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

2. Influence of molar masses

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Summary

The process of stereocomplexation in blends of isotactic poly(methyl methacrylate)s and polybutadiene-syndiotactic poly(methyl methacrylate) diblock copolymers was studied by differential scanning calorimetry as a function of molar mass of the constituents, 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 annealing temperature. Complex formation can be observed in blends containing a copolymer with a very low molar mass syndiotactic poly(methyl methacrylate) block (Mn=700). In contrast to homopolymer blends, for which two endotherms of decomposition were generally reported, only one endotherm is observed for copolymer-homopolymer blends. This behavior is attributed to the elastomer block.

Introduction

Stereocomplex formation between isotactic and syndiotactic poly(methyl methacrylate)s (iPMMA and sPMMA), in solution in suitable solvents and in bulk, has been extensively studied (1-8). The stoichiometry of the stereocomplex has been a point of controversy for a long time (9). From a series of papers by Challa et al. (8,10-12), a composition i/s=1/2 was finally proposed for the stereocomplex whatever the conditions of preparation. Thermal analysis of the stability of the complex revealed the existence, in the more general case, of two overlapping endotherms of decomposition. A model of the stereocomplex formation developped by Challa et al. (8) attributed the two endotherms to the decomposition of the complex involved in superstructures of different thermal stability, namely fringed micellar clusters and lamellar crystallites (endotherms referred as T_{m1} and T_{m3} respectively).

In a previous paper (13), we have shown that complex formation could be observed in annealed blends of a polybutadiene-syndiotactic poly(methyl methacrylate) AB block copolymer (PB-sPMMA) with iPMMA. Among the differences with homopolymer blends, the more striking feature was the observation of only one endotherm of decomposition whatever the i/s ratio, annealing time (t_a) and temperature (T_a). Furthermore, the temperature of decomposition (T_d) was

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found to depend only on T_a, and the variation of T_d versus T_a was in complete agreement with that observed for T_{m1} by Challa et al.. Hence, on the basis of the model proposed by these authors, one could conclude that no lamellar crystallites were formed in PB-sPMMA/ iPMMA blends. This behavior could be attributed to the "foreign" PB block preventing the formation of highly organized superstructures. These results were obtained for a given homopolymer-copolymer pair. The present paper deals with the influence of the molar masses of the sPMMA block of the copolymers and iPMMA homopolymers on the stereocomplex formation.

Experimental

The methods of synthesis and characterization of the polymers have been described in previous papers (13,14). Molar masses and stereoregularity of iPMMA and PB-sPMMA samples used are reported in Table 1.

Table 1 Molar masses and stereoregularity of iPMMA and PB-sPMMA samples used. Mp/Mn corresponds to the molar mass distribution for iPMMA and copolymers

	Acronym	PMMA			PB	
		$\bar{M}n$	%Tacticity	$\bar{M}p/\bar{M}n$	$\bar{M}n$	1,4 (%)
iPMMA	H1	44000	94	1.2	-	-
	H2	5000	95	1.2	-	-
PB-sPMMA	C1	4500	80	1.3	4500	85
	C2	2700	81	1.1	4500	85
	C3	700	76	1.2	4500	85

Preparation of the blends

The blends were prepared by dissolution of PB-sPMMA and iPMMA in chloroform and subsequent quantitative precipitation in hexane, except those containing C3. They were then dried under vacuum for two days at room temperature.

C3 is a viscous liquid at room temperature. The corresponding blends were obtained by direct evaporation under vacuum of the chloroform.

Differential scanning calorimetry

D.s.c. measurements were conducted using a Perkin-Elmer DSC-4 apparatus calibrated with indium and cyclohexane. Glass transition temperatures T_g 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 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 minutes 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 minutes at 200°C, the samples were cooled to the selected annealing temperature (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 minutes 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 copolymers and some blends but no systematic measurements were performed on the different annealed samples.

Results and Discussion

In a previous paper (13), using H1C1 blends, we have shown that complex formation was dependent on blend composition, annealing time and temperature. The larger amount of complex was obtained for i/s=42/58, whatever the annealing time and temperature. In the work presented here, this composition was used for all the blends. The formation of the stereocomplex was studied for annealing temperatures ranging from 90 to 140°C and four annealing times (2,15,40 and 64h).

General aspect of the d.s.c. trace

As mentioned in the introduction, stereocomplex formation in H1C1 homopolymer-copolymer blends previously studied (13), led to thermograms presenting only one endotherm of decomposition. Here again, only one endotherm was observed whatever the annealing time and temperature.

Influence of the annealing time

The variation of the enthalpy of decomposition ΔH versus t_a is illustrated in Figure 1. The rate of complex formation is high at short annealing times and tends towards zero for times larger than 64h, for all the blends. Furthermore, in the limits of ± 2°C, no variation of the temperature of decomposition Td versus t_a was observed. These results are similar to those previously obtained for H1C1 blends. For H1C3, complex formation was only observed for t_a=64h at T_a=110°C, and ΔH was very weak (1 J/g). For H2C3 no complex formation was observed whatever the time and temperature of annealing. These two results will be discussed in the chapter devoted to the influence of molar masses.

Influence of the annealing temperature

The variation of ΔH versus T_a for t_a=64h, is presented in Figure 2 together with the results previously obtained for H1C1 (and completed for T_a=90°C). For H1C2, H2C2 and H2C1, no complex is formed at T_a=140°C. For the blends containing H1

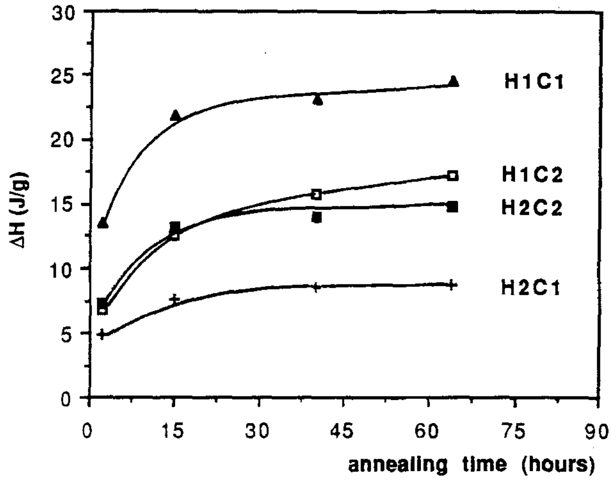

Figure 1: Enthalpy of decomposition as a function of annealing time at Ta = 110°C

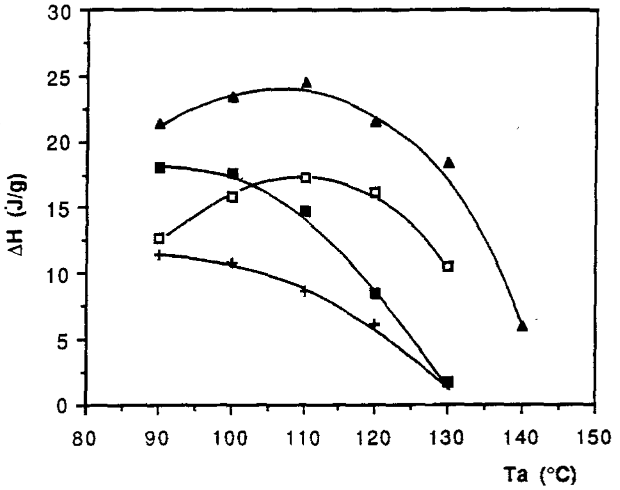

Figure 2: Enthalpy of decomposition as a function of annealing temperature at ta = 64h.
▲ H1C1 ; □ H1C2 ; ■ H2C2 ; + H2C1

a maximum is observed at T_a=110°C, while a continuous decrease occurs for H2 blends. Owing to the shape of the curves for H2C2 and H2C1, a maximum could be expected at a temperature near or lower than 90°C. Unfortunately, this assumption could not be verified for experimental reasons. Indeed, as previously discussed (13), the width of the endotherm increases as T_a decreases. Then, the lower are the annealing temperature and the amount of complex formed, the larger is the error on the determination of the endotherm area. Moreover, as T_d decreases with

T_a, the endotherm of decomposition tends to overlap the end of the glass transition signal at low annealing temperatures.

The variation of T_d versus T_a (Figure 3) is linear, close to that previously observed for H1C1 and independent of the homopolymer-copolymer pair. The single value obtained for H1C3 (T_d=151°C) is on the same line. Assuming that the value of T_d is associated with the size of the complexed sections, one can conclude that the annealing temperature is the size governing parameter.

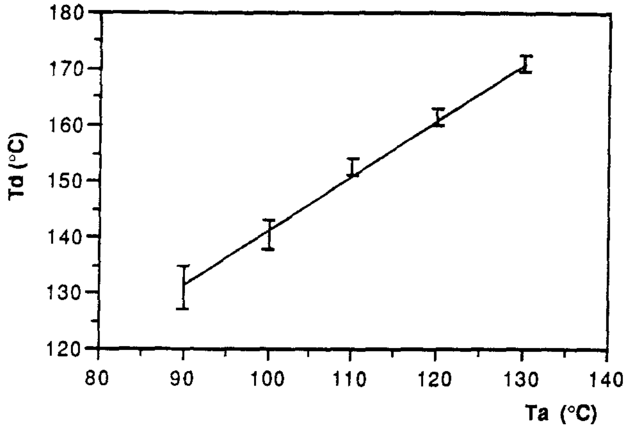

Figure 3: Variation of Td as a function of annealing temperature for the different blends. Bars represent the maximum dispersion observed.

Influence of the molar mass

As shown in Figure 2, the influence of the molar mass of the iPMMA homopolymer and the sPMMA block of the copolymer on ΔH cannot be separated from the influence of the annealing temperature. Indeed, on the one hand at T_a=110°C a large difference is observed between H1C1(ΔH=24.6 J/g) and H2C1(ΔH=8.6 J/g), while for H1C2 and H2C2 similar values (17.2 and 14.8 J/g respectively) are obtained. On the other hand, at T_a=130°C, a large difference between H1C1 and H2C1 remains and is also observed for H1C2 and H2C2. As previously reported (13), this dependence on T_a is related to the increase of the minimum stereoregular sequence length necessary for complex formation as T_a increases. Consequently, at a given annealing temperature, the number of stereoregular sequences having the appropriate length decreases with the molar mass. Thus, at T_a=140°C, complex formation is only observed for H1C1 while, at T_a =130°C, it takes place also in H1C2 . This indicates that the critical chain length of the sPMMA block at T_a = 140°C is larger than 27 monomer units and lower than 45.

At T_a = 130°C, a decrease of the molar mass of iPMMA does not impede complex formation, but the values of ΔH are low and similar for H2C1 and H2C2. This shows that the critical chain length for iPMMA is approximately the same as for sPMMA. However, as T_a decreases, the amount of complex is larger for H2C2 than for H2C1. This could be attributed to both the restricted mobility of sPMMA chains, attached to the PB sequences which are in a separate phase, and the mean number of sPMMA chains which is, for the same i/s composition, two times larger for H2C2 than for H2C1.

The maximum observed in figure 2 for H1C1 and H1C2 at T_a=110°C and expected for H2C1 and H2C2 at (or near) 90°C could result from a balance, as T_a decreases, between the easiness of complex formation (resulting from the decrease of the minimum stereoregular sequence length) and the increase of the viscosity. The later is governed by the difference T_a - T_g and, as complexation takes place, by the amount of complex already present. On this basis, one could expect a decrease of the temperature of the maximum as a result of the decrease of the glass transition temperature of the blends with the molar mass of the constituents. This assumption does not hold. Indeed, as shown in Table 2, a decrease of T_g with the molar mass is observed for the polymers but not reflected on the blends.

Table 2 Glass transition temperatures of PMMA for polymers, copolymers and blends used

	iPMMA		PB-sPMMA			Blends			
Acronym	H1	H2	C1	C2	C3	H1C2	H2C2	H2C1	H1C3
T_g (°C)	55	51	120	89	55*	68	60	70	60*

* heating rate 40°C/min.

Though numerous studies have been devoted to PMMA stereocomplex formation, nearly all have been for polymers with molar masses greater than 20,000. In the low molar mass range, only some examples on complex formation (in solution) have been reported (1,15,16). For Spevacek and Schneider (1) a critical syndiotactic sequence length of about 10 units is necessary for complex formation whatever the molar mass of sPMMA, while Schomaker et al. (15) reported a critical chain length (for sPMMA in the presence of a long iPMMA matrix) depending on the fraction x_s of sPMMA oligomers and corresponding to approximately 60 units for x_s = 0.4. Furthemore, Buese et al. (16), observed some complexation using sPMMA with a degree of polymerization of 37 and a syndiotactic content of 80.9%. In the present study, as already indicated, some complex formation was observed with H1C3 at T_a=110°C. This shows that the degree of polymerization can be as low as 7. Moreover, as the temperature of decomposition is the same as for the other blends, one can conclude that the size of the complexed entities is small, included with polymers of high molar mass. The increase of the annealing temperature leads to complexed entities of larger size and consequently of higher temperature of decomposition, but the size remains limited to some tens of units despite the use of polymers of very high molar mass. Indeed, Challa et al. (8), using PMMAs with molar masses larger than 10^6 reported a temperature of decomposition of 180°C for blends annealed at T_a=140°C, i.e. the same value as observed in our previous study for H1C1.

The last point to discuss is the observation of only one endotherm for copolymer-homopolymer blends. It may be reminded that the observation of a second endotherm, with homopolymer blends, was attributed by Challa et al. (8) to complexed sections involved in lamellar crystallites. The absence of this endotherm was previously attributed (13) to the elastomer block which is in a separate phase, preventing the formation of highly organized superstructures. The present work tends to confirm this assumption. However, the model developped by Challa et al. was based on results obtained with homopolymers of molar masses more than ten times larger than the samples used in this work. Consequently, the influence of the molar mass cannot be totally excluded. In order to check this point, complex formation in homopolymer blends using low molar mass PMMAs has been carried out. The results will be reported in a forthcoming paper.

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