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CRYSTALLIZATION BEHAVIOR AND STRUCTURAL CHARACTERIZATION OF POLYPROPYLENE BLENDS.

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Two Polypropylene homopolymers, with different molecular weights (MW) and molecular weight distributions (MWD), were blended at different compositions in order to study the crystallization phenomenon. The kinetic data obtained by isothermal crystallization show that the crystallization rate increases with the amount of HMW PP, up to a critical value of 10%, above which the kinetic parameters reach a plateau. The spherulitic texture of samples, observed by optical microscopy, shows several differences in morphology, number and size of spherulites.
In order to check zonal crystallographical polymorphism (α, β, γ in iso-PP) we used a microarea X-ray diffraction technique. In spite of strong morphological differences, only crystallographical α form is present. We also observe a higher level of orientation at the border than at the center of spherulites.

PP, blend, crystallization kinetic, DSC, XRD

1. INTRODUCTION

One of the most common Polypropylene application is in bioriented film production (BOPP) to obtain a very thin, transparent, highly glossy product with good physical-mechanical properties.
In the last ten years the state of the art developed a PP homopolymeric matrix with a very large molecular weight distribution in order to optimize the BOPP production. This material can be obtained by direct mixing of two polypropylene homopolymers with different molecular weights.
This work is a preliminary investigation into the thermal behavior and the structural characteristics of these blends, in order to study how high and low molecular weight polymers affect the properties of the final product. This is only a first qualitative approach to the problem, that will be closely examined in another work.
The final aim is to understand the mechanism of crystallization in order to control the characteristics of these materials that depend on crystallinity and on crystal morphology.

2. EXPERIMENTAL METHODS AND MATERIALS

Two Polypropylene homopolymers with intrinsic viscosity 6.80 (sample A; HMW) and 0.95 (sample B; LMW) dl/g and isotactic index 98.6 and 98.8% respectively were synthesized in liquid monomer with high yield Himont catalyst system.
The PP blends were prepared via dissolution of the required amounts of the A and B fractions in xylene at 130°C under nitrogen atmosphere, in the presence of 100 ppm of Irganox 1010 and Irgafos 168 as thermal stabilizers. The samples were precipitated by adding cool methanol (rougly using a volume ratio of 5:1, methanol:xylene) until complete recovery of the polymer was achieved. The precipitated blends were then washed with acetone, filtered and dried; the relative molecular characteristics are collected in Table I.

Table I. Molecular characterization of HMW/LMW PP blends.

Sample	%HMW wt	$[\eta]$* dl/g	$\bar{M}w$# g/mol	$\bar{M}w/\bar{M}n$
A	100	6.80	1658000	7.3
B	0	0.95	203000	6.6
Blend 1	5	1.20	252000	6.9
2	10	1.26	338000	10.1
3	20	1.88	525000	14.5
4	30	2.22	614000	13.1

*Obtained in tetrahydronaphtalene at 135°C.
#Obtained via GPC measurement.

Thermal analyses were performed by differential scanning calorimetry and optical microscopy, using the same thermal treatment.
The DSC experiments were carried out in a Perkin-Elmer DSC-7 in nitrogen flow. The temperatures and heat flux were calibrated with high purity standards.
The hot stage microscopy work was performed by an optical polarizing Orthoplan microscope, produced by Leitz and equipped with a Mettler FP52 heating device and a Mettler FP5 temperature programmer.
The crystallization process has been studied after melting at 200°C for 5 min and quenching at 80°C/min to the chosen temperature Tc. After crystallization for a time tc long enough to complete the crystallization process, the specimen was heated at 10°C/min to 200°C. The Tc range

(118-135°C) avoids too slow (Tc>135°C) and fast (Tc<118°C) crystallizations.
X-ray diffraction measurements were carried out by means of a Chesley microbeam X-ray camera (Cu Kα =1.54 Å) and a X-ray generator produced by Italstructure (Riva del Garda, Italy).

3. RESULTS and ANALYSES

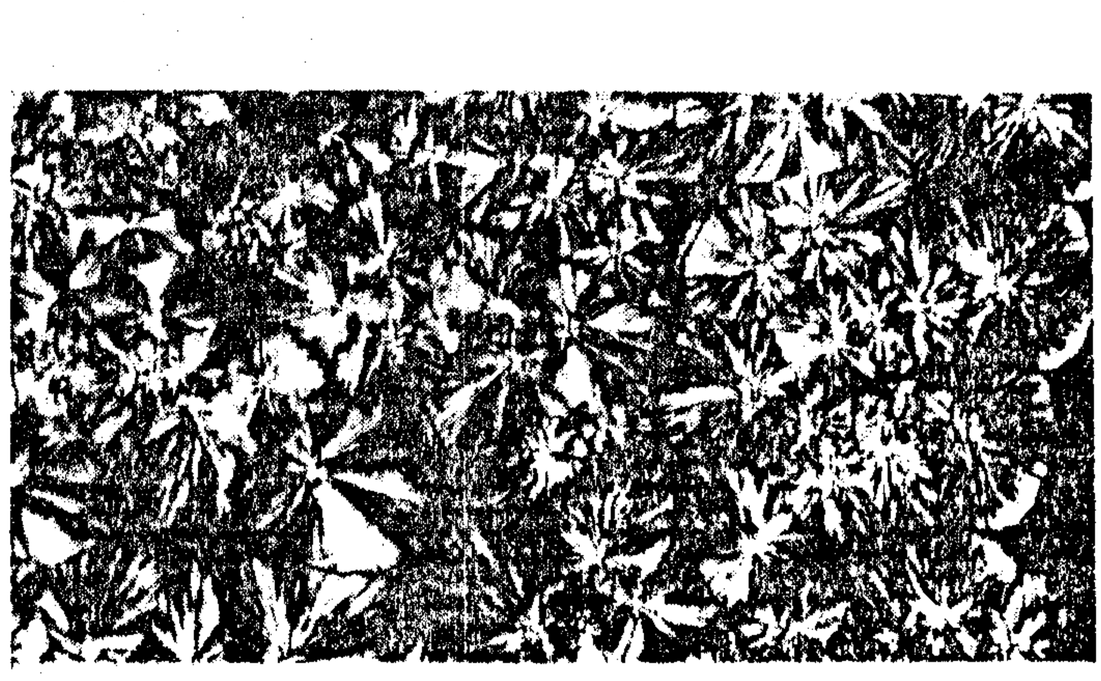
In order to evaluate the effect of high molecular weight on the crystallization of low molecular weight Polypropylene, a study was carried out by using isothermal crystallization.

Homopolymers.
Table II reports the kinetic data related to the overall process of crystallization of the homopolymers. The crystallization half-time, i.e. the time to reach 50% of total crystallinity, is a function of Tc.

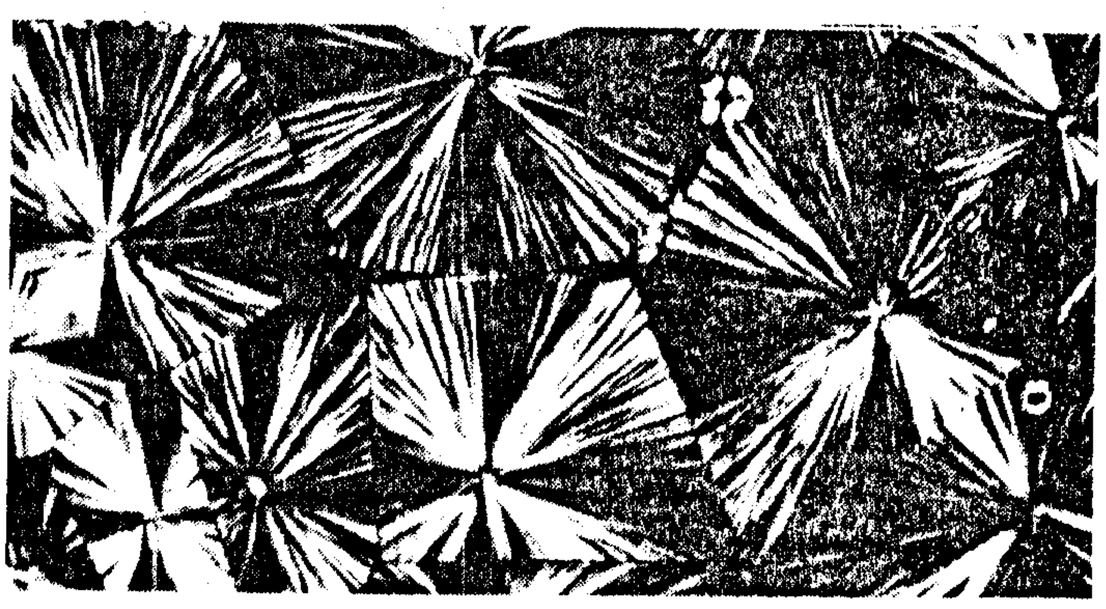
Table II. Isothermal crystallization parameters for PP samples A and B.

	Sample A		Sample B	
Tc °C	$t_{1/2}$ min	ΔHm J/g	$t_{1/2}$ min	ΔHm J/g
118	1.2	91	0.7	109
119	1.6	95	0.9	110
120	1.7	96	1.0	122
121	2.0	90	1.2	111
122	2.5	88	1.6	113
123	3.1	94	1.8	116
124	3.8	89	2.2	113
125	4.3	82	2.7	109
126	5.1	93	3.6	117
127	6.6	93	4.6	118
128	7.9	96	5.6	117
129	10.3	94	6.8	120
130	13.5	101	8.3	118
131	15.0	97	11.3	121
132	18.3	94	14.0	122
133	22.6	98	16.4	124
135	28.1	97	23.5	126

It can be observed that the LMW sample crystallizes faster than HMW at all temperatures Tc. The crystallization experiments in DSC are characterized by a secondary crystallization phenomenon, that is more important for sample A.
The overall degree of crystallization obtained in the isothermal crystallization is lower for the high molecular weight sample, as we can see from enthalpies of melting reported in Table II. We have to point out that the melting process occurs with a double endothermic peak, which can be related to a melting-recrystallization phenomenon (1).
However, in general ΔHm varies little with crystallization temperature, even if a small increase at high Tc is noticeable. This is consistent with the observation that annealing at higher temperature usually increases the degree of crystallinity. In any way, the differences between the ΔHm of samples A and B remain nearly constant at each Tc.
All these experimental results suggest that the crystallization rates are governed by kinetic rather than thermodynamic effects (2): the most important parameter for the crystallization process is the diffusion rate in the melt, which is higher for smaller chains, i.e. for low molecular weights.
Note, however, that the supercooling ΔT = Tm°-Tc varies considerably with the samples. The equilibrium melting points Tm° were evaluated according to Hoffman and Weeks procedure (3): the extrapolations of melting versus crystallization temperatures (Tm vs Tc) give values of 200 and 185°C for samples A and B respectively.
Morphological observation was carried out in optical microscopy on samples which were isothermally crystallized. In Figure 1, for example, samples A and B crystallized at 130°C are shown. It can be observed that both samples present a spherulitic texture, but there are some differences. The most important is the nuclei number, from which the spherulitic size originates: large for LWM and small for HMW.
Besides, the spherulitic morphology is more regular for the LMW sample. Long chains do not reach a high perfection in the fold structure: intercrystalline links and chain entanglements are abundant. Those affect molecular motion in the polymer melt and increase the degree of disorder in the intercrystalline region (4).



SAMPLE A



SAMPLE B

Figure 1. Optical micrographs of samples A and B isothermally crystallized at 130°C (100x).

Blends.
The effect of blending of the two homopolymers on the crystallization process is shown in Figure 2, where some kinetic data are reported. All results are shown in Table III.

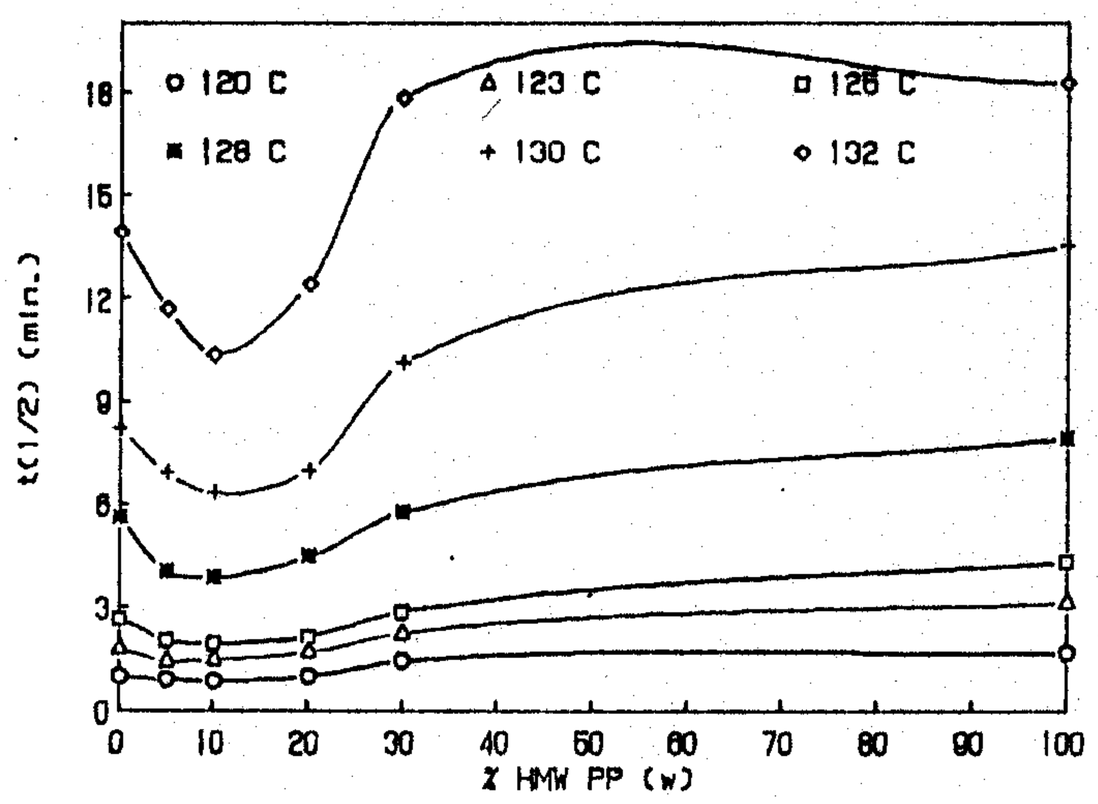


Figure 2. Semi-crystallization time versus blend composition for crystallization experiments at different Tc, as indicated in figure.

Table III. Isothermal crystallization parameters for blends 1, 2, 3, 4.

	blend 1		2		3		4	
Tc °C	$t_{1/2}$ min	ΔHm J/g	$t_{1/2}$	ΔHm	$t_{1/2}$	ΔHm	$t_{1/2}$	ΔHm
118	0.6	107	0.7	111	0.8	103	1.0	100
119	0.7	109	0.8	106	0.9	107	1.0	103
120	0.9	102	0.9	113	1.0	104	1.4	111
121	1.1	110	1.0	107	1.3	108	1.5	107
122	1.4	113	1.3	116	1.6	110	2.0	107
123	1.4	114	1.5	114	1.7	115	2.2	109
124	1.8	112	1.7	110	2.0	108	2.8	106
125	2.0	114	2.0	107	2.2	115	2.9	107
126	2.7	115	2.7	112	3.2	110	3.7	107
127	3.5	114	3.5	113	4.0	111	5.2	107
128	4.0	118	3.8	118	4.4	113	5.8	111
129	5.3	119	5.1	116	5.8	114	8.0	109
130	6.9	122	6.4	122	7.0	116	10.1	115
131	8.7	117	8.4	117	10.2	115	13.2	112
132	11.7	115	10.4	121	12.5	122	17.9	113
133	13.1	122	13.0	119	16.3	116	20.0	113
135	25.0	124	21.2	118	26.1	120	28.4	116

It can be observed that small amounts of sample A in sample B matrix cause an increase in the crystallization rate: this effect is more important when the HMW percentage is 10%, as shown in Figure 2.
This behavior is more visible at low supercooling: when ΔT increases, the crystallization rates become very similar for every sample, independently of its composition. This could be due to the incomplete destruction of the original nuclei before the crystallization experiments. In fact, it is worth speculating that 5 minutes at 200°C may be ineffective melting condition. The radial growth of the spherulites should not be affected by this incomplete melting (5), whereas the nucleation process could be.
The overall degree of crystallization, evaluated by enthalpies of melting, is very similar between sample B and blends 1, 2 and 3. Only blend 4 shows a decrease in ΔHm: this behavior suggests that high percentage of HMW (30%) causes a slower and more difficult crystallization process.
In general, the rate constant of crystallization is written as (6):

$$k = k_0 \exp(-U^*/R(Tc-T_\infty)) \exp(-Kg/Tc\,\Delta Tf)$$

where K_0 is a constant, U^* is the activation energy for segmental transport at the interface, T_∞=Tg-30 is the temperature below which molecules become immobile; f is a correction term introduced to account for the temperature dependence of the heat of crystallization and is equal to $2Tc/(Tm^0+Tc)$.
The first exponential term refers to the local mobility of the system; the second refers to the nucleation process, which depends on the degree of supercooling.
At low ΔT the second exponential term is more important, but in our case also the first is very significant, because it refers to the diffusional aspect of the system.
The molecular weight dependence of a diffusion process in a binary mixture has been a controversial issue in recent years. Theoretically two limiting cases have been calculated: the "slow mode" model, in which the slow component controls the mobility of the system, and the "fast mode" model, in which the mutual diffusion coefficient is controlled by the mobility of the faster moving (i.e. shorter) polymer chains.
Recently Feng at al. (7) have shown, by experimental measurements, that the blend mobility can be represented by the "fast mode" model when the polymeric matrix has low molecular weight. Therefore, we can reasonably assume that this is our case.
The results show that long chains modify the local mobility of the system and, if they are present until 10%, cause an increment in the overall crystallization kinetic.
The same phenomenon was observed for growth rates in similar blends of PP (between homopolymers at lower MW) and was described as a nucleanting effect of HMW crystalline regions for LMW sample (8).
Unfortunely we do not have any data about growth and nucleating rates, but only about the overall crystallization kinetic: this makes it difficult to assess the influence of the two processes on the total phenomenon.

Other significant information can be obtained by morphological observation on samples crystallized in the hot stage. Samples show an increasing degree of the heterogeneity with increasing the HMW percentage: this is evident in the number of nuclei which can vary in the same specimen. The supermolecular structure that develops depends on the crystallization temperature and blend composition: it is very difficult to classify the spherulite types obtained in the blends, due to the complex crystalline architecture that we can observed also in

isotactic homopolymer (9).
Using microbeam XRD we have checked whether there was some crystallographical polymorphic forms associated to the different morphological views. Only iso-PP α form is present in all microarea examined, for each sample.
Figure 3 shows an example of spherulitic morphology obtained for crystallization at 130°C in blend 3: the sample heterogeneity appears in presence of small and large spherulites as well. XRD analysis shows a random crystallites orientation in the more disordered zone of the sample and at the center of the spherulites; at the border, instead, an a*-axis in uni-orientation along the radius of the spherulite is present (10).

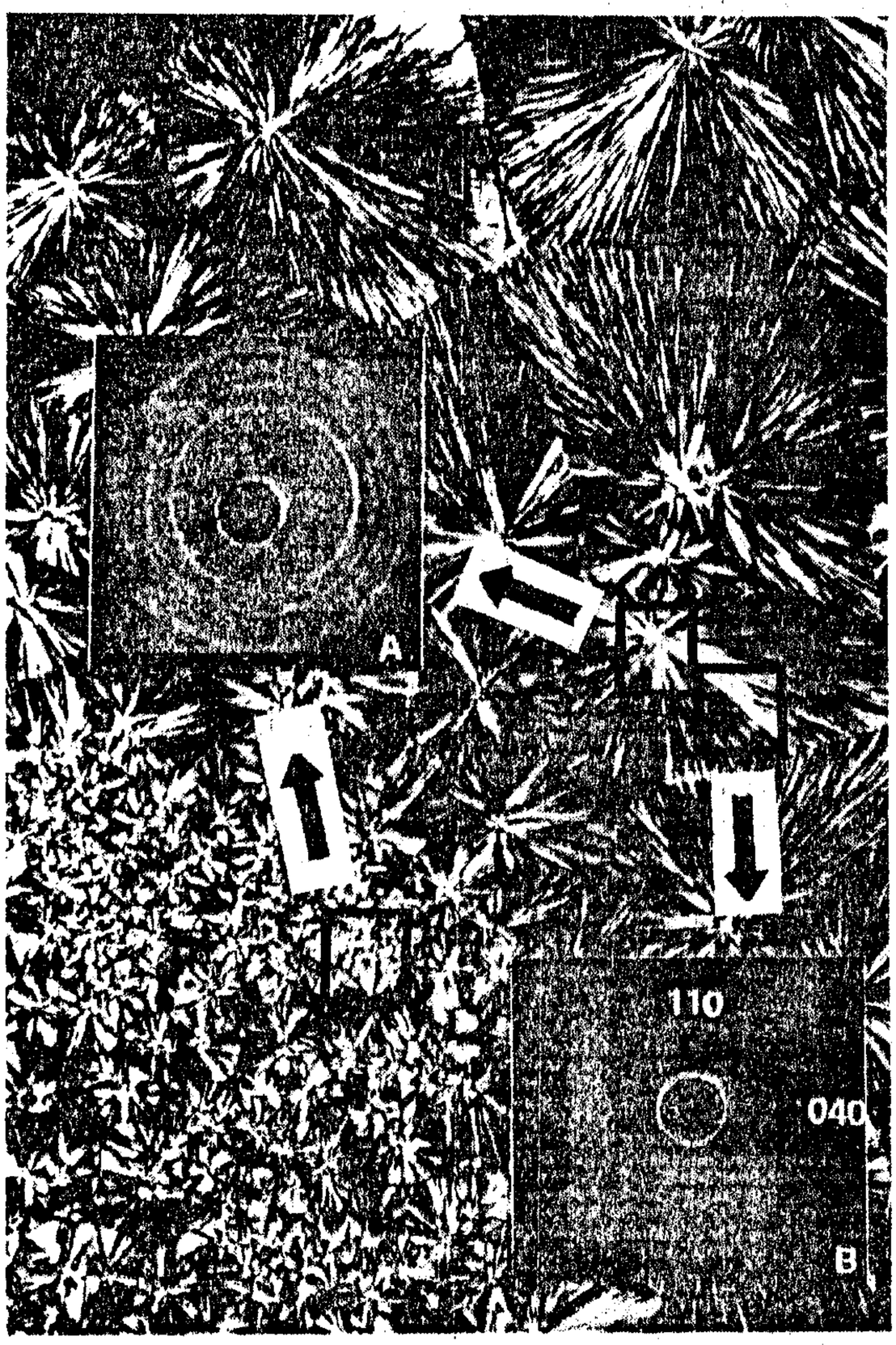


Figure 3. Optical micrograph of blend 3 isothermally crystallized at Tc=130°C (100x). Microarea XRD, reported in figure, refer to: a) small spherulites and central zone of large spherulites; b) border zone of large spherulites.

4. CONCLUSION

Blends of HMW and LMW Polypropylene homopolymers show a complex behavior during the crystallization process. A percentage of HMW up to 10% causes an increase in the overall crystallization kinetic. It is difficult to assess the changes in the numbers of nuclei in the samples because of the heterogeneity of the specimens.
XRD analyses show that no PP polymorphic forms are present: only α form with different degree of orientation is observed.
Certain open problems remain: more in depth sample analysis and data management are required in order to gain a better comprehension of the crystallization mechanism and regimes.

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