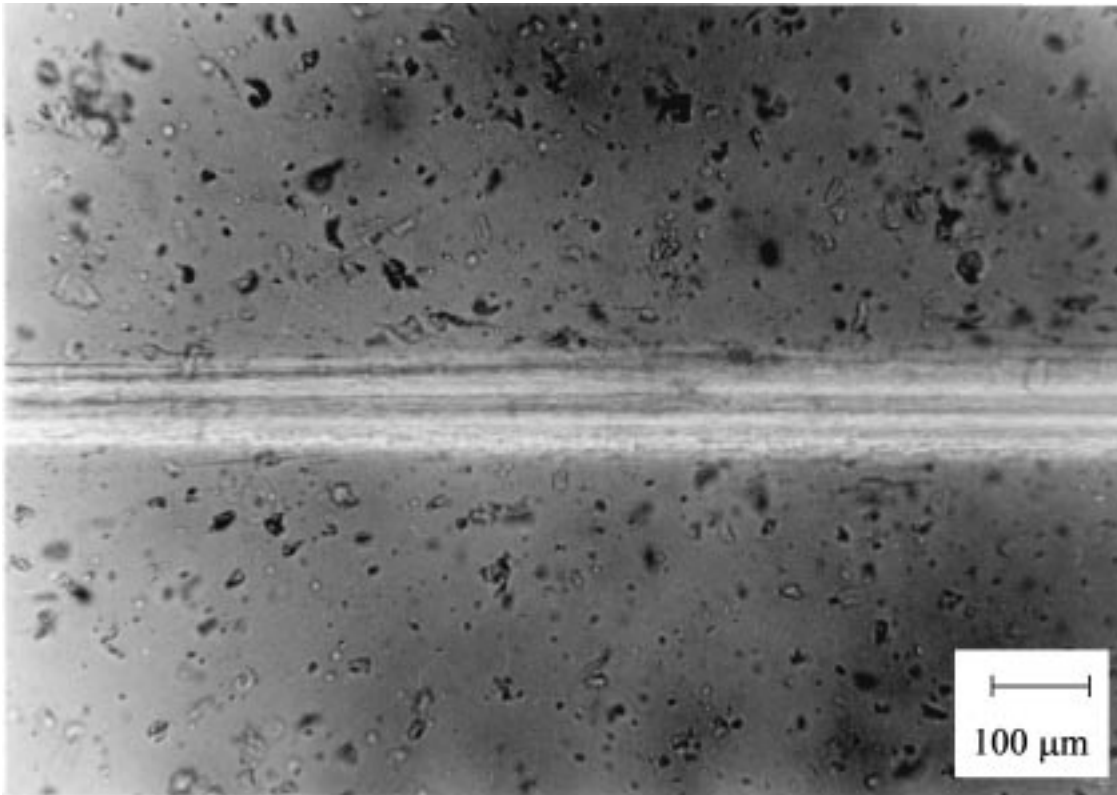
(b)

Figure 4 Crystallization under shear of different polypropylenes after 20 s at 126°C: (a) L1 (RE-PP), (b) L7 (CR-PP), (c) L0 (RE-PP), (d) B-L0/L5-50/50, (e) L5 (RE-PP). (Continued)

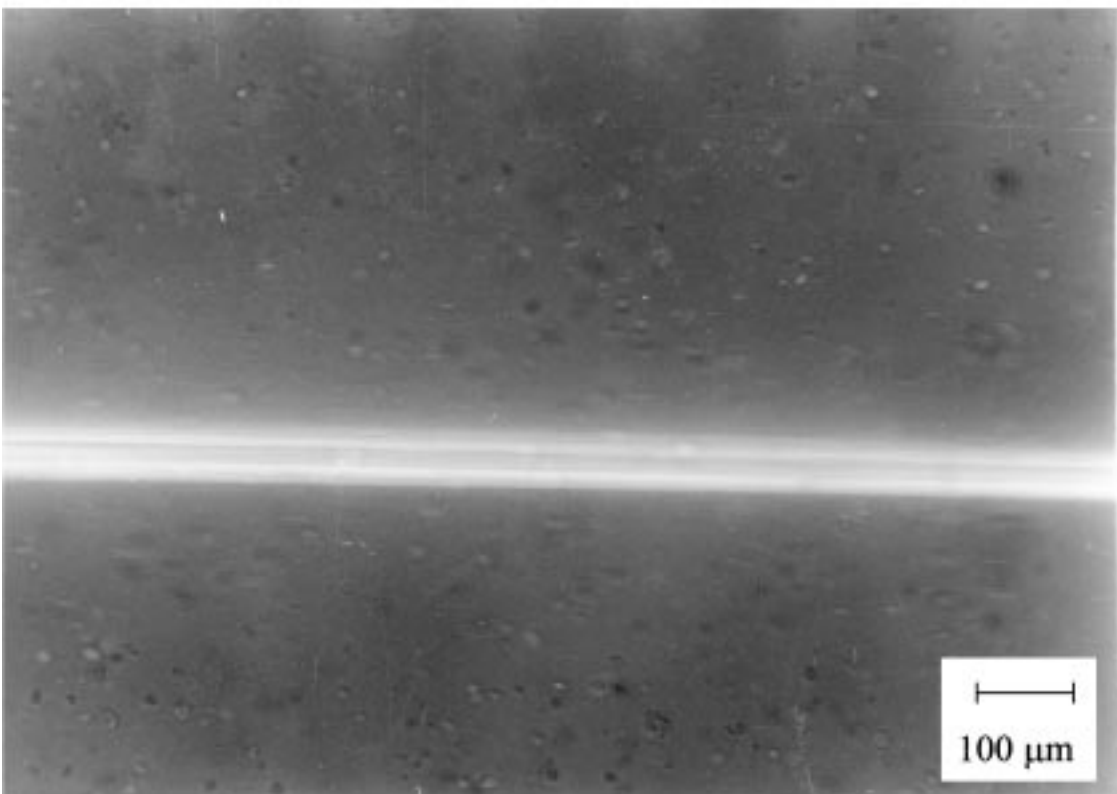
L0 to L6 (Tables I and IV). The same trend is observed for the peroxidized polymers (Tables II and IV), for which the growth-rate values are close to those of the previous polymers, for equivalent molecular weights. As has been shown under static condition, the peroxide degradation seems to have a negligible influence on the growth-rate under shear flow. For the blends,

the growth-rate increases with the proportion of the polymer L0, i.e., with the molecular weights, following the same trend as the other series of polypropylene (Tables III and IV).

From these experiments, an increase of the growth-rate under shear is observed with an increase of the molecular weights.

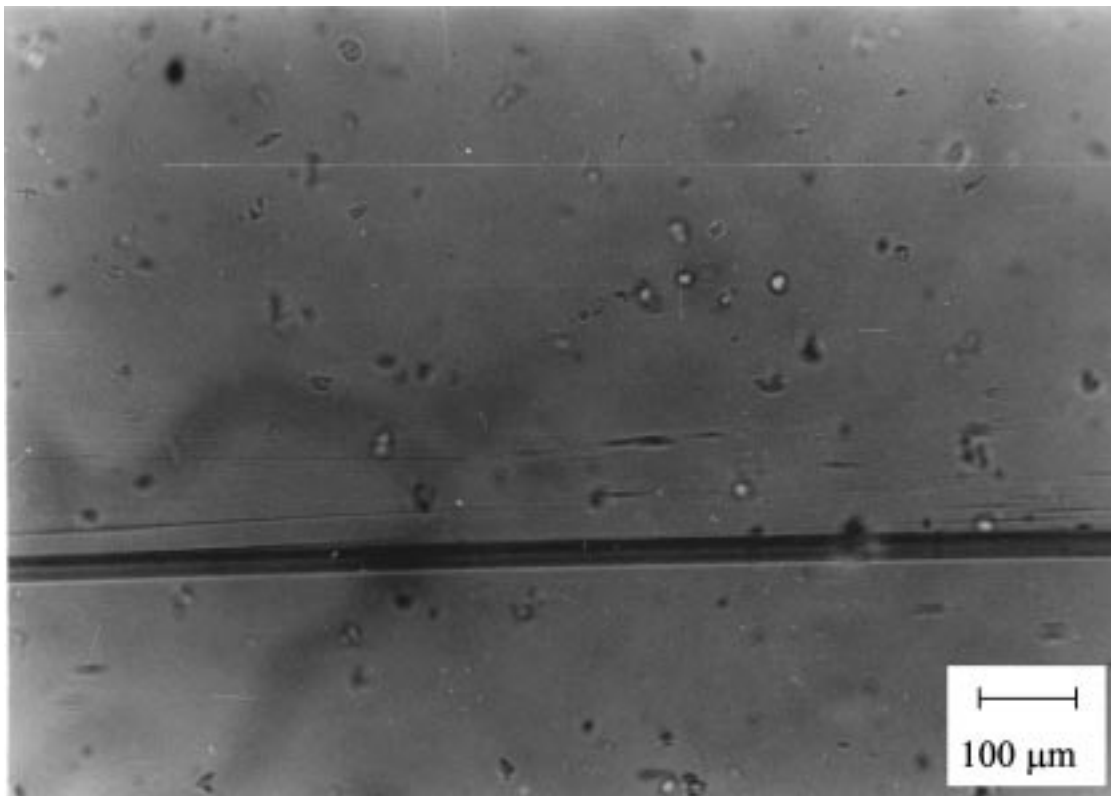


(c)



(d)

Figure 4 (Continued)



(c)

Figure 4 (Continued).

#### 4. Discussion: Influence of the molecular structure

Under static condition (Fig. 5), the growth-rate seems to be independent of the molecular weight, in the range  $109\,000 \leq \bar{M}_w \leq 374\,000$  g/mol. This can be partly explained by the high polymerization degree, i.e., the high molecular weight of these polymers. In fact, during the growth mechanism, at the most 100 monomers are involved in the deposit of a crystalline segment at the growth front. Only a small portion of chain is involved in the deposit of each sequence. The amount of 100 monomer units is negligible in comparison with the high degree of polymerization  $\overline{DP}_w$ ,  $2\,600 \leq \overline{DP}_w \leq 9\,000$ . This fact could be related to the works of Parrini and Corrieri [34], Avella *et al.* [35], Gahleitner *et al.* [36] and Eder *et al.* [37], where the

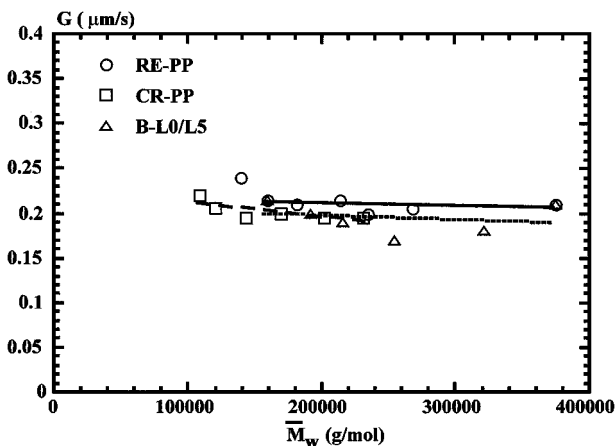


Figure 5 Growth-rate  $G_{\text{static}}$  under static condition versus  $\bar{M}_w$ .

influence of the molecular weight is not clearly established. Gahleitner *et al.* [36] and Eder *et al.* [37] speak about a critical mass, above which the growth-rate under static condition is not affected by the molecular weight. However, Parrini and Corrieri [34] and Avella *et al.* [35] have observed a slight decrease of the growth-rate for a high molecular weight or narrow molecular weight distribution polypropylene. In the present work, in the range  $109\,000 \leq \bar{M}_w \leq 374\,000$  g/mol, no significant dependence of the growth-rate  $G$  on the molecular weight is observed. Furthermore, the very slight decrease of  $G$  with an increase of the polydispersity is in contradiction with the results previously reported. The low dependence of the static growth-rate on the molecular weight is, therefore, not surprising. In addition, all the present polypropylenes are characterized by the same isotactic index around 95%. As the polymers are obtained by the same catalytic system, the measured stereoregularity is almost the same for blends and is not significantly modified by peroxidic degradation within the accuracy of the measurements. Martuscelli *et al.* [38] and Paukkeri and Lehtinen [39] have demonstrated that the global crystallization kinetics was controlled by the amount and the distribution of the defects along the macromolecular chains. Considering these conclusions, the different polypropylenes studied in the present work should have almost the same growth-rate under static condition, which is actually observed.

The growth mechanism is the same under static condition and under shear ( $\alpha$ -phase with a growth-rate independent of time). Under shear condition, the different polypropylenes can be classified according to the sensitivity of their growth-rate to flow (Table IV). The



growth-rate sensitivity to shear, denoted by  $S$ , is defined as the growth-rate under shear  $G_{\text{shear}}$  divided by the growth-rate of the same polypropylene under static condition  $G_{\text{static}}$ . The molecular structure obviously influences the crystalline growth-rate. A linear dependence of  $\log S$  as a function of molecular weight is observed (Figs 6–8). An excellent correlation is found for the average molecular weight  $\bar{M}_w$  (Fig. 6). The correlation is worse for the average molecular weight  $\bar{M}_z$  (Fig. 7) and especially for  $\bar{M}_n$  (Fig. 8). It appears surprising that the correlation is better with  $\bar{M}_w$  than with  $\bar{M}_z$ ,

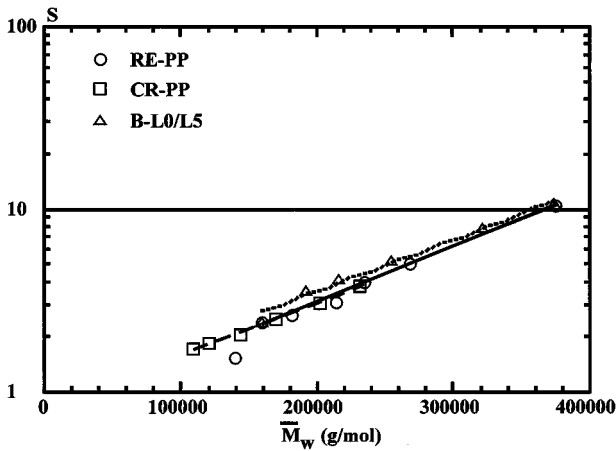


Figure 6 Flow sensitivity of the growth-rate  $S$  versus  $\bar{M}_w$ .

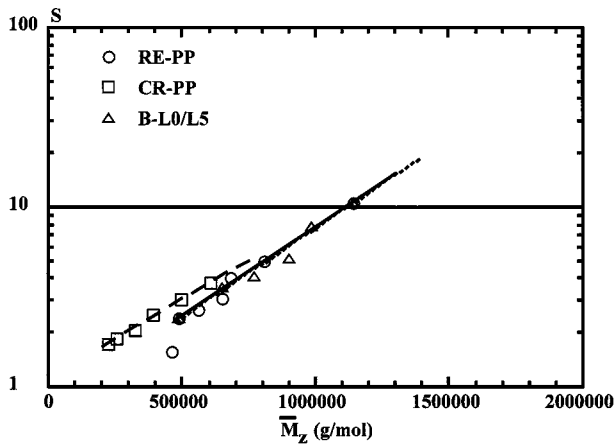


Figure 7 Flow sensitivity of the growth-rate  $S$  versus  $\bar{M}_z$ .

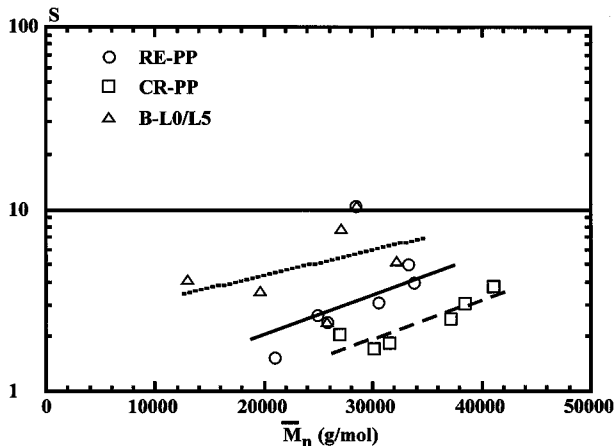


Figure 8 Flow sensitivity of the growth-rate  $S$  versus  $\bar{M}_n$ .

when the high molecular weights are considered to be more efficient on the orientation of polymer chains and the subsequent crystallization under flow. Indeed, Haas and Maxwell [1], Lagasse and Maxwell [5], Liedauer *et al.* [11, 12] and Jay *et al.* [17, 18] underline in their works the influence of the highest molecular weights on the extension of macromolecular chains under flow, which leads to an enhancement of the overall crystallization kinetics. Further investigations based on rheological parameters could help in the understanding of these observations.

Considering the sensitivity  $S$  versus  $\bar{M}_w$  curve for the RE-PP family (Fig. 6), the polymer L6, with the lowest molecular weight, is away from the trend. It is certainly due to the measurement precision, because of the low sensitivity to shear of this polymer. Regarding the other polypropylenes of the RE-PP family, the correlation is excellent. The curves of the growth-rate  $G$  and sensitivity  $S$  versus  $\bar{M}_w$  can surprisingly be approximated by exponential functions, with correlation coefficients  $\sigma$  close to 1, as shown in the Equations 5 and 6. If the polymer L6 is not considered, the expressions are as follows ( $G$  in  $\mu\text{m/s}$ ):

$$G_{\text{shear}} = 0.159 \exp(6.97 \times 10^{-6} \bar{M}_w) \quad (\sigma = 0.998) \quad (5)$$

$$S = 0.745 \exp(7.05 \times 10^{-6} \bar{M}_w) \quad (\sigma = 0.997) \quad (6)$$

The same trend is observed for the series of peroxidized polypropylene CR-PP. The  $G$  or  $S$  versus  $\bar{M}_w$  curves can be approximated by exponential functions, where the slopes are slightly smaller than those of the RE-PP:  $5.76 \times 10^{-6}$  instead of  $6.97 \times 10^{-6}$  mol/g for  $G$  and  $6.4 \times 10^{-6}$  instead of  $7.05 \times 10^{-6}$  mol/g for the sensitivity  $S$ . This leads to a variation of 20% and 10%, respectively. The correlation is as good as for the precedent series RE-PP. For the CR-PP family, the expressions are as follows ( $G$  in  $\mu\text{m/s}$ ):

$$G_{\text{shear}} = 0.186 \exp(5.76 \times 10^{-6} \bar{M}_w) \quad (\sigma = 0.985) \quad (7)$$

$$S = 0.840 \exp(6.40 \times 10^{-6} \bar{M}_w) \quad (\sigma = 0.998) \quad (8)$$

The peroxidic degradation has not really modified the crystallization behavior of the polypropylene under shear, though the molecular weight distribution is lower.

Polymer blending is one way to increase this molecular weight distribution in the same range of molecular weight. The series of blends follows the same trend as the previous ones (Fig. 6). The  $G$  or  $S$  versus  $\bar{M}_w$  curves can be also fitted by exponential functions, with a correlation as good as in the other series. The slopes are very close to those of the peroxidized polypropylenes:  $6.32 \times 10^{-6}$  instead of  $5.76 \times 10^{-6}$  mol/g for  $G$  and  $6.55 \times 10^{-6}$  instead of  $6.4 \times 10^{-6}$  mol/g for the

sensitivity  $S$ . This leads to a variation of 10% and 3%, respectively. The respective equations are ( $G$  in  $\mu\text{m/s}$ ):

$$G_{\text{shear}} = 0.194 \exp(6.32 \times 10^{-6} \bar{M}_w) \quad (\sigma = 0.985) \quad (9)$$

$$S = 0.948 \exp(6.55 \times 10^{-6} \bar{M}_w) \quad (\sigma = 0.993) \quad (10)$$

Only the blends could be distinguished from the other series, as is shown in Fig. 6. A slight influence of the molecular weight distribution is observed. Considering in Fig. 6 the blend 36/64, we can observe, for the same average molecular weight  $\bar{M}_w = 215\,000$  g/mol as polymer L3, a slightly higher sensitivity for a wider molecular weight distribution. This effect is certainly due to the higher proportion of long chains resulting from a wider distribution. Nevertheless, if we consider, in Figs 9 and 10, the evolution of  $S$  versus the two molecular weight distributions  $\bar{M}_w/\bar{M}_n$  and  $\bar{M}_z/\bar{M}_w$ , only a slight trend is observed. The correlation is not so obvious as for  $\bar{M}_w$ . It may be the result of a too narrow molecular polydispersity, especially for  $\bar{M}_z/\bar{M}_w$ , which does not allow us to conclude definitely about the influence of the polydispersity on the growth-rate under shear (Fig. 10). Another reason could be directly related to the homogeneity of the blends. If the blends

are not homogeneous, the longest macromolecules will crystallize easily under shear and then induce a higher sensitivity to shear of the growth, though the average molecular weights are close to those of a “reactor grade” polypropylene. So, the molecular weight distribution would have a second order effect on crystallization under shear flow, compared with the molecular weight  $\bar{M}_w$ .

A master curve can be drawn for all the investigated polymers, except for the polymer L6. Its expression is obtained with an excellent correlation coefficient  $\sigma$  of 0.99 ( $G$  in  $\mu\text{m/s}$ ):

$$G_{\text{shear}} = 0.163 \exp(6.83 \times 10^{-6} \bar{M}_w) \quad (11)$$

$$S = 0.789 \exp(6.93 \times 10^{-6} \bar{M}_w) \quad (12)$$

The extrapolation of the  $S$  versus  $\bar{M}_w$  curve to the point with a sensitivity of 1 gives a molecular weight of 30 000 g/mol. This point corresponds to a mass, below which shear would not have any influence on the growth-rate. It seems related to the critical molecular weight, i.e., the mass between entanglements. This  $\bar{M}_w$  critical value of 30 000 g/mol corresponds to a  $\bar{M}_n$  value between 3 500 g/mol and 8 500 g/mol, for an average  $\bar{M}_w/\bar{M}_n$  dispersity between 3.5 and 8.5. This  $\bar{M}_n$  range is in agreement with the value of the critical mass between entanglements for polypropylene, which is about 7 000 g/mol according to the literature [40]. This threshold was already demonstrated by Fritzsche *et al.* [4], Ulrich and Price [7], and Sherwood *et al.* [8]. They observed an induction time saturation for the lowest molecular weights in the case of poly(ethylene oxide). They recognized a value of the critical mass between entanglements of 10 000 g/mol. Below this value, the orientation of the macromolecules becomes too weak to induce crystallization. The relaxation time of a short chain is too low to induce the orientation necessary for crystallization under flow. It is why, in the present work, it is difficult to study the growth-rate enhancement of low molecular weight polypropylene.

In previous works [13, 14, 17–19], the growth-rates of various polypropylenes were obtained using the fiber pull-out device. Especially in the last one [19], the polymers were obtained with different ways of catalysis, which lead to a series of materials with various molecular structures. Their growth-rates, as measured under static condition, were different according principally to the isotacticity index and more generally to the defects along the macromolecular chains. In the present work, it is now possible to conclude that the molecular weight does not act on the growth-rate under static condition, when the isotactic content is constant. The chemical structure seems to have a great influence mainly on the growth-rate under static condition. Under shear conditions, the growth-rate of these polymers increases. The growth-rate measured under shear condition takes into account both the shear flow effect and the deposit mechanism during crystallization. The latter should be directly related to that under static crystallization, since the growth mechanisms are the same and depend on the chemical structure (configuration, defects) of the polypropylene. Therefore, the sensitivity

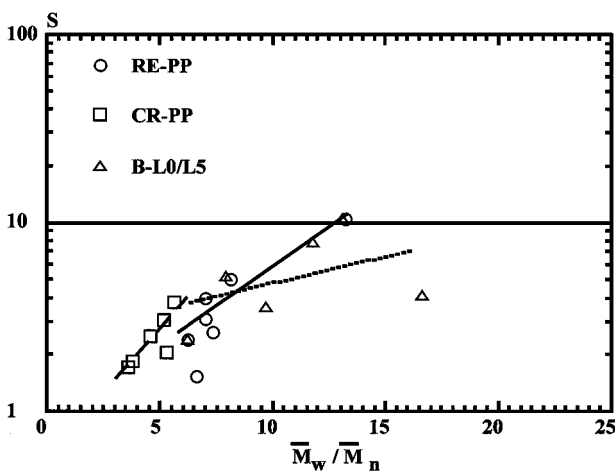


Figure 9 Flow sensitivity of the growth-rate  $S$  versus  $\bar{M}_w/\bar{M}_n$ .

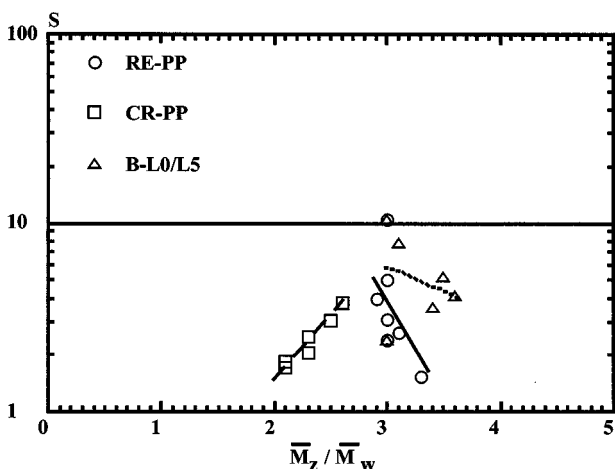


Figure 10 Flow sensitivity of the growth-rate  $S$  versus  $\bar{M}_z/\bar{M}_w$ .

is more representative of the flow effect on the growth-rate. In this previous work [19], we have observed the preponderant influence of the average molecular weight  $\bar{M}_z$  and the tacticity, but these parameters were coupled and a clear conclusion was uncertain.

In the present study, the investigated polypropylenes are obtained by the same catalytic system. They have the same molecular structure, in terms of nature and distribution of the defects along the macromolecular chains. This is partly proved by the similar values of the growth-rate measured under static conditions. In order to compare the behavior of these polypropylenes, the growth-rate under shear  $G_{\text{shear}}$  could only be used, due to the same growth-rate under static conditions. As another consequence, there is almost no difference between the correlation coefficients and the slope values of the expressions of  $G_{\text{shear}}$  and  $S$  versus  $\bar{M}_w$  (Equations 5–10). The variations do not exceed a few percents.

## 5. Conclusions

In previous works dealing with the crystallization of polypropylene under shear, using a fiber pull-out device, it has been established that a shear flow significantly increases the growth-rate of polypropylene. In the present study, it is then possible, for polypropylenes with the same isotacticity, to reveal molecular differences, which were almost indiscernible under static condition. Shear-induced crystallization is an efficient tool to study molecular structure differences in polypropylene. Indeed, these polypropylenes have the same configuration in terms of nature, amount and distribution of defects along the macromolecular chains. The selection of the present materials allows us to observe a high influence of the molecular weight, and more precisely of the average molecular weight  $\bar{M}_w$ , on the enhancement of the growth mechanism due to the presence of a shear flow. For example, in the case of the polymer L0, the growth-rate is multiplied by a factor of 10. An extrapolation of the sensitivity  $S$  versus  $\bar{M}_w$  curve to the point of sensitivity 1 leads to a critical mass, below which the shear would have no influence on the growth-rate. This critical mass can be related to the mass between entanglements. The molecular weight distribution seems to have a secondary order effect under shear flow. The comparison of these new results with previous ones [19] reveals the particular care which must be taken when comparing polymers from different origins.

In order to study the influence of the presence of defects along the macromolecular chains on the growth mechanism, we will consider in further work new series of polypropylenes, having similar molecular weights, but different amounts of defects related to the presence of comonomers or the modification of the catalytic system. In addition, we will consider the rheological behavior of the molten polypropylene in the fiber pull-out device to have a better correlation with the molecular structure.

## References

1. T. W. HAAS and B. MAXWELL, *Polym. Eng. Sci.* **9** (1969) 225.

2. K. KOBAYASHI and T. NAGASAWA, *J. Macromol. Sci. Phys.* **B4**(2) (1970) 331.
3. A. WERETA and C. GOGOS, *Polym. Eng. Sci.* **11** (1971) 19.
4. A. K. FRITZSCHE, F. P. PRICE and R. D. ULRICH, *ibid.* **16** (1976) 182.
5. R. R. LAGASSE and B. MAXWELL, *ibid.* **16** (1976) 189.
6. V. TAN and C. GOGOS, *ibid.* **16** (1976) 512.
7. R. D. ULRICH and F. P. PRICE, *J. Appl. Polym. Sci.* **20** (1976) 1077.
8. C. H. SHERWOOD, F. P. PRICE and R. S. STEIN, *J. Polym. Sci. Polym. Symp.* **63** (1978) 77.
9. M. D. WOLKOWICZ, *ibid.* **63** (1978) 365.
10. G. EDER and H. JANESCHITZ-KRIEGL, *Colloid Polym. Sci.* **266** (1988) 1087.
11. S. LIEDAUER, G. EDER, H. JANESCHITZ-KRIEGL, P. JERSCHOW, W. GEMAYER and E. INGOLIC, *Intern. Polym. Process.* **8** (1993) 236.
12. S. LIEDAUER, G. EDER and H. JANESCHITZ-KRIEGL, *ibid.* **10** (1995) 243.
13. C. TRIBOUT, Thesis, Ecole des Mines de Paris (Sophia Antipolis), 1993.
14. C. TRIBOUT, B. MONASSE and J.-M. HAUDIN, *Colloid Polym. Sci.* **274** (1996) 197.
15. B. MONASSE, *J. Mater. Sci.* **30** (1995) 5002.
16. *idem.*, *ibid.* **27** (1992) 6047.
17. F. JAY, Thesis, Ecole des Mines de Paris (Sophia Antipolis), 1996.
18. F. JAY, J.-M. HAUDIN and B. MONASSE, *J. Mater. Sci.* **34** (1999) 2089.
19. C. DUPLAY, B. MONASSE, J.-M. HAUDIN and J.-L. COSTA, *Polym. Intern.* **48** (1999) 320.
20. E. DEVAUX and B. CHABERT, *Polym. Comm.* **32** (1991) 464.
21. J. L. THOMASON and A. A. VAN ROOYEN, *J. Mater. Sci.* **27** (1992) 897.
22. J. VARGA and J. KARGER-KOCSIS, *J. Polym. Sci. Polym. Phys. Ed.* **34** (1996) 657.
23. J. VARGA, in "Polypropylene: Structure, Blends and Composites, Vol. 1," edited by J. Karger-Kocsis (Chapman and Hall, London, 1995) p. 56.
24. G. NATTA and P. CORRADINI, *Nuovo Cimento Suppl.* **15** (1960) 40.
25. S. Z. D. CHENG, J. J. JANIMAK and J. RODRIGUEZ, in "Polypropylene: Structure, Blends and Composites, Vol. 1," edited by J. Karger-Kocsis (Chapman and Hall, London, 1995) p. 31.
26. F. J. PADDEN JR and H. D. KEITH, *J. Appl. Phys.* **30** (1959) 1479.
27. A. TURNER-JONES, J. M. AIZLEWOOD and D. R. BECKETT, *Makromol. Chem.* **75** (1964) 137.
28. D. R. MORROW and B. A. NEWMAN, *J. Appl. Phys.* **39** (1968) 4944.
29. P. CORRADINI, V. PETRACCONE and B. PIROZZI, *Eur. Polym. J.* **19** (1983) 299.
30. C. TZOGANAKIS, J. VLACHOPOULOS and A. E. HAMIELEC, *Polym. Plastic Tech. Eng.* **28** (1989) 319.
31. *idem.*, *Polym. Eng. Sci.* **29** (1989) 390.
32. G. LUX, in Speciality Plastics Conference, 1988, p. 139.
33. D. CAMPBELL and M. M. QAYYUM, *J. Polym. Sci. Polym. Phys. Ed.* **18** (1980) 83.
34. P. PARRINI and G. CORRIERI, *Makromol. Chem.* **62** (1963) 87.
35. M. AVELLA, R. DELL'ERBA, L. D'ORAZIO and E. MARTUSCELLI, *Polym. Networks Blends* **5** (1995) 47.
36. M. GAHLEITNER, K. BERNREITNER and W. NEISSEL, *Polym. Testing* **14** (1995) 173.
37. G. EDER, H. JANESCHITZ-KRIEGL and S. LIEDAUER, *Progr. Polym. Sci.* **15** (1990) 629.
38. E. MARTUSCELLI, C. SILVESTRE and G. ABATE, *Polymer* **23** (1982) 229.
39. R. PAUKKERI and A. LEHTINEN, *ibid.* **34** (1993) 4075.
40. R. P. WOOL, in "Polypropylene: Structure, Blends and Composites, Vol. 1," edited by J. Karger-Kocsis (Chapman and Hall, London, 1995) p. 227.

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