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MORPHOLOGY AND CRYSTALLIZATION OF POLY(4-METHYLPENTENE-1) AND ITS BLENDS WITH HYDROGENATED OLIGOCYCLOPENTADIENE

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Key Words: Poly(4-methylpentene-1), Hydrogenated Oligo(cyclopentadiene), Blends, Crystallization, Miscibility, Morphology

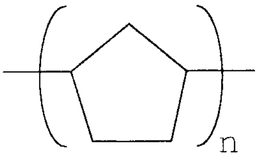
ABSTRACT

The paper discusses the morphology, melting behavior, and process of crystallization of poly(4-methylpentene-1) (P4MP1) and its blends with an amorphous oligomer, hydrogenated oligocyclopentadiene (HOCP). The study was performed by using optical and electron microscopy, differential scanning calorimetry and X-ray scattering.

In all ranges of compositions and temperatures investigated, P4MP1 and HOCP components were not miscible. The HOCP formed segregated domains in the P4MP1 matrix. Depending on thermal treatment, different melting behaviors and morphologies were obtained. In particular, varying the crystallization conditions and composition one or two populations of lamellae of different thickness formed. The half-time of crystallization drastically increased following the addition of HOCP. This increase was mainly accounted for by the additional energy required to perform the occlusion of the HOCP domains by the P4MP1 molecules during the crystallization.

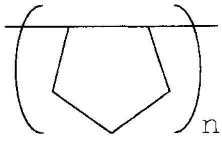
INTRODUCTION

Several years ago, in order to reduce the permeability to oxygen and odors, hydrogenated oligocyclopentadiene (HOCP) was added to isotactic polypropylene (iPP) [1-5]. HOCP is an oligomer with Mw = 630. It can be obtained from 1,3 cyclopentadiene. The commercial HOCP, produced by Esso Chemical, is a mixture of *cis* and *trans* isomers of the following structures:



A

1,4 structure
(cis and trans)



B

1,2 structure
(cis and trans)

Bi-oriented films of iPP/HOCP blends were successfully introduced into packaging. Besides the remarkable commercial side, the iPP/HOCP blends turned out to be a very interesting system from the scientific point of view. In fact, for this system a phase diagram with both lower and upper cloud point curves was found. The knowledge of the phase diagram allowed the attainment of films for packaging applications. The morphology, phase structure, miscibility, crystallization process, and thermal and mechanical properties of bulk materials and films were thoroughly investigated. Subsequently, studies were carried out to analyze the influence of HOCP on the crystallization process, and properties of other semicrystalline polyolefins $(\text{-CH}_2\text{-CHR-})_n$ with different side groups [6-10]. Interesting results were found in the system with high density polyethylene (HDPE), polyolefin containing no side group (R = H). The melt of a HDPE/HOCP system separated into two phases: a HDPE-rich phase and a HOCP-rich phase. At the crystallization temperatures, the HDPE crystallized from both phases.

Recently, in order to complete the study on the influence of the polyolefin side group on the properties of the polyolefin/HOCP blends, isotactic poly(4-methylpentene-1), (P4MP1) was used [11, 12]. Isotactic poly(4-methylpentene-1), is a semicrystalline polyolefin, with a bulky side group, $R = CH_2\text{-}CH(CH_3)_2$. P4MP1 has several interesting properties, [13-15], such as high chemical and thermal stability, and low dielectric constant. P4MP1 is the only semicrystalline polymer in which the density of the amorphous fraction is higher than the density of the crystalline fraction at room temperature . Although semicrystalline, the P4MP1, at room temperature, is transparent because the crystals present a birefringence close to zero. The intrinsically desirable characteristics have led to several studies of the structure and properties of this polymer. Most of these studies have been described in a comprehensive review by Lopez *et al.* [16]. P4MP1 is employed extensively for a number of applications, such as medical and chemical equipment, microwave oven cookware, and food packaging.

In a previous paper, the relationships between the properties and the morphology of P4MP1/HOCP blends, up to the composition 60/40 wt%, were reported [11, 12]. The study pertained only to samples quenched from the melt state. The authors report that the P4MP1 and HOCP are not miscible in the melt state, and that the solidified blends form a three-phase system: the pure HOCP phase, present as very small domains homogeneously distributed in the matrix, and the amorphous and the crystalline phases of P4MP1 forming the matrix. The hypothesis is that the HOCP was not even partially miscible with P4MP1, whereas a partial miscibility was found with iPP and HDPE, derived from the DSC and DMTA results. These indicated the presence of two distinct Tgs, whose values were equal to those of the pure components. The mechanical properties depended on composition, phase struc-ture, amount of crystallinity and physical state of the amorphous phase. The tensile mechanical properties at 20°C were particularly surprising. The films of the 90/10 and 80/20 blends, materials containing small domains of a phase (HOCP) not miscible with the matrix, had, in fact, a tensile behavior similar to that of plain P4MP1. These findings, together with the reduced permeabilityof the films to CO_2, O_2 and N_2 [12], make the P4MP1/HOCP films potentially useful for replacing pure P4MP1 films in those applications where reduced permeability is required.

The aim of this paper is to complete the study of this system. The morphological, kinetic and thermal parameters related to the overall isothermal crystallization process of the P4MP1 samples and its blends with HOCP, and their dependence on temperature, blend composition, and preparation conditions are reported.

EXPERIMENTAL

Material and Preparation of the Blends

The following materials were used: Poly(4-methylpentene-1), (P4MP1), from Scientific Polymer Products and Hydrogenated oligo(cyclopentadiene) (HOCP), Escorez 512 produced by Esso Chemical Co.

The molecular characteristics of the materials are reported in Table 1.

Table 1. Molecular Weights and Glass Transition Temperatures of the Used Polymers

Polymer	M_w	M_n	T_g (°C)
P4MP1	6.0×10^5	6.5×10^4	40
HOCP	630		85

The P4MP1/HOCP blends were obtained by melt mixing the two components in a Brabender-like apparatus at 240°C and 32 rpm, for 10 minutes.

The blends were also obtained by solution casting from n-octane at about 130°C and then dried under vacuum at 100°C.

Thermal Analysis

The overall kinetics of crystallization and the thermal properties of the homopolymers and blend films were analyzed by differential scanning calorimetry (Mettler TA 3000). The isothermal crystallization process was studied using the following procedure: the samples were heated from room temperature to 260°C and kept at this temperature for 10 minutes. Then they were cooled to different crystallization temperatures and the heat evolved during crystallization was recorded as a function of time. The weight fraction, X_t, of the material crystallized at time t was calculated from the ratio of the heat generated at time t and the total heat corresponding to the completion of crystallization. After the completion of crystallization, the samples were cooled to room temperature. Finally, they were heated at a scanning rate of 10°C/min from room temperature to melting. The observed calorimetric T_m was obtained from the maximum of the melting peak.

(Thermogravimetric analysis has shown that the samples do not decompose under the above thermal treatment.)

Optical and Electron Microscopy

The morphology of the blends and the growth rate of P4MP1 spherulites in the blends as a function of crystallization temperature, composition and blend preparation were analyzed by optical and electron microscopy. A Zeiss polarizing microscope, equipped with a hot stage, and a SEM 501 Philips microscope were used. Before the electron microscopy observation, the surfaces were coated with Au-Pd alloy with a SEM coating device (SEM Coating Unit E5150-Polaron Equipment Ltd.).

X-ray Diffraction

Wide-angle X ray scattering measurements were carried out on a Philips (PW 1050 model) powder diffractometer (CuNi-filtered radiation) equipped with a rotating sample holder device. Small-angle X-ray studies were performed with the 10m SAXS camera at the Oak Ridge National Laboratory (USA).

RESULTS AND DISCUSSION

Morphology

Figure 1 shows optical micrographs of pure P4MP1 and P4MP1/HOCP blends in the melt at 260°C. For all blends, the melt is not homogeneous in the range of temperature investigated. In fact, in the melt discrete spherical particles dispersed in the matrix are visible. This result is in agreement with the results of a previous paper [12] and confirms that the two components are not miscible.

Figure 2 shows optical micrographs of samples of P4MP1 and P4MP1/HOCP blends isothermally crystallized at T=220°C. For all samples, birefringent microspherulites can be observed. During the crystallization the microspherulites do not develop completely into mature spherulites, because of the great number of nuclei. At T_c many nuclei become stable and start to grow into micro-spherulites that are unable to further develop into mature spherulites before termination of their growth due to impingement.

It should be noted that the birefringence of all samples is observed only at temperatures above 60°C. In fact, at room temperature, even if the sample is crystalline, no birefringence is shown, in agreement with the findings of Saunders [17].

In Figure 3, scanning electron micrographs of the pure P4MP1 and P4MP1/HOCP blends are shown. The micrographs always reveal the presence of stacks of lamellae that are the constituents of the microspherulites observed in the optical micrographs. For the blends, the small HOCP domains are occluded by the P4MP1 lamellae, that during the growth, bend to encompass the particles. The occlusion of the particles and bending of the P4MP1 lamellae require extra energy, resulting in the decrease of the crystallization rate observed for the blends. (See next section).

P4MP1 is a polymorph material and five crystalline modifications have been reported [18-20]. Crystallization from the melt generates the form known as modification I. This modification has a tetragonal cell with a=b=18.66 and c=13.80 A.

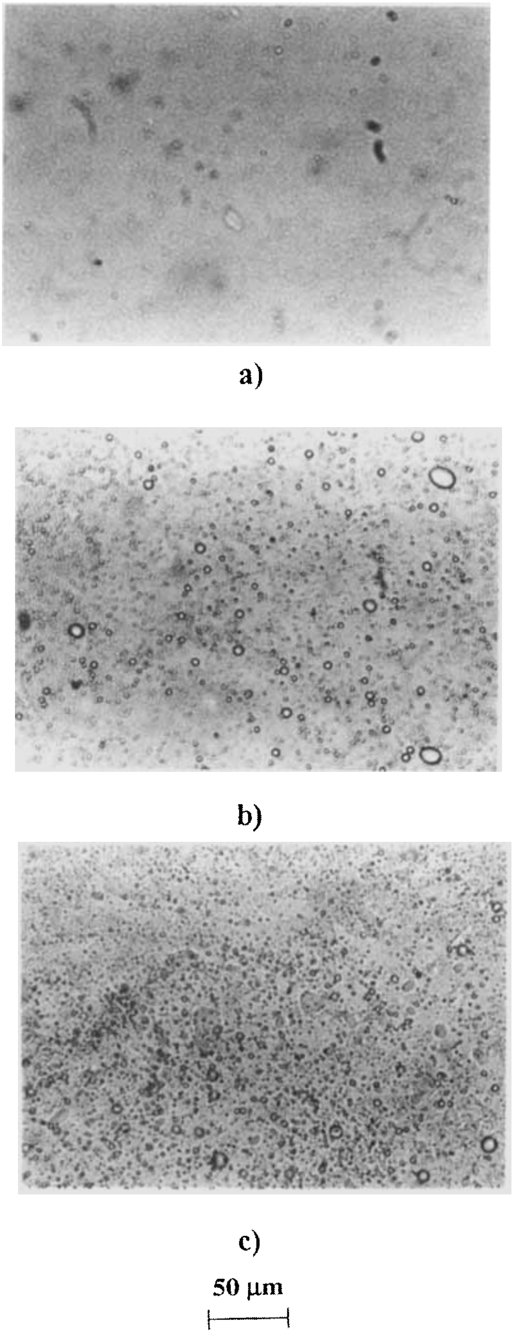


Figure 1. Optical micrographs of thin films of P4MP1/HOCP blends in the melt: a) 90/10; b) 80/20; c) 60/40.

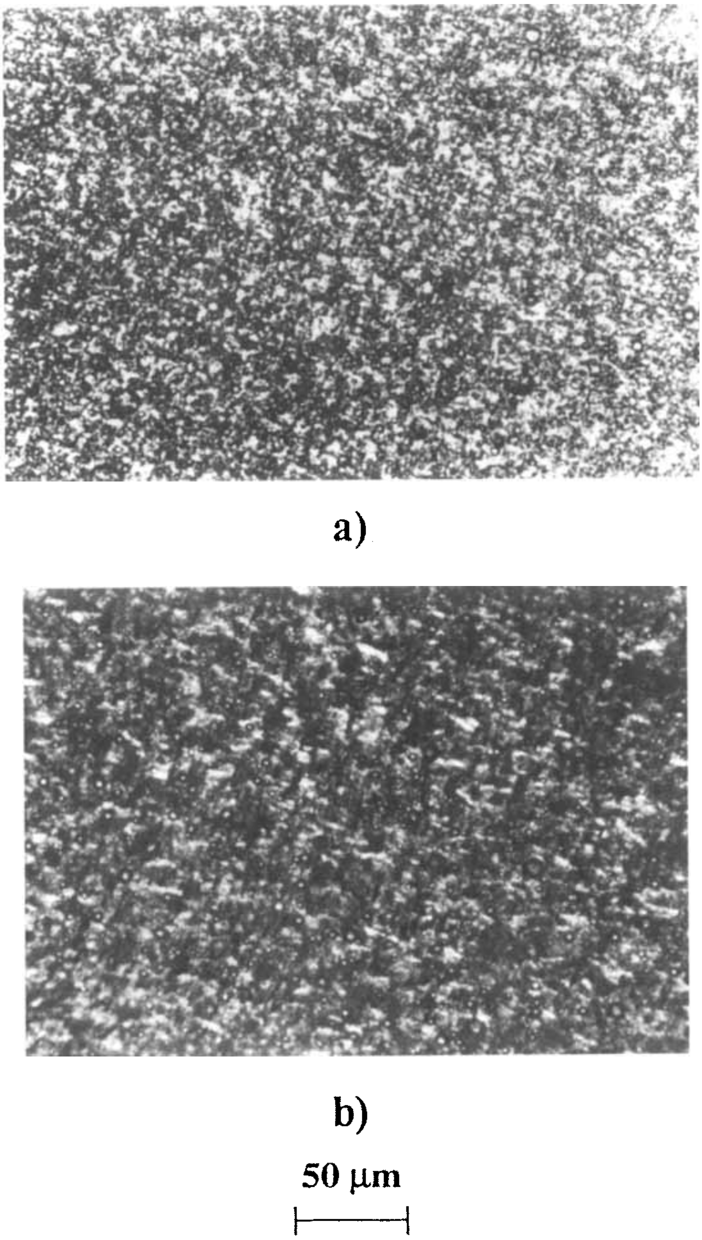
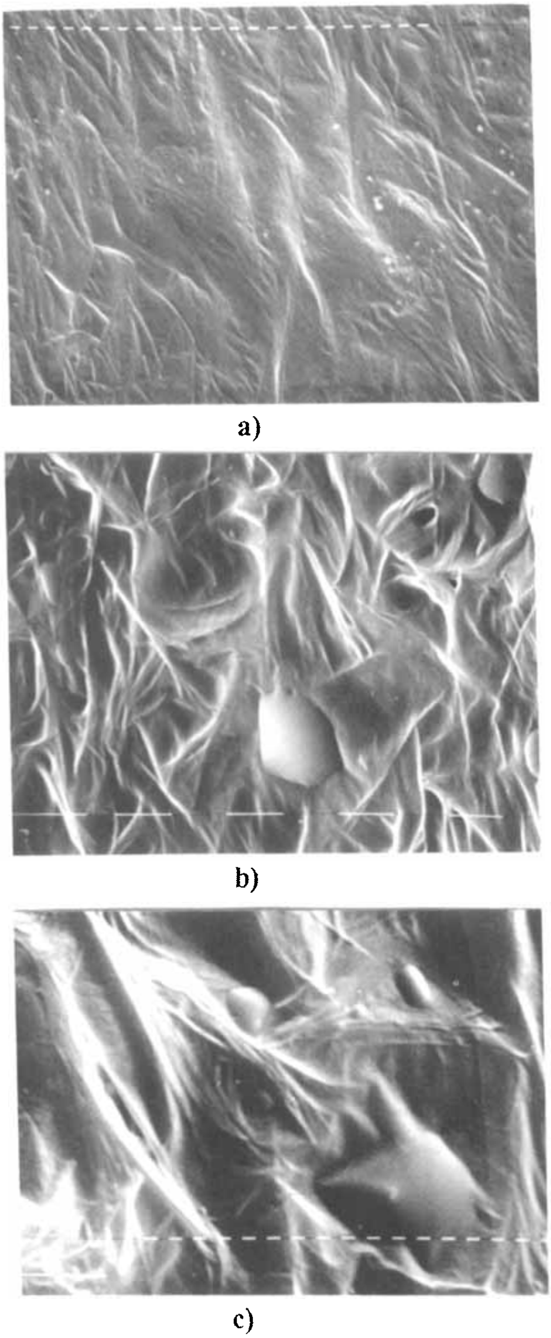


Figure 2. Optical micrographs of thin films of P4MP1/HOCP blends isothermally crystallized at T_c=220°C. a) 90/10; b) 80/20.



a)

b)

c)

Figure 3. Electron micrographs of P4MP1/HOCP blends isothermally crystallized at T_c=220°C, a) 100/0; b) 90/10; c) 80/20,

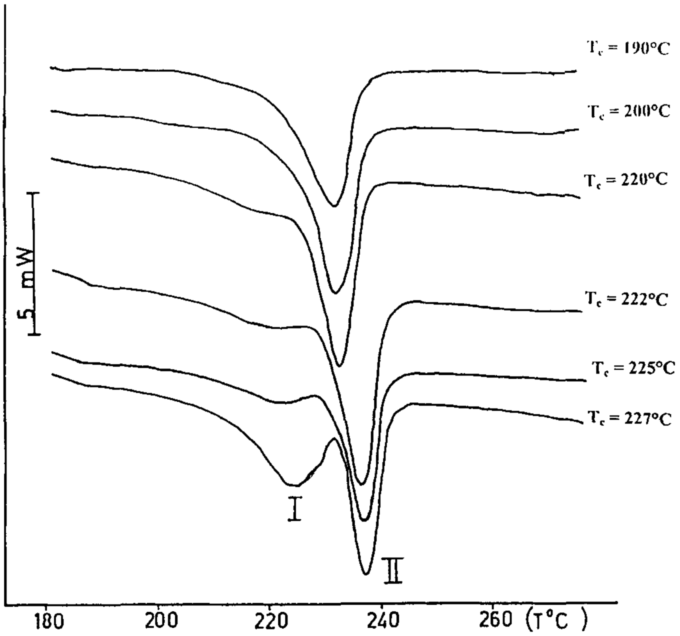


Figure 4. Melting scans of P4MP1 samples isothermally crystallized at different crystallization temperatures.

The WAXD patterns of the pure P4MP1 and the P4MP1/HOCP blends isothermally crystallized are identical and show that the polymer crystallizes always according to modification I, independently of the presence of HOCP.

Thermal Behavior

The samples were subjected to the following thermal treatment: they were first melted at 260°C for 10 minutes, and then cooled rapidly to a crystallization temperature T, ranging between 180 and 227°C. After completion of the crystallization, the samples were cooled to 180°C and then scanned at 10°C/min up to 290°C.

The DSC curves relative to the last scan are reported in Figure 4 for P4MP1 crystallized at different T_c. For samples crystallized from 180 to T<220°C, where the crystallization is not isothermal, a single broad melting peak, centered at about 233°C is present. For the samples isothermally crystallized (T_c range between 220 and 227°C) two melting peaks are detected: a lower temperature peak (peak I) and a higher temperature peak (peak II). We consider the higher endotherm as being

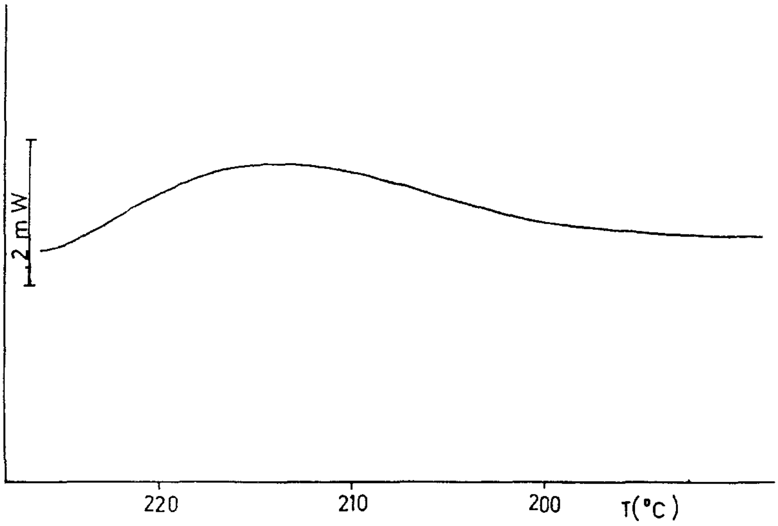


Figure 5. DSC scan of P4MP1 sample crystallized at 225°C registered during the cooling from 227 to 180°C.

indicative of the crystals formed prevalently at T_c and the lower one as being due to the melting of material formed not isothermally during the cooling. In fact, this last melting starts at a temperature lower than T_c, indicating that some crystals are not isothermally crystallized at T_c. These crystals probably form during the cooling from T_c to 180°C. The ratio of the area under peak I to the area under peak II increases with crystallization temperature. The overall crystallinity is about 65%, independently of T_c.

These results lead to the following conclusions: at temperatures lower than 220°C, all the crystallizable material crystallizes. At crystallization temperatures higher than 220°C, on the contrary, less material crystallizes; the remaining part of P4MP1, crystallizable at $T<220$°C, being in the melt state along with the amorphous P4MP1. Decreasing the temperature, a second crystallization takes place during the cooling, as it is evident from Figure 5. In this figure, a scan of a P4MP1 sample , crystallized isothermally at 227°C, following cooling from T_c=227 to 180°C is shown. A crystallization curve is observable starting from T=220°C. The heat evolved during this transition is 4.4J/g. Taking into consideration that the heat required for the entire crystallization is 17 J/g, it can be deduced that at 227°C only 80% of the crystallinity can develop.

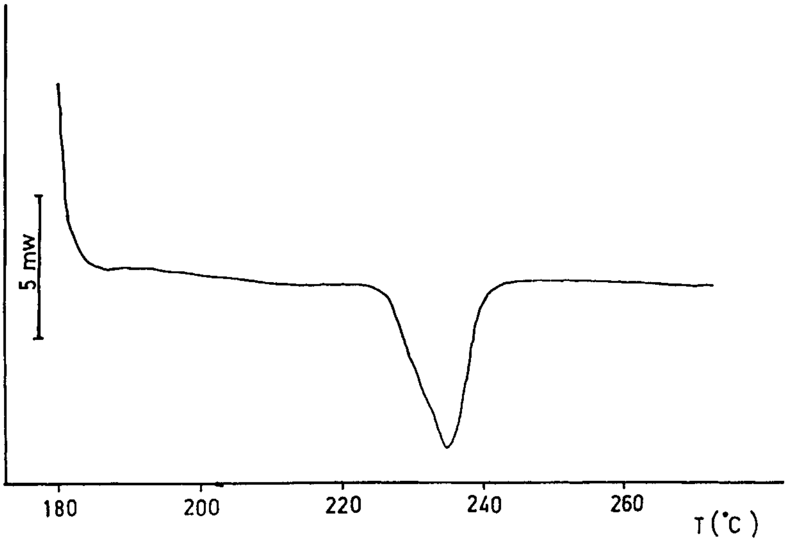


Figure 6. DSC scan of a P4MP1 sample crystallized at 180°C and annealed at 227°C.

We could attribute the two melting peaks to two populations of lamellae with different thicknesses, formed in two stages of crystallization, in agreement with Bassett *et al.* [21]. The first lamellae (primary lamellae), formed isothermally at higher T_c, are thicker and have the highest melting point. During the second crystallization, thinner lamellae (secondary lamellae) can form with a lower T_m. They are thinner, not only because of the higher undercooling, but also as a consequence of the difficulties of the lamellae to accommodate to the environment of previously formed lamellae.

The importance of the environment in the crystallization of P4MP1 is also evident from the scan of samples obtained by varying the crystallization conditions.

In fact, the second crystallization can be avoided by changing the thermal treatment. A sample of P4MP1 was, in fact, subjected to the following thermal treatment: I step: crystallization at 180°C; II step: annealing at 227°C for 30 minutes; III step: cooling to 180°C, IV step: heating from 180 to 290°C. Figure 6 shows the DSC curve relative to the IV step. A single melting peak is observed centered at 233°C and a value of crystallinity of 50% is computed. The presence of a single melting peak centered at high temperature and the low value of crystallinity indicate that the second crystallization during the cooling does not occur. It can be speculated

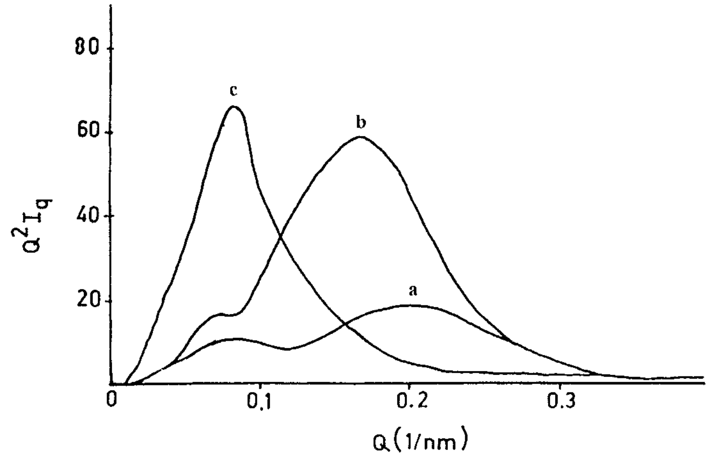


Figure 7. Lorentz corrected intensities curves for plain P4MP1 for selected temperatures: a) T=150°C; b) T=210°C and, c) T=230°C.

that the environment in this case probably does not allow the second crystallization. At 180°C (I step), primary and secondary lamellae are formed, the crystallinity of the samples is 65%. During the annealing at 227°C (II step), the secondary lamellae melt and at the same time the primary lamellae thicken occupying part of the space left by the melting of the secondary lamellae. Therefore, on cooling the material to 180°C (III step), the secondary lamellae cannot form again because having enough space for this crystallization is not available.

The hypothesis that one or two populations of lamellae can form, depending on crystallization conditions, is in agreement with the morphology, that shows stacks of lamellae with different thickness for samples crystallized isothermally at T_c=220°C, (see Figure 3). Moreover, preliminary X-ray results seem to confirm the hypothesis. Figure 7 shows, in fact, the Lorentz corrected intensity for pure P4MP1 crystallized at 150, 210, and 230°C as a function of the scattering variable, $Q = 4\pi\sin\theta/\lambda$. At T_c=150, 210°C two peaks are observed, whereas at 230°C, a single peak is present. From this result, it can be concluded that for the samples crystallized at 150 and 210°C, two long periods are obtained, a thinner long period and a thicker long period. At 230°C, only the thicker long period is present. For the samples crystallized at 150 and 210°C, the presence of the two long periods probably confirms the two populations of lamella. For samples crystallized at a higher temperature (230°C), the single long period indicates a single lamellar structure. At this

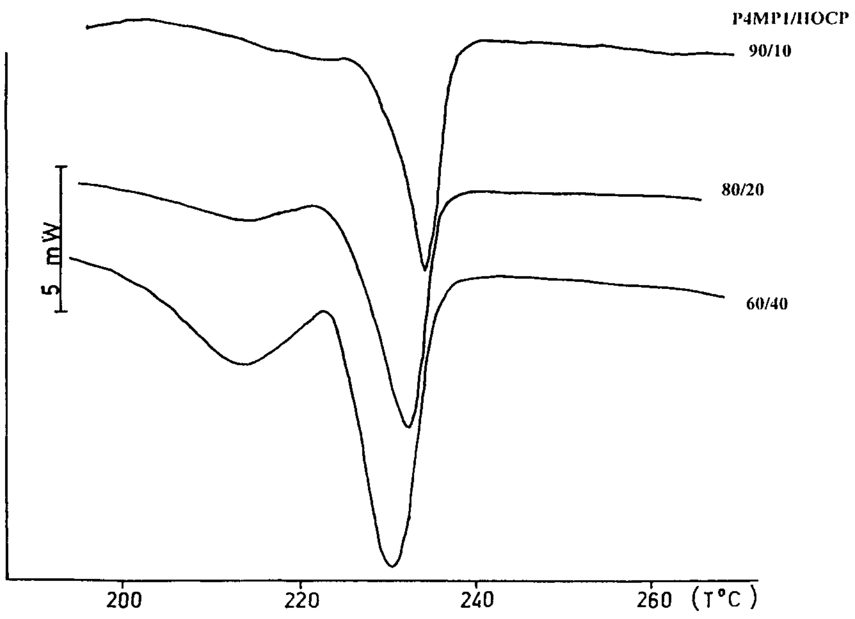


Figure 8. Melting scans of P4MP1/HOCP blends isothermally crystallized at $T_c = 220°C$.

temperature, the lamellae having shorter thickness cannot form, because their melting point is below 230°C, as shown in the *Thermal Behavior* section. P4MP1 lamellae of different thicknesses were also observed by Rybnikar and Geil [22], several years ago.

The presence of HOCP influences the thermal behavior of the P4MP1.

In the case of blends, two melting peaks are always detected, for all crystallization temperatures investigated, as reported in Figure 8. For a given T_c, the higher melting peak shifts to lower temperature with composition. The position of the lower melting peak is independent of composition. The ratio of the area under peak I to the area under peak II increases with temperature and at a given crystallization temperature with composition. Therefore, HOCP disturbs mainly the primary isothermal crystallization of P4MP1. The blends are probably characterized by a small number of dominant lamellae and a large number of subsidiary lamellae. This is in accordance with the hypothesis of two kinds of lamellae formed in two steps of crystallization. X-ray and electron microscopy works are in progress in order to confirm this hypothesis.

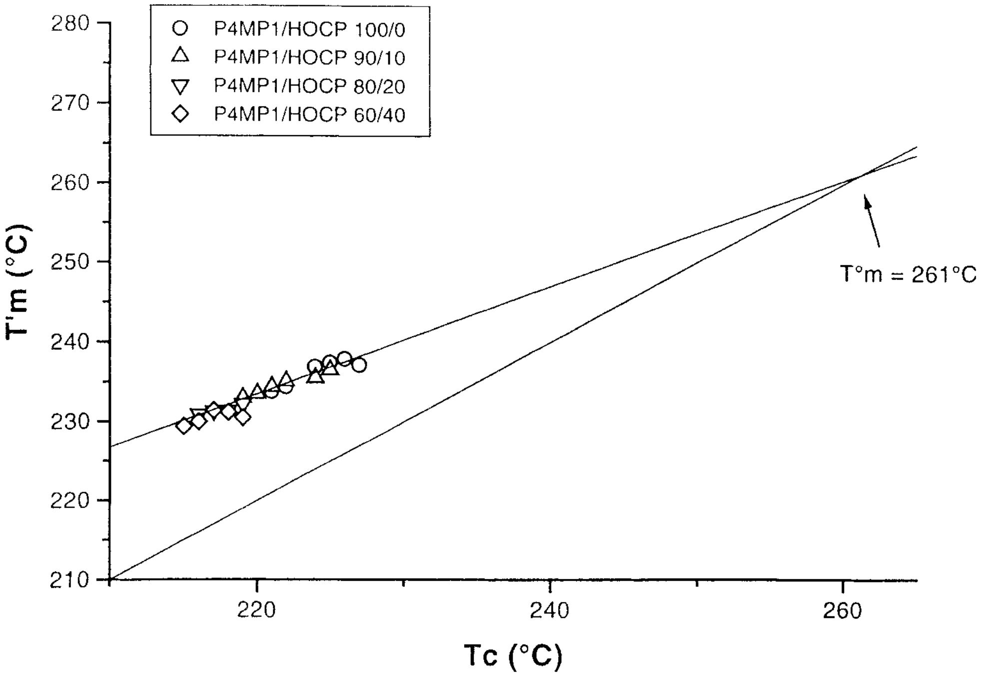


Figure 9. Hoffman-Weeks plot for P4MP1 and P4MP1/HOCP blends.

Figure 9 reports the Hoffman-Weeks plots for all the samples [23]. All the points can be fitted by a single straight line, that can be extrapolated to give a single value of $T_m°$, independent of composition. The constancy of $T_m°$ with composition indicates that the two polymers are not miscible, at the least in the range of compositions and temperatures investigated [24]. In fact, thermodynamic considerations predict that the chemical potential of a polymer decreases following the addition of a miscible diluent. In the case of a crystallizable polymer, such a decrease results in a depression of the equilibrium melting temperature.

Crystallization Behavior

The study of the bulk crystallization of P4MP1 has not received much attention. Only two studies, to our knowledge, describe the crystallization kinetics of this polymer from the melt [25, 26]. Crystallization behavior of copolymers of 4MP1 with other α-olefins is also reported [27], whereas no study of the crystallization of P4MP1 in presence of a second component has been reported.

Isothermal crystallization was conducted for samples obtained both by casting and by melt mixing. The preparation conditions and the presence of HOCP greatly influence the crystallization behavior of the crystalline polymer.

The half-time of isothermal crystallization, as a function of composition and temper-ature is reported in Figures 10 and 11 for samples obtained by casting and by melt mixing, respectively. For both sample preparations, at a given T_c, a continuous decrease of $\tau_{1/2}$ with composition is observed.

The crystallization for the blends can be performed in a T_c range that shifts to lower temperatures, compared to pure P4MP1. So, taking into consideration that the equilibrium melting point is independent of composition, a higher undercooling is required in order to crystallize isothermally the blend in a finite time. This fact gives rise to a more disordered polycrystalline structure with a lower melting point.

The crystallization behavior can be explained by considering the phase structure and the morphology of the system.

In the entire range of compositions and temperatures investigated, the two components are not miscible, so the crystallization of P4MP1 starts from a phase-separated melt.

The increase of $\tau_{1/2}$ with composition certainly indicates that the HOCP domains in the melt at T_c influence the energy related to the motion of the P4MP1 macromolecules in the melt. In fact, as indicated by the electron micrographs, during the crystallization, the stacks of P4MP1 lamellae bend around the HOCP domains to occlude them. The energies required for the bending and the occlusion are probably responsible for the decrease of the crystallization rate [28-30].

For a given composition and T_c, the samples prepared by melt mixing crystallize in a shorter time than the samples obtained by casting. This result underlines the fact that the preparation conditions greatly influence the overall crystallization process of a polymer material. In the samples prepared by casting, a certain amount of nuclei is probably dissolved in the solvent, and/or during the dissolution, they lose their activity.

The bulk kinetics of crystallization of P4MP1 and its blends with HOCP were analyzed using the Avrami treatment for the kinetics of phase change [31]. Both for the pure P4MP1 and the P4MP1/HOCP blends an Avrami index equal to 2 was obtained. Different values of the Avrami index are reported in the literature for the P4MP1. Griffith and Ranby [25] found a value of n=4, whereas Yadav *et al.* [26] reported a value of 3.

In agreement with the Avrami theory, a value of n=4 indicates a three-dimensional growth with a homogeneous nucleation. As reported [32], homogeneous nucleation requires large undercooling ($\Delta T > 100$), and therefore, can be ignored for the crystallization of P4MP1 at the crystallization temperatures applied in the present work and in those in the literature.

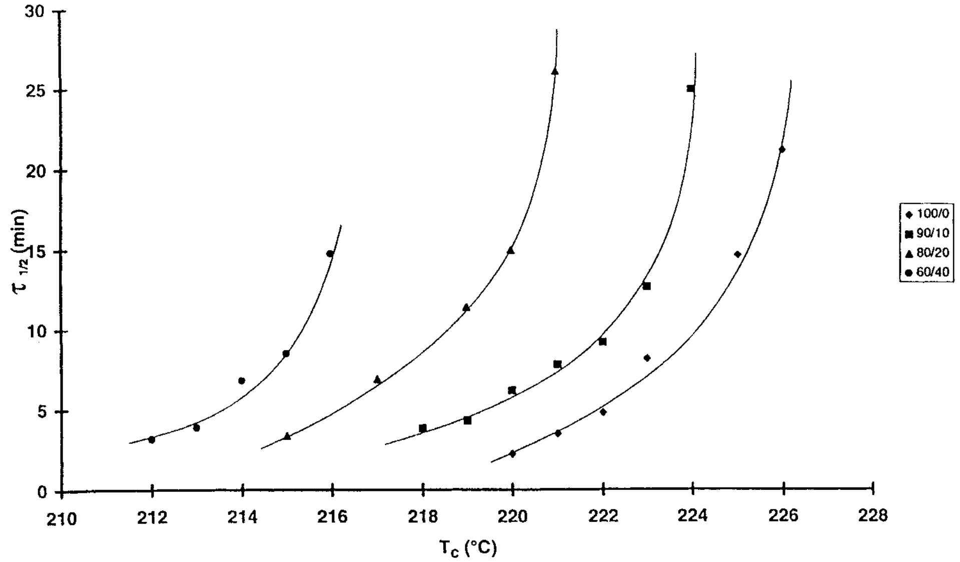


Figure 10. Half-time of crystallization, $\tau_{1/2}$, as a function of composition and temperature for samples obtained by casting.

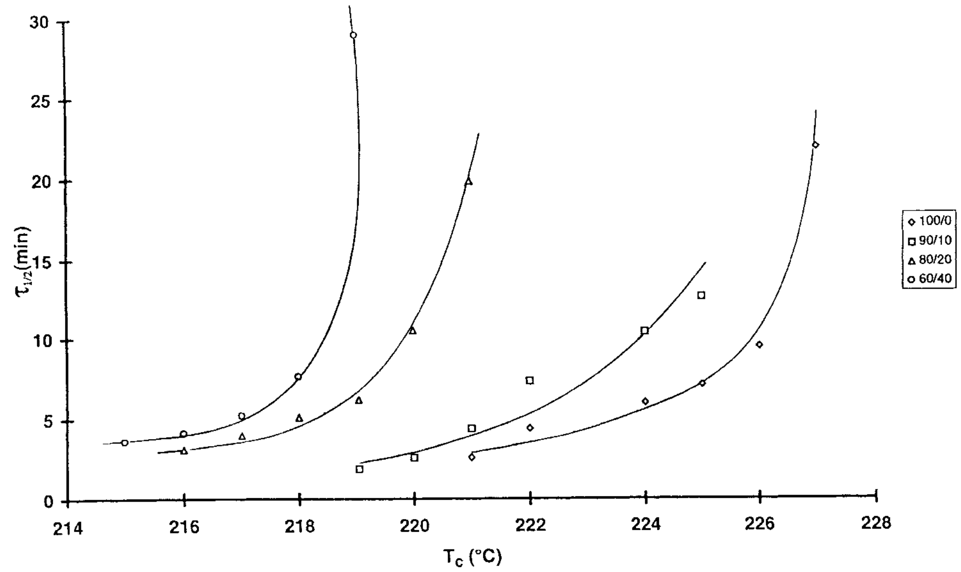


Figure 11. Half-time of crystallization, $\tau_{1/2}$ as a function of composition and temperature for samples obtained by melt mixing.

Therefore, in our opinion, the value of n=4 obtained by Griffith and Ranby does not describe the crystallization process of P4MP1 well.

Assuming therefore, that the nucleation process is heterogeneous, according to Avrami, n=3 indicates a three-dimensional growth, whereas n=2 a bi-dimensional one. In the *Morphological Section*, it was shown that the crystals are made of stacks of bi-dimensional lamella. Therefore, the value of n=2 describes rather well the crystallization of P4MP1 and P4MP1/HOCP blends.

CONCLUSION

A study of the crystallization kinetics of P4MP1 and its blends with HOCP has been performed over a wide range of crystallization temperatures and several compositions.

The results reported have shown that:

The thermal behavior and SAXS analysis seem to indicate that one or two populations of lamellae, different in thickness, can form depending on the crystallization conditions and presence of HOCP. The relative amount of the two kinds of lamellae is a function of the crystallization temperature, composition and thermal treatment.

The P4MP1/HOCP system is not homogeneous. In the melt, two phases, composed of the pure components, are present. After crystallization, the system is formed by three phases: a crystalline phase of P4MP1 and two amorphous phases: one of P4MP1 and the other of HOCP. The HOCP phase is homogeneously distributed in the P4MP1 matrix.

The crystallization behavior is dependent on crystallization conditions, and composition. For a given crystallization temperature, a depression in the overall crystallization rate is observed, following the addition of HOCP to P4MP1. At a given composition and temperature the samples prepared by melt mixing crystallize in a shorter time than the samples obtained by solvent casting.

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