

Crystallization behaviour of stereocomplexed poly(methyl methacrylates): influence of thermal history

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The influence of thermal history on the stability of stereocomplexes of isotactic and syndiotactic poly(methyl methacrylate) PMMA was investigated using differential scanning calorimetry. It was found that a prolonged annealing of the stereocomplex not only increases its crystallinity but also leads to the appearance of another, yet rather small, endotherm with a maximum located close to the beginning of the melting of the stereocomplex. Crystallization from the melt and partial melting of samples indicate that the isotactic PMMA also is able to crystallize the stereocomplex crystals, the ratio of these two crystalline species being very sensitive to the stoichiometric ratio of the mixture and the isotactic content of the PMMA. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The synthesis of stereoregular poly(methyl methacrylates) (PMMA) by Fox *et al.*¹ in 1958 led rapidly to the concept of stereocomplexation between isotactic (i) and syndiotactic (s) chains². Since then, several studies have been devoted to a better understanding of the nature of the stereocomplex and to the determination of the experimental conditions that are necessary to favour such associations in solution^{3–5}. It was found that the solvent used has a considerable influence on complex formation and that solvents for PMMA can be divided into three groups: those strongly complexing (e.g. acetone, tetrahydrofuran); those weakly complexing (e.g. toluene, benzene); and others non-complexing (e.g. chloroform, dichloromethane)⁶. Other factors, such as molecular weight, polymer concentration, mixing ratio of the stereoregular polymers, contact time, complexation temperature and stereosequence lengths, must also be taken into account^{7–9}.

Although ratios of 1/1 and 1/1.5 have been reported in the literature^{5,10}, it is now generally accepted that the stereocomplex stoichiometry corresponds to an isotactic to syndiotactic molar ratio of 1/1¹¹. The complementarity of the chains suggests that an interaction of the ester groups of isotactic PMMA occurs with the α -methyl groups of syndiotactic PMMA^{12,13}: in a strongly complexing solvent, structures having a 1/2 stoichiometry associate in the form of compact particles having approximately 50 nm in dimension^{14–16}; these particles can aggregate thereafter and the complex is isolated from the solvating medium by centrifugation.

The formation of a stereocomplex between isotactic PMMA and syndiotactic PMMA was also known to occur in the bulk: after annealing between 403 and 433 K, a melting

endotherm is observed at about 463 K, even with samples precipitated from a non-complexing solvent^{17,18}. However, the formation of a complex in the bulk is a less favourable process than complexation in dilute solution since the maximum degree of crystallinity then measured is half the value found from solution.

Nevertheless, differential scanning calorimetry and wide-angle X-ray scattering indicate that the melting point and crystalline structure of stereocomplexes formed in the bulk or in solution are independent of the isotactic to syndiotactic ratio of the initial mixture^{11,19} and, therefore, that there is only one type of stereocomplex. Kusanagi *et al.*²⁰ have suggested that the structure of the stereocomplex is closely related to the double-stranded helix conformation of isotactic PMMA²¹. Bosscher *et al.*²², and later Schomaker and Challa²³ have confirmed this assumption by investigating its X-ray fibre pattern. It seems, from the Schomaker and Challa study²³, that the stereocomplex is made of a 9/1 double-stranded helix, having an asymmetric unit consisting of one isotactic unit and two syndiotactic units, having a pitch of 1.84 nm, the energy barrier required for screwing the isotactic PMMA and syndiotactic PMMA chains through each other being only 0.8 kJ/mol. It is interesting to note that this conformation is very close to the conformation of pure isotactic PMMA, with a 10/1 helix structure^{20,21}, and that of syndiotactic PMMA, with a 37/4 helix²³.

Although several studies have been devoted to the thermal properties of this stereocomplex^{11,17,19,24–27}, its crystallization behaviour seems to have been neglected. Konnecke and Rehage^{24,26} investigated the crystallization rate of a stereocomplex in the gel state, which is controlled by the short sequence length of the syndiotactic units in the polymer. Allen *et al.*²⁷ compared the crystallization behaviour of blends of isotactic PMMA with syndiotactic PMMA or atactic PMMA induced by a solvent or by a thermal treatment, and measured the crystallinity and dynamic mechanical properties of such systems.

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It is expected that the extent of crystallization of a solvent-free stereocomplex can be controlled since its stability depends strongly upon its physical environment. Therefore, it is the purpose of this article to study the effect of thermal history on the crystallization behaviour of stereocomplexed poly(methyl methacrylates). This investigation will focus on three points: first, the influence of thermal treatments on complexation and crystallization processes; second, the contribution of the stoichiometric ratio of the stereoregular chains on the nature of the stereocomplex; and, finally, the influence of a decrease in stereoregularity of the chains on the thermal stability of the stereocomplex. Crystallization will be carried out in the melt and the thermal behaviour of the stereocomplex will be compared with that of isotactic PMMA.

EXPERIMENTAL SECTION

Table 1 lists the poly(methyl methacrylates) used in this study along with their triad characteristics (i, isotactic; h, heterotactic; and s, syndiotactic triad fraction), weight-average molecular weight (M_w), polymolecularity index (M_w/M_n), glass transition (T_g) and melting (T_m) temperatures. Six isotactic and five syndiotactic PMMAs have been investigated. The crystallization behaviour of the isotactic samples has been reported elsewhere²⁸. Samples ISO-2 and ISO-3 are commercial samples used without further purification; they exhibit a broad polymolecularity index. All remaining samples were kindly supplied by the Laboratory of Macromolecular Chemistry and Organic Synthesis, University of Liège, Belgium. Details about the synthesis and the characterization of these samples have been reported elsewhere^{29,30}.

Tacticity values were obtained by nuclear magnetic resonance spectroscopy³¹ from 10% *o*-dichlorobenzene solutions, at 408 K, with a Varian XL-200 instrument. Molecular weights were determined by size-exclusion chromatography (SEC) using μ -styragel columns and a Waters chromatograph. The measurements were conducted at 298 K in tetrahydrofuran, and the apparatus was calibrated with polystyrene standards.

Stereocomplexes were prepared by mixing 1 wt.% spectroscopic acetone solutions of isotactic PMMA and syndiotactic PMMA in various ratios under continuous stirring at 298 K (it must be noted that acetone is a strongly complexing solvent). After 1 h, the crystallized material was separated from the solution by centrifugation at 10 000 rpm.

The precipitate was then dried in a vacuum oven at room temperature until it reached constant weight.

Annealing and crystallization experiments were performed in a wax bath which allowed the simultaneous treatment of 10 different samples with a temperature control of ± 0.5 K³⁰. Prior to its thermal treatment, each sample was weighted in a d.s.c. pan and left in the wax bath inside a small-diameter glass tube. Some samples were brought to the annealing temperature T_a at a rate of 10 K/min and kept at T_a for several days. Other samples were heated up at a rate of 10 K/min above their melting temperature T_m , maintained at that temperature for 1 min, cooled at 5 K/min to the crystallization temperature T_c and kept at T_c for several days.

Differential scanning calorimetry (d.s.c.) measurements were conducted with a Perkin-Elmer DSC-4 apparatus equipped with a TADS microcomputer. The d.s.c. was calibrated with ultrapure indium. The glass transition temperatures T_g reported in this article were recorded at the half-height of the corresponding heat capacity jump, while the melting points correspond to the end of the melting peak. After their insertion into the d.s.c. apparatus, all samples were first cooled to 273 K and maintained at that temperature for 5 min. Scans were made at a heating rate of 20 K/min.

RESULTS

For reasons of uniformity, all results mentioned in the next two sections refer to an ISO-2/SYN-2 stereocomplex. Similar results could be achieved by combining various stereoregular PMMAs, as will be shown in the third section.

THERMAL TREATMENTS

Figure 1 illustrates the influence of annealing (after solvent precipitation) on the thermal behaviour of a 1/2 stereocomplex in comparison with that of solvent-free isotactic PMMA. The annealing was carried out for 7 days at 363, 383 and 403 K.

Upon heating the complex recovered from solution (curve A), one can see that the melting endotherm covers a range of 100 K. Furthermore, several irregularities appear on top of this melting curve, which suggest that traces of solvent have been trapped during the aggregation of the complex and are suddenly released upon melting.

In contrast, the annealed stereocomplex is characterized

Table 1 Characterization of the polymers used

Sample	<i>i/h/s</i>	M_w (kg/mol)	M_w/M_n	T_g (K)	T_m (K) ^a
ISO-2	100/0/0	294	7.4	331	427
ISO-3	85/15/0	60	6.0	324	428 ^b
ISO-4	63/24/13	291	3.0	348	430
ISO-5	60/25/15	256	3.0	343	428
ISO-6	56/29/15	166	2.8	349	429
ISO-7	46/33/21	120	3.0	355	—
SYN-1	5/26/69	92	1.4	400	—
SYN-2	5/21/74	130	1.7	404	—
SYN-3	0/24/76	126	1.3	396	—
SYN-4	2/18/80	85	1.3	403	—
SYN-5	0/18/82	117	1.1	406	—

^aFirst d.s.c. scan

^bThis low-molecular weight sample crystallizes after a short annealing treatment at 393 K

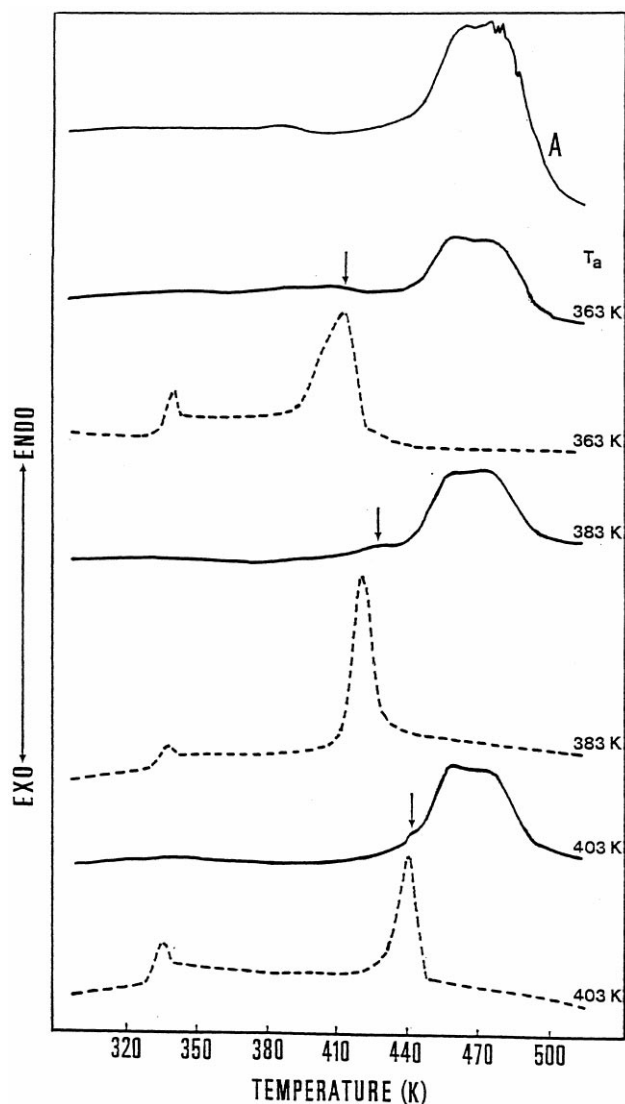


Figure 1 Influence of the annealing temperature T_a on the thermal behaviour of a 1/2 stereocomplex (full line) and an isotactic PMMA (dashed line) after 7 days at $T_a = 363, 383$ and 403 K. For comparison, curve A (at the top) gives the melting behaviour of the same stereocomplex before annealing

by a broad but uniform melting endotherm occurring between 430 and 510 K. The uniformity of the melting endotherm proves the efficiency of the annealing treatment for the removal of the solvent. Also, the enthalpy of fusion of the melting species increases from 33 to 40 J/g which suggests an increase in the degree of crystallinity of the complex.

Beside this big endotherm, a rather small peak (indicated by an arrow) is noticed, and shifts to higher temperatures as the annealing temperature is increased. If a similar thermal treatment is used for solvent-free isotactic PMMA, its melting peak occurs at about the same temperature as the small peak observed on the melting curve of the annealed stereocomplex. In addition, they show a glass transition temperature (T_g) at about 333 K. This glass transition, as well as others observed in this and the next figures, exhibits a small endotherm which is often present for samples undergoing enthalpy relaxation. This phenomenon is seen in many cases in this work since the samples have often been heat treated for long periods of time, a condition that favours the enthalpy relaxation.

This indicates that the annealing treatment not only

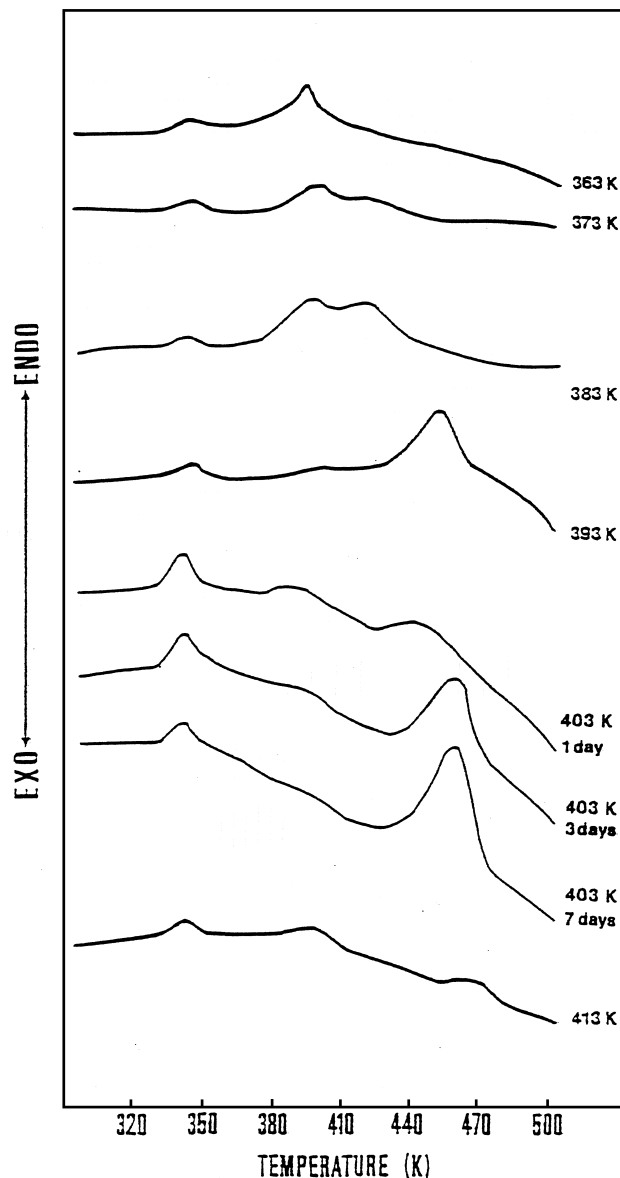


Figure 2 Influence of the crystallization temperature T_c on the thermal behaviour of a 1/2 stereocomplex melted at 513 K for 1 min and crystallized for 7 days between 363 and 413 K. The influence of time of crystallization is shown by curves obtained at 403 K for $1, 3$ and 7 days of crystallization

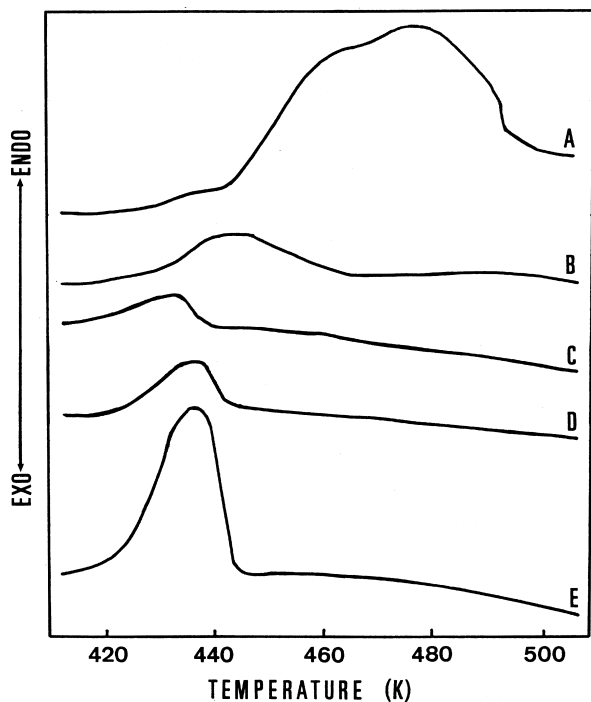
enhances the crystallinity of the complex but also allows a partial dissociation of the system and/or the crystallization of isotactic chains which, somehow, never got to associate with their syndiotactic counterpart. The fraction of crystallized isotactic chains relative to that of the stereocomplex is rather small and points out that dissociation is not favoured by annealing, at least between 363 and 403 K which is below the beginning of the melting of the stereocomplex.

Figure 2 shows the thermal behaviour of a 1/2 stereocomplex which has been melted for 1 min at 513 K and then crystallized at T_c up to 7 days, between 363 and 413 K. At $T_c = 363$ K, there are only traces of crystallized material, but two sharp T_g values are observed (again with a small endotherm due to enthalpy relaxation) at about 329 and 389 K. A melting endotherm can be observed for crystallization temperatures ranging between 373 and 413 K, with a maximum intensity at $T_c = 393$ K.

The crystallization of mixtures of stereoregular PMMA chains from the melt is a very slow process^{11,24,28,32}, as

Table 2 Glass transition temperatures (T_{g1} and T_{g2}) and melting point (T_m) of a 1/2 stereocomplex as a function of the crystallization temperature T_c

T_c (K)	T_{g1} (K)	T_{g2} (K)	T_m (K)	ΔH_m (J/g)
363	332	389	442	3
373	338	392	446	4
383	333	395	453	6
393	337	396	471	9
403	334	—	474	6
413	337	392	479	4

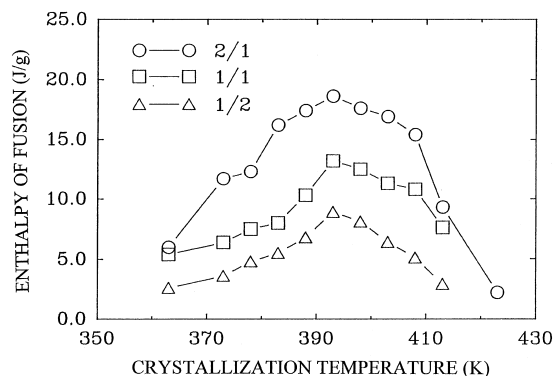
**Figure 3** Thermal behaviour of a 1/2 stereocomplex annealed for 7 days at 393 K (curve A), a 1/2 stereocomplex crystallized for 7 days at 393 K (curve B), and an isotactic PMMA (curves C, D and E) crystallized at 393 K for 7, 20 and 60 days, respectively

shown in *Figure 2* by a 1/2 stereocomplex melted for 1 min at 513 K and crystallized at 403 K for 1, 3, and 7 days. It is necessary to keep the sample at 403 K for at least 1 day before any quantitative measurements can be carried out but, at that temperature, the enthalpy of fusion reaches a constant value after 7 days.

Since two T_g values can be observed, phase separation of the system occurs in the melt and remains for a long period of time in the 383–403 K range. From the position of these T_g values, the system contains an isotactic-rich amorphous phase ($T_{g1} \approx 334$ K), which is not strongly influenced by the crystallization time, and a time-dependent syndiotactic-rich amorphous phase. The T_g of the latter broadens and decreases in relative intensity as the crystallization time is increased.

Table 2 shows that both T_{g1} , associated with the isotactic-rich amorphous phase₁, and T_{g2} , associated with the syndiotactic-rich amorphous phase, are not influenced by the crystallization temperature. As we have mentioned above, the observation of two T_g values indicates the presence of two amorphous phases.

Figure 3 shows the melting curve of a 1/2 stereocomplex annealed for 7 days at 393 K (curve A), which is compared with that of a 1/2 stereocomplex (curve B) melted for 1 min

**Figure 4** Evolution of the melting endotherm as a function of the crystallization temperature for 2/1, 1/1 and 1/2 ISO-2/SYN-2 systems. Crystallization period, 7 days

at 483 K and then crystallized for 7 days at 393 K. These two curves are compared against those of isotactic PMMA which was melted for 1 min at 483 K and then crystallized for 7 (curve C), 20 (curve D), and 60 days (curve E) at 393 K. These curves show that the crystallization of isotactic PMMA requires a longer period of time to achieve a similar heat of fusion as the one observed for the decomplexed 1/2 system (roughly, 7 days for the stereocomplex as compared to 20 days for isotactic PMMA). In addition, a shift of the T_m of isotactic PMMA to higher temperatures can be followed with time but its limiting value is always below the maximum of the melting peak of the crystallized stereocomplex mixture.

STOICHIOMETRIC RATIO

In a binary blend made of a crystallizable polymer 1 and a non-crystalline polymer 2, the crystallization rate of component 1 decreases with an increase in concentration of component 2. Such a trend was demonstrated by Keith and Padden³³ who followed the radial growth rate of spherulites in blends, and later by several other groups^{34–36}. For a given blend composition, as a function of temperature, the crystallization rate goes through a maximum corresponding to optimum values of the nucleation and diffusion rates. In first approximation, the same trend is obtained by plotting the heat of fusion corresponding to the melting endotherm of the crystallized material against T_c ³⁷.

Such a plot is illustrated in *Figure 4* where three different compositions of the isotactic/syndiotactic mixture, i.e. 2/1, 1/1 and 1/2, were first melted for 1 min at 513 K and then crystallized for 7 days at various crystallization temperatures. For each composition, the enthalpy of fusion was calculated by integrating the peak area from 420 to 480 K if we take as an example the 403 K curve of *Figure 2*. This curve, exhibiting a broad melting endotherm, without

Table 3 Thermal properties of 1/1 and 1/2 stereocomplexes partially dissociated at T_a and crystallized for 7 days at $T_c = 393$ K

T_a (K)	1/1 stereocomplex						1/2 stereocomplex					
	T_{g1} (K)	T_{g2} (K)	T_{m1} (K)	ΔH_{m1} (J/g)	T_{m2} (K)	ΔH_{m2} (J/g)	T_{g1} (K)	T_{g2} (K)	T_{m1} (K)	ΔH_{m1} (J/g)	T_{m2} (K)	ΔH_{m2} (J/g)
393	326	382	—	—	512	37	320	386	—	—	512	37
463	323	389	459	5	502	12	320	397	455	1	503	17
473	326	390	464	8	502	4	325	396	457	3	503	6
483	336	392	468	11	—	—	336	398	463	7	—	—
513	339	390	473	13	—	—	337	396	471	9	—	—

distinguishable peaks due to the isotactic fraction and to the complex, is typical of what we observed not only for the 1/2 complex but also for the 1/1 and 2/1 mixtures. As a function of temperature, there is a maximum value of the heat of fusion (expressed in Joules/total mass of the sample) at $T_c = 393$ K, in accordance with previous observations (Figure 2). In addition, the heat of fusion is larger at all temperatures for the 2/1 system than for the two other compositions investigated. If the stereocomplex with an isotactic/syndiotactic stoichiometry of 1/2 would be the only crystallizable component, its heat of fusion should be larger since this composition does not contain an excess of isotactic PMMA relative to the stereocomplex composition. The observation of an opposite trend suggests that isotactic PMMA also crystallizes in these blends, under the specific conditions of crystallization used (see Figure 3), leading to the coexistence of both types of crystals and a broad melting peak.

As suggested above, the melting of the stereocomplex at 513 K leads to a dissociation of the complex. Partial dissociation was also attempted by heating stereocomplexes of 1/1 and 1/2 isotactic/syndiotactic ratios for 1 min at various temperatures T_a in its melting zone, i.e. above 440 K. Then, these samples were allowed to crystallize for 7 days at $T_c = 393$ K. Data obtained following these thermal treatments are listed in Table 3. Each of these samples exhibits two T_g values, the low-temperature one (T_{g1}) corresponding to the isotactic-rich amorphous phase, and the second one (T_{g2}) to the syndiotactic-rich amorphous phase. In addition, samples which have been partially dissociated in the 463–473 K range show two well-defined melting peaks. At higher dissociation temperatures, only the first melting peak which corresponds to the isotactic PMMA fraction is observed.

Table 3 indicates that there is a regular increase of T_{m1} and ΔH_{m1} as a function of T_a , the dissociation temperature. It appears that the higher the dissociation temperature, the greater the amount of isotactic PMMA separating from the complex and available for crystallization. In addition, the melting endotherm ΔH_{m1} is larger with the 1/1 stereocomplex than with its 1/2 counterpart, in accordance with the evolution of the melting endotherms reported in Figure 4, although the results of Table 3 and those of Figure 4 were generated under different crystallization conditions. In contrast, increasing T_a leads to a decrease in ΔH_{m2} which is larger with the 1/1 stereocomplex than with its 1/2 counterpart. This shows a certain tendency of the 1/1 system to be less stable than the 1/2 complex.

CHAIN STEREOREGULARITY

A decrease of the tacticity of PMMA inhibits the associating forces between the stereoregular chains and, consequently, the thermal stability of the stereocomplexes. This case is

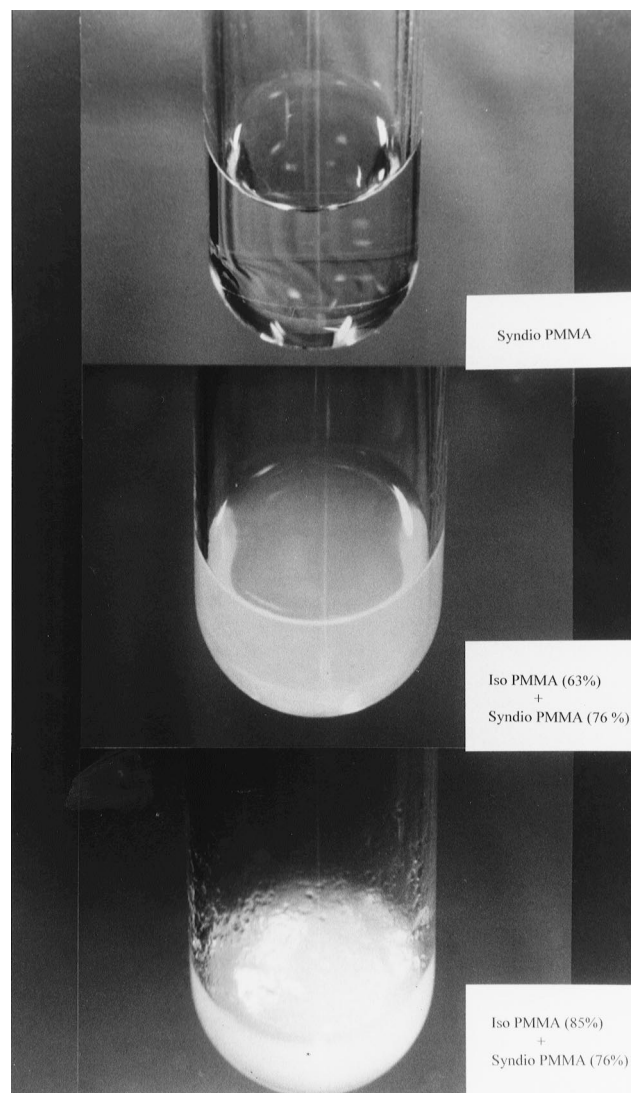


Figure 5 Influence of the stereoregularity of the PMMA chains on the formation of a stereocomplex. At the top, there is no stereocomplexation, as indicated by the transparent solution. In the middle, an isotactic PMMA of relatively low degree of tacticity (63%) leads to weak complexation (turbid solution). At the bottom, an isotactic PMMA of higher degree of stereoregularity (85%) gives more complexation, as indicated by the milky appearance

illustrated in Figure 5 where equimolar acetone solutions of stereoregular PMMAs having a concentration of 1% were mixed in glass tubes and kept at room temperature for 3 months. Solutions which contain syndiotactic PMMA only (top of Figure 5), remain clear without any sign of complexation. However, by combining a solution of PMMA which has an isotactic triad fraction of 63% [ISO-4] to a

Table 4 Influence of time on partial dissociation at 463 K of 1/2 stereocomplexes crystallized for 7 days at 393 K

Dissociation time at 463 K (min)	ISO-2/SYN-5		ISO-2/SYN-2	
	ΔH_{m1} (J/g)	ΔH_{m2} (J/g)	ΔH_{m1} (J/g)	ΔH_{m2} (J/g)
0	0	43	0	37
1	1	17	1	12
3	1	14	2	9
5	3	9	2	9

solution of PMMA having a syndiotactic triad fraction of 76% [SYN-3], a significant amount of turbidity can be observed (middle of *Figure 5*). Finally, by replacing this isotactic PMMA [ISO-4] by a PMMA having a degree of isotacticity of 85% [ISO-3] (bottom of *Figure 5*), the turbidity becomes even greater: the concentration of solid particles is more important, which demonstrates a stronger complexation as compared to the previous case.

Therefore, the isotactic triad content of isotactic PMMA plays an important role in the stereocomplex formation. The influence of this parameter was investigated by comparing the thermal properties of five different stereocomplexes, ISO-3/SYN-4, ISO-4/SYN-4, ISO-5/SYN-4, ISO-6/SYN-4 and ISO-7/SYN-4, which all have a 1/2 stoichiometric ratio and the isotactic triad content of which is 85%, 63%, 60%, 56% and 46%, respectively (see *Table 1* for more details). The heats of fusion of these stereocomplexes, prepared from the solution, were, respectively, equal to 35, 24, 17, 17 and 16 J/g. Except for the ISO-3/SYN-4 and ISO-4/SYN-4 systems, all samples were shown to be totally amorphous after annealing for 7 days at 393 K, a thermal treatment previously used to remove residual complexation solvents from stereocomplexes.

Table 4 compares the melting endotherms for stereocomplexes ISO-2/SYN-5 and ISO-2/SYN-2 which both have a 1/2 stoichiometric ratio and syndiotactic contents of 82% and 74%, respectively. After being partially molten at 463 K for 1, 3 and 5 min, both complexes were crystallized for 7 days at 393 K and their melting behaviour recorded thereafter. A significant decrease in the melting endotherm of the stereocomplexes (ΔH_{m2}) can be observed at relatively short melting times. On the other hand, partial melting for longer times (5 min) provides ΔH_{m2} values which are about the same, whatever the stereoregular components within the complex. In contrast, the low-temperature melting endotherm (ΔH_{m1}) increases as a function of dissociation time. Both observations confirm that dissociation is more pronounced for ISO-2/SYN-2 as compared to ISO-2/SYN-5.

To complete this analysis, three stereocomplexes having a 1/2 stoichiometric ratio were partially molten between 463 and 483 K for a constant melting time of 1 min and then allowed to crystallize for 7 days at 393 K. These are identified as ISO-2/SYN-5, ISO-2/SYN-2 and ISO-2/SYN-1, in which the syndiotactic content for each syndiotactic PMMA was, respectively, 82%, 74% and 69%. *Figure 6* gives the melting endotherms ΔH_{m1} and ΔH_{m2} of these samples. In all three cases, a significant difference in ΔH_{m2} is seen below 470 K; beyond this temperature, it becomes small (*Figure 6*, bottom). The dissociation of the complex can be considered to be complete at 480 K.

At the same time, the melting endotherm ΔH_{m1} of PMMA ISO-2 increases with the melting temperature (*Figure 6*, top). In addition, there is a decrease in the thermal stability

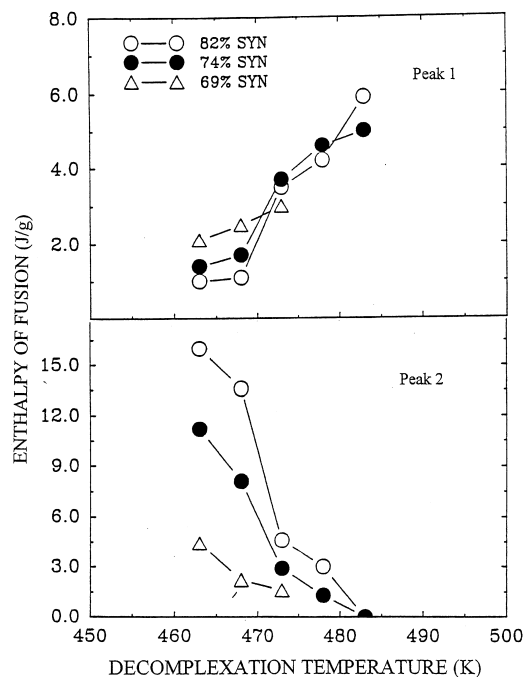


Figure 6 Variation of the melting endotherms ΔH_{m2} (bottom) and ΔH_{m1} (top) related, respectively, to the stereocomplexes and isotactic PMMA, as a function of the partial melting temperature. Heats recorded after crystallization for 7 days at 393 K

of 1/2 stereocomplexes with a reduction of their syndiotactic triad content, as previously shown in *Table 4*, since ΔH_{m2} decreases at any temperature when going from SYN-5 to SYN-1. This does not influence, however, the crystallization of isotactic PMMA.

DISCUSSION

The measurements presented above indicate that, after the stereocomplexation of isotactic/syndiotactic PMMA mixtures from solution in a so-called complexing solvent, there is a dissociation in the melt state. Afterwards, upon cooling the system, a melting endotherm appears at a much lower temperature and corresponds to the crystallization of pure isotactic PMMA. In addition, stereocomplex crystals are present but they are found in a much more disordered state than when crystallized from solution, with a melting temperature of about 430 K as compared to 480 K from solution (*Figure 3*). Moreover, annealing (without melting) the stereocomplex between 363 and 403 K also leads to a slow partial dissociation of the stereocomplex and to some crystallization of isotactic PMMA.

This phenomenon is also supported by experiments carried out with 2/1 and 1/1 isotactic/syndiotactic mixtures which lead to a larger melting enthalpy than the classical 1/2

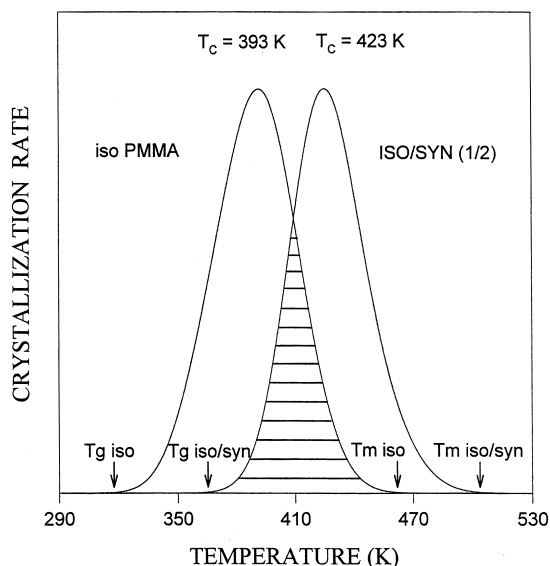


Figure 7 Schematic representation of the optimized conditions required to crystallize a mixture of isotactic and syndiotactic PMMAs

ratio (Figure 4) since the relative amount of isotactic PMMA present in these samples is larger. Similarly, a decrease in the degree of tacticity of PMMA leads to a decrease of the melting enthalpy of the stereocomplex and, simultaneously, to an increase in the melting enthalpy of the low melting peak (Figure 6). Therefore, a model is proposed to explain, first, the crystallization behaviour of an uncomplexed mixture of stereoregular PMMA chains and, second, some of the features observed during the crystallization of a partially dissociated complex.

The model assumes the coexistence of two crystalline species, isotactic PMMA and an isotactic/syndiotactic stereocomplex. As illustrated in Figure 7, the crystallization of isotactic PMMA is possible between $T_{g\text{ISO}}$ and $T_{m\text{ISO}}$, whereas crystallization of the isotactic/syndiotactic stereocomplex occurs only between $T_{g\text{ISO/SYN}}$ and $T_{m\text{ISO/SYN}}$. Therefore, at relatively low temperatures, the crystallization of isotactic PMMA is favoured, whereas, at relatively high temperatures, the crystallization of the stereocomplex occurs predominantly. In between, an intermediate zone can be found, between $T_{g\text{ISO/SYN}}$ and $T_{m\text{ISO}}$, i.e. between 370 and 450 K, where both crystalline species can exist. However, above 423 K, no melting endotherm has been observed which seems to indicate that the crystallization of the complex from the melt can only occur in a narrow range of temperature.

Schomaker and Challa also proposed the possibility of stereocomplex dissociation, following crystallization for long periods of time¹⁸ (n.b. the samples in Ref. 18 were maintained at a constant temperature, following melting for 5 min at 513 K. This thermal treatment is called 'crystallization' in this paper, instead of 'annealing' which was preferred in Ref. 18). For example, they observed that crystallization at low temperature ($T < 398$ K) leads to the formation of multiple endotherms (T_m^1 and T_m^3) at 433 and 457 K, respectively. Note that the T_m^2 peak was also mentioned but assigned to the decomplexation of complexes formed during scanning in the d.s.c. apparatus. The position of T_m^1 is strongly affected by thermal history while T_m^3 is almost constant. Schomaker and Challa also proposed that complexation occurs in two steps. First, stereoregular chains interpenetrate during complexation; then, micellar

crystallites are formed at low crystallization temperatures while more stable crystals are produced through lamellar growth at higher temperatures. According to this model, T_m^1 would correspond to the melting of complexed domains that have not sustained any lamellar growth while T_m^3 would be associated to the melt of the most stable species, the complex lamellae.

Our experiments carried out by varying the crystallization temperature and time confirm the existence of two melting endotherms that do correlate with the T_m^1 and T_m^3 peaks proposed by Schomaker and Challa. However, we suggest that peak 1 represents, more likely, the melting of crystallized isotactic chains that have not yet complexed, whereas peak 3 represents the melting of stereocomplex crystals that have crystallized more or less simultaneously with the isotactic PMMA chains.

We have attempted to obtain direct X-ray evidence of the complexation/decomplexation of PMMA chains and of the presence of isotactic PMMA crystals. Unfortunately, the powder diagrams recorded are inconclusive because the amount of crystallinity present, with enthalpies of the order of 10 J/g, is small, and the characteristic peak at $2\theta = 8.6^\circ$, which is seen in isotactic PMMA samples, is at the limit of resolution.

Finally, the times of crystallization used (and needed) here are large as compared to previous studies^{38,39}. This phenomenon must be related to the molecular weight distribution of the isotactic samples used (Table 1), which is large as compared to many published data. For example, the ISO-2 sample has a M_n similar to that of the H1 sample of Berkoukchi *et al.*³⁸, but a much larger M_w . This long chain fraction certainly slows down the crystallization and/or stereocomplexation and in addition, it favours the crystallization of the isotactic chain rather than complexation, the crystallization of isotactic PMMA being notoriously slow.

CONCLUSIONS

The stereocomplex formed in acetone, a strongly complexing solvent, between isotactic and syndiotactic PMMA leads to a broad melting peak ending at about 510 K. Annealing between 363 and 403 K, i.e. below the melting peak of the stereocomplex, leads to a significant increase of the degree of crystallinity of the stereocomplex but, also, to the appearance of a small melting peak, at about 420 K, which is assigned to the crystallization of some free isotactic PMMA chains which, obviously, are not complexed with syndiotactic PMMA.

The fusion of the stereocomplex leads to an amorphous heterogeneous phase having two broad T_g values which are close to the ones expected for immiscible blends of isotactic and syndiotactic PMMAs. In the bulk, at temperatures well below its melting peak, there is a slow crystallization of isotactic PMMA which reaches its largest enthalpy of fusion at $T_c = 393$ K.

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