Stereocomplex formation in polybutadiene–syndiotactic poly(methyl methacrylate) block copolymers blended with isotactic poly(methyl methacrylate)

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The process of stereocomplexation in the bulk between isotactic poly(methyl methacrylate) and a polybutadiene–syndiotactic poly(methyl methacrylate) diblock copolymer was studied by differential scanning calorimetry as a function of composition of the blends, annealing time and temperature. The amount of complex formed is dependent on these three parameters, while the temperature of decomposition of the complex is only dependent on the temperature of annealing. One endotherm of decomposition was observed, in contrast to poly(methyl methacrylate) homopolymer blends, for which two endotherms referred to as T_{m1} and T_{m3} were generally reported. On the basis of a model proposed by Challa *et al.*, the endotherm can be identified with T_{m1}. The absence of the second endotherm can be explained by the presence of the 'foreign' elastomer sequence preventing the formation of the lamellar crystals attributed to T_{m3} in the model. For annealing temperatures larger than 140°C, no complex is formed.

(Keywords: stereocomplexes; poly(methyl methacrylate); polybutadiene; block copolymers; blends; differential scanning calorimetry)

INTRODUCTION

It has been known for a long time that mixing of syndiotactic poly(methyl methacrylate) (sPMMA) and isotactic poly(methyl methacrylate) (iPMMA) in suitable solvents leads to the formation of a stereocomplex[1]. The parameters that govern the process of stereocomplexation have been extensively studied by Spevacek[2–4], Challa[5–7] and others[8–10] and recently reviewed by Spevacek[11].

Over the past few years, by means of differential scanning calorimetry, Challa *et al.*[12,13] have shown that this phenomenon also occurs in bulk. In that case, multiple endotherms with different characteristics assigned as T_{m1}, T_{m2} and T_{m3} are observed. The endotherm labelled T_{m2} is ascribed to the decomposition of the complex formed during scanning. The two endotherms T_{m1} and T_{m3} are interpreted respectively as the decomposition of complexed PMMA sections partly organized into fringed micellar clusters and the decomposition and melting of lamellar crystallites.

The temperature of decomposition is mainly governed by the temperature of annealing of the blends, and values of the order of magnitude of 210°C have been reported. The stoichiometry of the stereocomplex has been a point of controversy for a long time[11]. Challa and coworkers in a series of papers[13–16] have finally proposed a composition i/s = 1/2 for the stereocomplex whatever the conditions of preparation.

Until now, the formation of the stereocomplex was focused exclusively on homopolymer blends. Such complex formation in blends containing block copolymers (AB, ABA or star) is expected to lead to intermolecular physical linkages promoting enhanced or novel properties. For example, in blends of iPMMA homopolymers with ABA copolymers (where A is an sPMMA block and B an elastomer block), we can expect that the formation of the complex will increase the useful temperature range of the ABA thermoplastic elastomer, which is limited to the T_g of the sPMMA hard block in the absence of stereocomplex formation. Similarly, blending of iPMMA with a three-arm star block copolymer A_3B should lead to the formation of thermoplastic elastomers with enhanced properties.

As a first step, we have studied by means of d.s.c. the stereocomplex formation in bulk upon mixing polybutadiene–syndiotactic poly(methyl methacrylate) AB block copolymers (PB–sPMMA) with iPMMA. The influence of parameters such as annealing time, annealing temperature and composition upon the complexation process has been investigated.

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Table 1 Molar masses and stereoregularity of iPMMA and PB–sPMMA samples used. $\bar{M}_p/\bar{M}_n$ corresponds to the molar-mass distribution for iPMMA and copolymer

	PMMA			PB	
	$\bar{M}_n$	i-h-s	$\bar{M}_p/\bar{M}_n$	$\bar{M}_n$	1,4 (%)
iPMMA	44 000	94/4/2	1.2	–	–
PB–sPMMA	4 500	5/15/80	1.3	4 500	85

EXPERIMENTAL

Synthesis and characterization of the polymers

Polybutadiene–syndiotactic poly(methyl methacrylate) AB block copolymers were prepared according to the method described in a previous paper[17] and involved the t-butyllithium-initiated anionic polymerization of butadiene in benzene at room temperature followed by addition of a tetrahydrofuran (THF) solution of 1,1-diphenylethene. At this stage the precursor PB anion was separated into several portions, one of which was protonated (CH_3OH) and used to determine the polydispersity and M_n by s.e.c. using PB standards.

The other portions of the precursor PB anion were used for the preparation of several copolymers by addition of various amounts of MMA by distillation of the MMA into the reaction vessel kept at −78°C.

The 1,2 and 1,4 contents of the PB block were determined by ^1H n.m.r. spectroscopy of $CDCl_3$ solutions at 200 MHz (Varian XL 200 spectrometer) using the integrations of the signal at 4.9 ppm of the two protons of the 1,2 double bond and of the signal at 5.4 ppm of the proton CH= of the 1,2 double bond and of the two protons -CH=CH- of the 1,4 units.

From the above results, we can determine the DP_n corresponding to the 1,2 units. The comparison of the intensity of the signals due to the two protons of the 1,2 units with that of the O–CH_3 signal of the MMA units in the copolymer allows us to determine the M_n of the PMMA block.

Monodisperse isotactic poly(methyl methacrylate) was prepared according to the method of Hatada[18] (*Table 1*).

Average molar masses and molar-mass distribution of iPMMA were determined by size exclusion chromatography using a Waters 6000 A liquid chromatograph equipped with a Perkin–Elmer LC 75 u.v. detector. A calibration curve was used based on PMMA standards.

The tacticity of the iPMMA homopolymer and the sPMMA segments of the block copolymers was obtained from proton n.m.r. of the α-methyl groups. The results are summarized in *Table 1*.

Preparation of the blends

The blends were prepared by dissolution of PB–sPMMA and iPMMA in chloroform and subsequent quantitative precipitation in hexane. The samples were dried in high vacuum for two days at room temperature.

Differential scanning calorimetry

D.s.c. measurements were conducted using a Perkin–Elmer DSC-4 apparatus calibrated with indium and cyclohexane. Glass transition temperatures were recorded at the half-height of the corresponding heat capacity jump, and the decomposition temperatures T_d were determined at the maximum of the corresponding endotherm. A heating rate of 10°C min^{-1} and a cooling rate of 100°C min^{-1} were used unless otherwise stated.

After insertion of the pan in the d.s.c. cell, the samples were heated to 200°C and kept at this temperature for 2 min in order to remove any traces of solvent and thermal history. Then, they were cooled to 0°C. A second run from 0 to 200°C was performed to obtain the T_g values of the non-complexed blends, and after 2 min at 200°C the samples were cooled to the selected annealing temperatures (T_a). After annealing, the samples were cooled to 0°C. Then a third run from 0 to 200°C was performed to determine the T_g, T_d and ΔH (enthalpy of decomposition) of the complexed blends. Finally, after 2 min at 200°C and rapid cooling to 0°C, a fourth d.s.c. run was performed for the purpose of comparison with the results of the second run.

The T_g values of the elastomer blocks were measured for the copolymer and some blends but no systematic measurements were performed on the different annealed samples.

RESULTS AND DISCUSSION

The formation of the stereocomplex was studied for six blend compositions (i/s = 25/75, 35/65, 42/58, 50/50, 58/42 and 79/21), five annealing temperatures (100, 110, 120, 130 and 140°C) and five annealing times (1, 2, 15, 40 and 64 h).

Influence of the annealing time

Typical thermograms are represented in *Figure 1*. These thermograms show a glass transition T_g corresponding to the non-complexed part of the blend and one endotherm attributable to the decomposition. The area of the endotherm was found to increase with annealing time (t_a).

The corresponding enthalpy of decomposition ΔH reaches a limiting value after 64 h of annealing (*Figure 2*). This behaviour is observed whatever the i/s ratio and the annealing temperature. No endotherm is observed for samples of PB–sPMMA or iPMMA separately annealed in the same conditions. Thus, one can conclude that the presence of a PB block attached to the sPMMA chain does not prevent stereocomplex formation in bulk. Similar results have been obtained in solution[19].

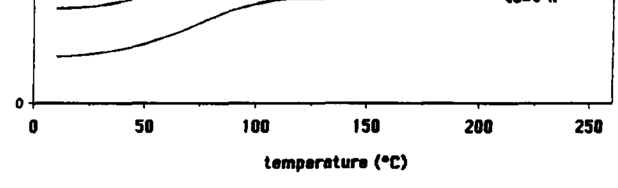

Figure 1 D.s.c. traces of (PB–sPMMA)/iPMMA blends after annealing at 120°C for various times (i/s = 42/58)

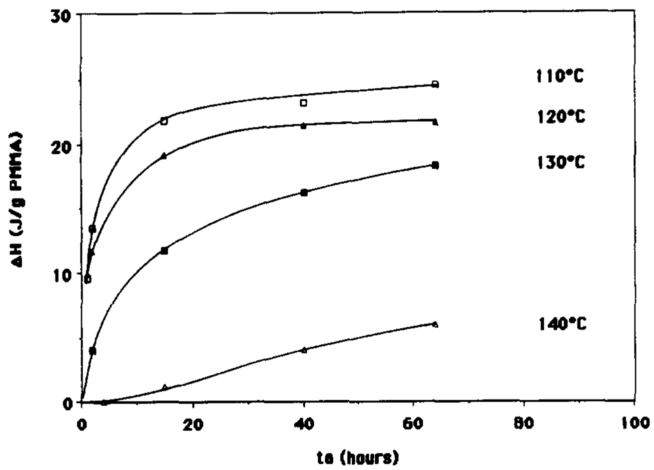

Figure 2 Heat of decomposition per gram of PMMA as a function of annealing time t_a at different annealing temperatures (i/s = 42/58)

Table 2 Influence of PMMA blend composition on the enthalpy of stereocomplex decomposition (in J/g PMMA) for various annealing temperatures (t_a = 64 h)

Composition i/s	Annealing temperature, T_a (°C) 100	110	120	130	140
25/75	6.7	9.6	10.3	8.7	1.0
35/65	18.3	16.2	16.0	11.2	1.4
42/58	23.4	24.6	21.6	18.4	6.0
50/50	22.2	20.5	19.7	15.6	6.3
58/42	19.2	17.7	14.4	12.6	5.5
79/21	10.8	9.5	8.2	7.0	3.8

Though complex formation in our blends has many characteristics similar to those observed by Challa and coworkers for homopolymer blends (see below), the kinetics of the process presents some differences. In homopolymer blends, complex formation is detectable after annealing for 2 min[12] while with (PB–sPMMA)/iPMMA blends no endotherm is found for up to half an hour. After 1 h of annealing, a significant part of the complex is formed compared with the limiting value at 64 h. For example at $T_a = 110°C$ and for an i/s ratio of 42/58, ΔH increases from about $10\,J\,g^{-1}$ at 1 h to $25\,J\,g^{-1}$ at 64 h. Thus after 1 h 40% of the final value is reached. Keeping in mind the absence of a significant quantity of stereocomplex after 30 min, complex formation apparently proceeds in three steps: an induction period followed by a strong acceleration of the complexation rate during roughly 2 h and then a gradual decrease of the rate to reach zero for times higher than 64 h. This behaviour is observed whatever the i/s ratio.

It is noteworthy that for higher annealing temperatures, mainly at $T_a = 140°C$, the induction period increases. The induction period could be due to the influence of the elastomeric block. However, in preliminary experiments conducted with PMMA homopolymers of similar molar masses and stereoregularities, we have observed that the kinetics of complex formation presents similar induction periods. Thus the absence of an induction period in the case of the systems studied by Challa is more probably related to differences in molar masses of PMMA. Indeed, molar masses of PMMA samples used by Challa *et al.* were approximately 100 times higher than ours[12].

Influence of the annealing temperature

Figure 2 shows that, for a given annealing time, the amount of complex formed decreases as the annealing temperature T_a increases. No endotherm is found for $T_a > 140°C$ in the range of annealing times explored. The enthalpy of decomposition obtained after annealing for 64 h, at various i/s compositions and annealing temperatures, is reported in *Table 2*. We can see that the decrease of ΔH with increasing T_a is a general trend whatever the i/s ratio except for the 25/75 blend composition in the 100–120°C region. For this blend, owing to the high sPMMA content, the glass transition temperature of the PMMA blend is high ($T_g = 85°C$) compared to that of other blend compositions (*Figure 3*). Thus at $T_a = 100°C$ complexation takes place in a highly viscous medium, reducing the mobility of the PMMA chains. An increase of T_a reduces the viscosity so that more complex is formed ($\Delta H = 9.6\,J\,g^{-1}$ at $T_a = 110°C$; $\Delta H = 10.3\,J\,g^{-1}$ at $T_a = 120°C$). However, this effect is limited and for $T_a = 130°C$ the general tendency observed for other i/s ratios reappears.

This tendency is in contrast with the results of Challa *et al.*[13]. Although they observe an increase of ΔH *versus* annealing time as we do, the amount of complex increases with increasing annealing temperature. This behaviour is explained on the basis of a model taking into account the formation of two types of superstructures composed of complexed chains called fringed-micelle crystallites and lamellar crystals, leading to the observation of two endotherms referred to as T_{m1} and T_{m3} ($T_{m1} < T_{m3}$) respectively. At low annealing temperatures, the rapid formation of the complex and subsequent partial organization into fringed-micelle crystallites act as physical crosslinks, thus reducing the mobility of the non-complexed part of the PMMA chains and limiting the amount of complex formed. If T_a is increased, the formation of lamellar crystals more stable than fringed-micelle crystallites is favoured. In that case, Challa *et al.* claim that the mobility in the amorphous matrix is not influenced and a limiting value is reached only when the system approaches the state of complete crystallinity. Thus for $T_a > 135°C$, only one endotherm corresponding to T_{m3} is observed.

For (PB–sPMMA)/iPMMA blends, only one endotherm was found whatever the i/s ratio, the annealing time and the annealing temperature. The value of T_d corresponding to the maximum of the endotherm is independent of the i/s ratio and annealing time. It only depends on the annealing temperature and a linear

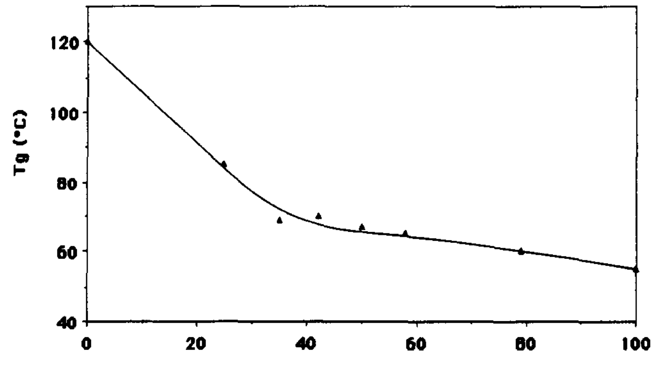

Figure 3 Glass transition of the PMMA phase as a function of isotactic content (unannealed blends)

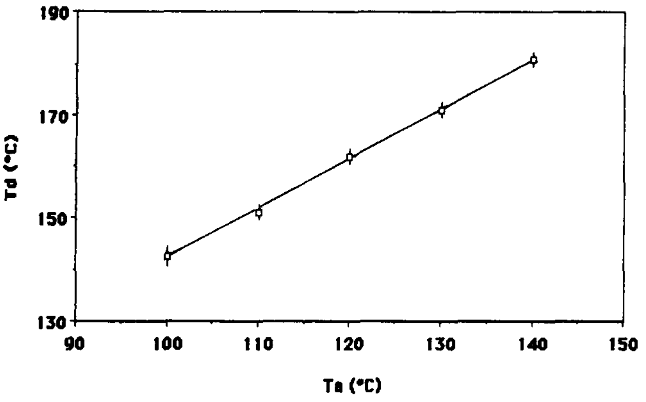

Figure 4 Variation of T_d as a function of annealing temperature T_a for different blend compositions and annealing time. Bars represent the maximum dispersion observed

correlation with a slope of one is obtained (*Figure 4*), in complete agreement with the results of Challa *et al.* for the variation of T_{m1}. On the basis of their model, the observation of only one endotherm for (PB–sPMMA)/iPMMA blends with characteristics identical to T_{m1} can be attributed to the presence of the 'foreign' elastomer sequence attached to the sPMMA chains preventing the formation of highly organized superstructures such as lamellar crystals.

The increase of T_d with T_a is of considerable interest. Here again, the reference is the model proposed by Challa *et al.*[13]. If the proposed lamellar crystals are formed, corresponding to T_{m3}, decomposition may be prevented below the melting temperature of these crystals. However, the endotherm can be ascribed for the major part to complex decomposition provided that the size of the crystals is sufficiently small. Challa *et al.* have proposed that the stability of the fringed-micelle crystallites is close to that of the complex itself. Using this assumption, in the case of our blends, T_d is a measure of the stability of the complex and the corresponding ΔH is a measure of the amount of complex formed as initially assumed in the first part of this paper. Then, the increase of T_d with T_a can be ascribed to the formation of complexed sections of sPMMA and iPMMA chains involving a larger number of monomer units as T_a increases. The limit of $T_a = 140°C$ for complex formation could then be attributed to the shortness of sPMMA chains ($M_n = 4500\ \mathrm{g\ mol^{-1}}$). On the other hand, despite the use of high-molar-mass sPMMA ($M_n = 380000\ \mathrm{g\ mol^{-1}}$), Challa and coworkers obtained the same value of T_d for a given value of the annealing temperature as we do and the disappearance of the endotherm T_{m1} corresponds to a value of T_a higher than 135°C (close to the value of 140°C obtained in our case).

This indicates that, even with polymers of high molar mass, each complexed entity is composed of a relatively small number of PMMA units. This number can be estimated to be smaller than 45 sPMMA units on the basis of the M_n value of the sPMMA segments of the block copolymer ($M_n = 4500\ \mathrm{g\ mol^{-1}}$).

The width of the endotherm of decomposition is also dependent on the annealing temperature. The width was defined as $\Delta T = T_f - T_i$, being the difference of the temperatures at the end (T_f) and the beginning (T_i) of the endotherm. For $t_a = 64$ h, ΔT decreases from ~60°C at $T_a = 100°C$ to 30°C at $T_a = 140°C$. For a given annealing temperature, T_i and T_f increase with t_a and ΔT decreases. The effect is the more pronounced the lower the annealing temperature. At $T_a = 140°C$, ΔT is independent of t_a. These results could be explained by the formation, in a first step at low annealing temperatures, of shorter complexed sections that are poorly organized and tend to rearrange with time in a longer, more perfect stereochemical match. As T_a increases, the formation of these short, poorly organized sections is more and more hindered owing to their instability. If T_a is sufficiently high, only well organized complexed sections are stable and no rearrangement with time is observed.

The decrease of ΔH as T_a increases can be related to the increase of the minimum stereoregular sequence length necessary for complex formation. As sPMMA and iPMMA are not perfectly stereoregular (*Table 1*), the number of stereoregular sequences having the appropriate length decreases as T_a increases. Owing to lower stereoregularity and molar mass, sPMMA is expected to have a stronger influence than iPMMA.

Influence of the composition

The variation of the enthalpy of decomposition *versus* blend composition represented in *Figure 5* shows a maximum for an iPMMA content of 42–45%. This optimal composition is not significantly dependent on annealing time. Curves for other annealing temperatures lead to the same maximum. These results do not permit one to draw conclusions about the stereocomplex stoichiometry itself but indicate only the overall blend composition for which the larger amount of complex is obtained.

The efficiency of complex formation E defined as:

$$E = \frac{\Delta H_{\mathrm{exp}}}{\Delta H_{\mathrm{m}}} \times 100$$

versus i/s ratio can be calculated assuming a stoichiometry i/s = 1/2 and an energy of stabilization of 100 J $\mathrm{g^{-1}}$ PMMA[16]. Here ΔH_{exp} is the measured enthalpy of decomposition for 1 g of PMMA (i + s) and ΔH_m is the corresponding value expected for maximum complex formation.

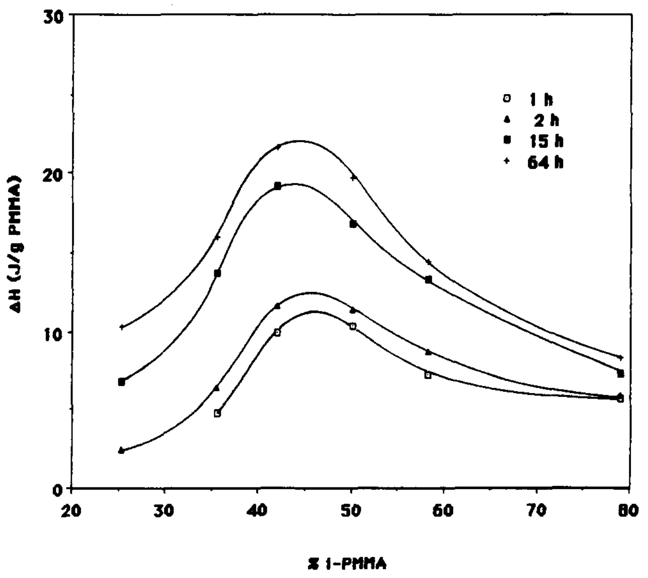

Figure 5 Heat of decomposition as a function of blend composition after different annealing times (annealing temperature $T_a = 120°C$)

Table 3 Efficiency of complex formation on assuming a 1/2 stoichiometry of the stereocomplex and an energy of complex formation $\Delta H = 100$ J/g PMMA. Annealing temperature is 110°C and annealing time 64 h

Composition i/s	ΔH_m (J/g PMMA)	ΔH_{exp} (J/g PMMA)	Efficiency, E
25/75	75	9.6	12.8
35/65	97.5	16.2	16.6
42/58	87	24.6	28.1
50/50	75	20.5	27.3
58/42	63	17.7	28.1
79/21	31.5	9.5	30.2

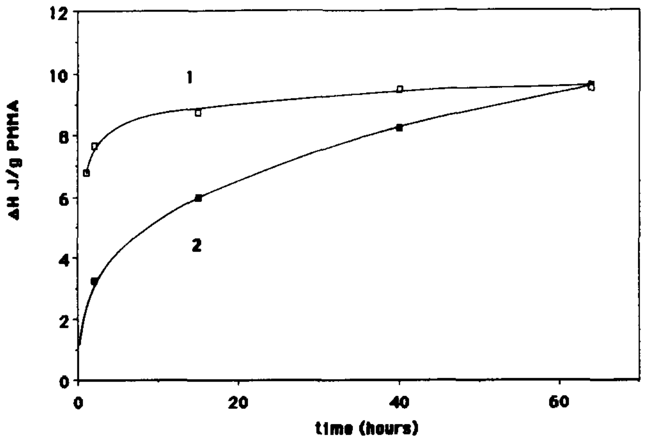

Figure 6 Variation of the enthalpy of decomposition as a function of annealing time for two i/s compositions: 79/21 (curve 1) and 25/75 (curve 2). Annealing temperature is 110°C

Table 4 Influence of the scan rate on the temperature and enthalpy of decomposition. i/s = 42/58, $t_a = 40$ h, $T_a = 110$°C

Scan rate (°C min^{-1})	T_d (°C)	ΔH ($\mathrm{J\,g^{-1}}$)
5	149	23.1
10	150	23.7
20	155	23.5
40	160	22

Thus, for a 50/50 blend composition, the potential maximum amount of complex in 1 g of blend is 0.75 g (0.25 g iPMMA + 0.50 g sPMMA; the residual 0.25 g corresponds to non-complexed iPMMA), leading to $\Delta H_m = 75\ \mathrm{J\,g^{-1}}$. Using ΔH values at 110°C and $t_a = 64$ h, the efficiency can be calculated for each blend composition (*Table 3*). One could expect to obtain the maximum efficiency for a blend composition corresponding to the stoichiometry of the complex. However, at an i/s composition of 35/65, which is close to stoichiometry, the calculated efficiency is low (16.6%). For higher iPMMA contents, E increases up to a value of about 28%, which remains roughly constant. The higher value (30.2%) is obtained for a large excess of iPMMA (i/s = 79/21). The same behaviour is observed for other annealing temperatures. This can be explained by the non-symmetrical role of iPMMA and sPMMA chains in the complex formation. Indeed, the iPMMA homopolymer chains are free to move while the mobility of sPMMA chains is restricted by the PB sequences, which are in a separate phase (as shown by the presence of a glass transition at −90°C).

Furthermore, although a single glass transition is observed for the PMMA phase whatever the i/s ratio, the width of the transition zone increases with increasing sPMMA content and for i/s = 25/75 exceeds (50–60°C) the width observed for iPMMA (15°C) and PB-sPMMA (40°C) scanned separately. This broadening has been observed in some miscible polymer blends and was generally interpreted as being due to incomplete miscibility at the molecular level[20]. One may expect then that for high sPMMA content the distribution of iPMMA and sPMMA units is not homogeneous and complexation is hindered for a portion of the sPMMA chains. An excess of iPMMA of course increases the probability to find iPMMA units in the vicinity of sPMMA units, and consequently increases the probability of complexation. This is illustrated in *Figure 6* for two blends corresponding to approximately opposite compositions and leading to similar end values of ΔH. With an excess of iPMMA (i/s = 79/21, curve 1), complexation takes place rapidly, and after a short annealing time ΔH is close to the end value corresponding to a high efficiency (30.2%). With an excess of sPMMA (i/s = 25/75, curve 2), complexation increases more slowly and reaches an end value corresponding to a very low efficiency (12.8%).

Influence of the scan rate

The influence of the scan rate on the characteristics of the endotherm of decomposition is presented in *Table 4*. The enthalpy of decomposition is unchanged, while T_d increases with the scan rate as observed by Challa *et al.*[13] for T_{m1} in the case of homopolymer blends.

CONCLUSIONS

In this paper, we have shown that the formation of a stereocomplex between isotactic PMMA and polybutadiene–syndiotactic PMMA block copolymers is not hindered by the presence of 'foreign' elastomer sequences linked to sPMMA chains. Despite the use of sPMMA of relatively short chain length ($DP_n \sim 45$), the stereocomplex formation is similar to that observed with homopolymers of higher molar masses. The minimum sequence length necessary for complex formation appears to be lower than the values previously reported. This point will be discussed in a following paper.

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