

Stereocomplexation of sPMMA–PBD–sPMMA triblock copolymers with isotactic PMMA. II: Effect of molecular weight

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Thermoplastic elastomers consisting of triblock copolymers (MBM) with outer syndiotactic poly(methyl methacrylate) (sPMMA) blocks associated to an inner polybutadiene (PBD) block have been modified by stereocomplexation with isotactic PMMA (iPMMA) at a constant 2/1 sPMMA/iPMMA (or s/i) mixing ratio. Toluene cast films of these stereocomplexes have been studied by thermal analysis as a function of molecular weight of the sPMMA blocks and the iPMMA homopolymer. Although the melting temperature of the stereocomplex (T_m) is independent of molecular weight of the sPMMA blocks (\bar{M}_n sPMMA) in the studied range from 7000 to 46 000, the melting enthalpy increases with increasing \bar{M}_n sPMMA. This effect is, however, erased by the sample annealing at 140°C for 15 h, and a melting enthalpy of ca. 33 J/g total PMMA is then observed whatever the copolymer composition. One melting endotherm is observed in case of low \bar{M}_n sPMMA, although two melting endotherms are reported for higher \bar{M}_n sPMMA depending, however, on the heating rate. Two endotherms are indeed observed at small \bar{M}_n sPMMA as the heating rate is low. Molecular weight of iPMMA has no significant effect on either the melting temperature or the melting enthalpy of the stereocomplexes. Dynamic mechanical analysis has confirmed the phase separation of the complexed triblock copolymers. At constant molecular weight of PBD and iPMMA, stereocomplexation increases the tensile strength of MBM copolymers containing small sPMMA blocks, whereas the opposite effect is observed for longer sPMMA blocks. When the same MBM copolymer is complexed by iPMMA, the tensile properties are independent of the molecular weight of iPMMA at least in the range from 5000 to 74 000. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Thermoplastic elastomers have been extensively investigated since the discovery of the styrene–butadiene–styrene triblock copolymers (SBS)^{1–11}. The increasing attention paid to these materials mainly results from their unique thermomechanical properties, controlled by the reversible crosslinking of the rubber phase by dispersed thermoplastic microdomains. The tensile properties of thermoplastic elastomers depend on the ability of the hard blocks to sustain a plastic deformation under stress. The upper service temperature of SBS is dictated by the glass transition temperature (T_g) of PS (100°C). Many efforts have been made in order to improve the thermal performances of these materials, such as chemical modification of the PS block^{4,5}, and blending of SBS with high T_g polymers miscible to PS⁶. Another efficient method consists in substituting a polymer of higher T_g for PS. For instance, Morton *et al.*¹ have explored the use of poly(α -methylstyrene), the T_g of which is higher than polystyrene by 70°C. The low ceiling temperature of this polymer, however, makes the synthesis of the triblock copolymer less attractive. Poly(ethylene sulfide)² has also been considered as a substitute for polystyrene, but the related triblock copolymers have poor ultimate mechanical properties. Poly(*t*-butyl methacrylate) has been considered by McGrath *et al.*^{7,8} as outer block of a T_g (115°C)

higher than polystyrene, with the additional advantage of forming ionomer upon hydrolysis⁹.

Very recently, poly(methyl methacrylate) (PMMA)^{10–14} has been reported as a valuable candidate for the outer block of triblocks. Indeed, syndiotactic PMMA (sPMMA) has a rather high T_g (ca. 125°C) and the unique properties of forming a stereocomplex with isotactic PMMA (iPMMA)^{15–18}. The melting temperature of the stereocomplex is indeed close to 190°C, which is a very interesting temperature for the upper boundary of the service range of thermoplastic elastomers.

Stereocomplexation of iPMMA and sPMMA has been largely investigated since the first report by Fox *et al.*¹⁵ on anomalous WAXS patterns for the related blends. These studies have recently been reviewed by Spevacek and Schneider¹⁶. Formation of iPMMA and sPMMA stereocomplexes has been reported to occur either in bulk or in some suitable solvents^{16,19}. The stereocomplex properties appear to be best at a 1/2 i-PMMA/s-PMMA molar ratio¹⁸. Stereocomplexation has been studied mainly in the case of blends of home PMMA stereoisomers. However, Hogen-Esch *et al.*^{20,21} have recently reported on the thermal behaviour of blends of iPMMA with PBD–sPMMA diblock copolymers. They have concluded that the rubbery PBD block does not prevent stereocomplexation from occurring, although only one endotherm is observed instead of two, as is usually reported¹⁸. Mechanical properties of blends of iPMMA with sPMMA–polyisobutylene–sPMMA triblock copolymers have been reported by Kennedy *et al.*^{10,11}, who have shown that stereocomplexation increases the tensile strength of triblock copolymers. Stereocomplexation has also been confirmed to

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occur when sPMMA–PDMS–sPMMA triblocks are mixed with iPMMMA and analyzed by d.s.c. and DMTA²².

In a previous paper²³, we have shown that solvent blending of MBM triblock copolymers with iPMMMA could also lead to stereocomplexation. Only one melting endotherm was observed by d.s.c. for the stereocomplex. The extent of stereocomplexation was highest at the 2/1 s/i mixing ratio as previously reported for blends of homo-PMMA. The effect of stereocomplexation on the mechanical properties of MBM was also studied and found to depend on the composition of the MBM copolymer. This paper deals with the effect of molecular weight of the sPMMA blocks and iPMMMA on stereocomplexation with special attention paid to crystallization, tensile properties and dynamic mechanical properties.

EXPERIMENTAL

Block copolymers

MBM triblock copolymers were synthesized by the sequential living anionic polymerization of butadiene and methyl methacrylate by using the diadduct of t-Butyllithium (t-BuLi) onto *m*-diisopropenylbenzene (*m*-DIB) as a difunctional initiator. Details of the experimental techniques and reaction conditions were reported elsewhere¹⁴. Molecular weight, polydispersity, composition and microstructure of the available block copolymers are reported in Table 1.

Synthesis of PMMA homopolymers

Isotactic PMMA was prepared in toluene at -78°C with tBuMgBr as initiator according to a method reported by Hatada *et al.*²⁴. Molecular weight, polydispersity, tacticity, glass transition and melting temperatures of iPMMAs are listed in Table 2.

Sample preparation

Films of block copolymers were prepared by solution casting. Block copolymers were added with 1 wt% hindered phenol antioxidant (tetrakis[methylene 3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl) propionate] methane, Irganox 1010, Ciba-Geigy Corp.) and dissolved in toluene. The 6 wt% solution was then allowed to evaporate at room temperature for 3 days in a glass Petri dish. Stereocomplexes were prepared from toluene solutions of the block copolymer stabilized by 1 wt% antioxidant and iPMMMA, respectively. These solutions were mixed at 100°C , and the 6 wt% final solution was poured into a Petri dish and allowed to evaporate at room temperature for 3 days. Films were dried for 2 extra days at 40°C under vacuum. Clear films with a smooth surface were formed in all cases.

Table 1 Characterization of the sPMMA–PBD–sPMMA (MBM) block copolymers

Sample	$\overline{M}_n \times 10^{-3}$ M–B–M	PMMA content (%)	$\overline{M}_w/\overline{M}_n$	PBD 1,2 units (%)	PMMA syndio (%)
T1	7–36–7	28	1.10	44	80
T2	9–36–9	33	1.10	46	79
T3	12–36–12	40	1.10	42	80
T4	20–36–20	53	1.10	44	78
T5	35–36–35	66	1.10	45	77
T6	46–36–46	72	1.10	43	77
T7	26–80–26	39	1.10	44	80
T8	6–85–6	12	1.10	43	80
T9	50–100–50	50	1.10	45	79
T10	84–90–84	65	1.20	45	80

Analysis

Molecular weight, molecular weight distribution and copolymer composition were measured as reported elsewhere¹⁴.

Differential scanning calorimetry (d.s.c.) was carried out with a DuPont 910 instrument, calibrated with indium. Glass transition temperature was reported as the inflection point of the corresponding heat capacity jump.

Tensile measurements were conducted with an Adamel Lhomargy tensile tester. Microdumbbells were cut from solution cast films and extended at 200 mm/min at room temperature. Strain was determined from the cross-head displacement. Sample thickness and width were 0.5 mm and 3.6 mm, respectively. Average values of three independent measurements were reported.

Dynamic mechanical analysis (DMA) was carried out with a TA 983 Dynamic Mechanical Analyser. Samples ($8 \times 6 \times 1$ mm) were deformed at a constant frequency (1 Hz) and a heating rate of $5^{\circ}\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Table 1 lists the MBM triblock copolymers used in this study. All these copolymers have a monomodal and narrow molecular weight distribution (<1.20). ¹H n.m.r. analysis confirms that the PMMA tacticity and the PBD microstructure are essentially the same for all the samples²³, with the syndiotactic content in the range from 77 to 80% and the content of PBD 1,2 units varying from 42 to 46%. The iPMMMA samples used have also a narrow molecular weight distribution (<1.15) and a constant isotacticity of 90% (Table 2). In a previous paper, we have shown that stereocomplexation of iMBM triblock copolymers by iPMMMA was dependent on the sPMMA/iPMMMA mixing ratio (or s/i) and the casting solvent. Since stereocomplexation was optimum for the 2/1 s/i mixing ratio, this mixing ratio has been systematically used in this work. Thermal properties of the stereocomplexes will be studied for the as-cast films (dried at 40°C for 2 days) and for the annealed films (as-cast films were further treated at 140°C for 15 h under vacuum). Mechanical properties will be reported for the as-cast films, which are optically clear and show a smooth surface.

THERMAL PROPERTIES

Effect of \overline{M}_n sPMMA

This effect on stereocomplexation of iPMMMA ($M_n = 30\,000$) with a series of MBM copolymers is shown in Figure 1 for the as-cast films and in Figure 2 for the annealed samples. Table 3 summarizes the melting temperature (T_m) and the melting enthalpy (ΔH_m) of the stereocomplexes formed when \overline{M}_n sPMMA is changed from 7000 to 46000. ΔH_m is expressed in joules per gram of PMMA in the polyblend. \overline{M}_n of the sPMMA blocks in

Table 2 Molecular characteristics of isotactic PMMA

Sample	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	Microstructure (%)			T_g ($^{\circ}\text{C}$)
			i	s	h	
I1	5	1.15	90	7	3	46
I2	30	1.10	90	6	4	50
I3	46	1.10	90	5	5	55
I4	74	1.10	90	6	4	60

Table 3 Thermal properties of blends of MBM triblock copolymers with iPMMMA

Sample	Copolymer	iPMMMA	PMMA (%)	20°C/min					40°C/min		
				As-cast films			Annealed		As-cast films		
				T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g PMMA)	T_m (°C)	ΔH_m (J/g PMMA)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g PMMA)
C1	T1	I2	37	–	182	18.0	185	34.0	–	185	17.2
C2	T2	I2	42	–	182	22.0	183	34.2	–	185	18.3
C3	T3	I2	50	–	182	27.0	182	33.2	–	184	28.0
C4	T4	I2	63	–	183	29.4	184	33.1	175	187	30.2
C5	T5	I2	74	–	182	32.8	184	34.0	177	190	30.4
C6	T6	I2	79	–	182	32.9	183	34.5	185	194	30.5
C7	T7	I1	48	–	179	28.3	183	30.0	nd	nd	nd
C8	T7	I2	48	–	187	32.0	186	36.0	nd	nd	nd
C9	T7	I3	48	–	185	35.0	184	34.6	–	190	34.6
C10	T7	I4	48	–	185	32.3	185	36.2	–	191	36.5
C11	T8	I4	17	–	174	20.0	nd	nd	nd	nd	nd
C12	T9	I1	60	167	181	28.3	nd	nd	165	185	26.0
C13	T10	I2	73	180	189	28.7	186	30.7	181	193	29.7

MBM triblocks is higher than the critical molecular weight above which stereocomplexation of the sPMMA block of sPMMA–PBD diblocks was observed to occur^{18,21}. In agreement with the observation by Hogen-Esch *et al.* for blends of sPMMA–PBD diblock copolymers with iPMMMA^{20,21}, a single melting endotherm is observed when samples are heated at a rate of 20°C/min (*Figure 1A*). However, these endotherms are not symmetric, which may indicate that they result from multiple events, when the heating rate is higher, i.e. 40°C/min (*Figure 1B*), two endotherms are as better resolved as the sPMMA molecular weight is high, particularly for samples C5 and C6 (*Table 3*). For samples C1 to C3, whose \bar{M}_n sPMMA is smaller (7000 to 12 000), only one broad endotherm is observed, whereas sample C4 seems to be an intermediate case, with a shoulder on the low temperature side of the melting endotherm. This effect of the heating rate (comparison of *Figure 1A* and *B*) is surprising, since two endotherms observed at low heating rate usually merge to one endotherm at the faster rate.

It is worth recalling that multiple endotherms have been reported in the scientific literature^{18,25,26} for blends of homoPMMA stereoisomers. Several explanations have been proposed for this observation, such as melting of solvent stabilized sPMMA crystallites followed by melting of stereocomplex crystallites²⁵, or disintegration of aggregates of stereocomplex particles followed by melting of these particles²⁶. Recently, Schomaker and Challa¹⁸ have investigated this phenomenon in detail and proposed the occurrence of two crystallization modes, leading to the formation of fringed micellar crystallites and lamellar crystallites, respectively, depending on the molecular weight and the experimental conditions. According to these authors, the superheating characteristics of the two types of crystallites are different since T_m of the fringed micellar crystallites increases with the heating rate in contrast to T_m of the lamellar crystallites which is essentially independent of it. On this basis, T_{m2} (*Table 3*) might be assigned to fringed micellar crystallites and T_{m1} to lamellar crystallites. In their study of the stereocomplexation of iPMMMA with the sPMMA block of sPMMA–PBD diblocks^{20,21} or sPMMA–PDMS–sPMMA triblocks²², Hogen-Esch *et al.* have observed only one endotherm and assigned it to fringed micellar crystallites. It must be noted that \bar{M}_n of the sPMMA blocks was relatively low (less than 15 000). From the results in *Table 3*, it thus appears that lamellar crystallites are formed in addition to fringed micellar crystallites, when the sPMMA block is long enough.

In top of the effect of two crystallization modes, the melting of the stereocomplex occurs over a temperature range that increases with molecular weight of the sPMMA block (*Figure 1A*). For instance, the melting domain extends over 30°C for sample C1, compared with *ca.* 50°C for sample C6. This observation indicates that crystallites of a larger distribution in size and perfection are formed as a result of the increase in molecular weight and loss in chain mobility when crystallization occurs. Consistently, *Figure 2* shows the d.s.c. thermograms for the same samples as in *Figure 1*, but annealed at 140°C for 15 h and scanned at a heating rate of 20°C/min (traces 1 to 6). The apparent effect of \bar{M}_n sPMMA is substantially reduced, since the melting domain is quite comparable for all the samples and only one endotherm is observed even for sample C6 that contains the longer sPMMA block upon heating at 40°C/min (trace 7, *Figure 2*). This observation indicates that the chain mobility is sufficiently high at a temperature (140°C) higher than T_g of sPMMA for crystallization to tend to equilibrium which did not occur during casting.

Figure 3 compares the dependence of the melting enthalpy (ΔH_m) of the stereocomplexes on \bar{M}_n sPMMA for the as-casts film and the annealed samples. ΔH_m of the as-cast films increases with increasing \bar{M}_n sPMMA in the low \bar{M}_n range and reaches a plateau value of *ca.* 33 J/g PMMA at \bar{M}_n sPMMA of 36 000, which is in good agreement with the value found for blends of homoPMMA stereoisomers prepared in solution¹⁸.

Effect of \bar{M}_n iPMMMA

It was previously observed that stereocomplexation of PBD sPMMA diblocks with iPMMMA of relatively low molecular weight, and particularly the melting enthalpy, increased with increasing \bar{M}_n iPMMMA for samples annealed above 100°C²¹. Thermograms of blends of the T7 triblock copolymer (*Table 1*) with iPMMMA of different molecular weight (*Table 2*) are shown in *Figure 4*. The melting temperature and melting enthalpy are reported in *Table 3* (samples C7–C10), and seem to be largely independent of \bar{M}_n iPMMMA in the range of 30 000 to 74 000 (samples C8–C10). Only the blend containing the lowest \bar{M}_n iPMMMA shows some lower *melting temperature* and melting enthalpy. This difference is apparently erased by annealing the samples at 140°C for 15 h. One endotherm is observed in all the cases even for sample C10 of the highest \bar{M}_n iPMMMA (74 000) scanned at a heating rate of 40°C/min (trace 6,

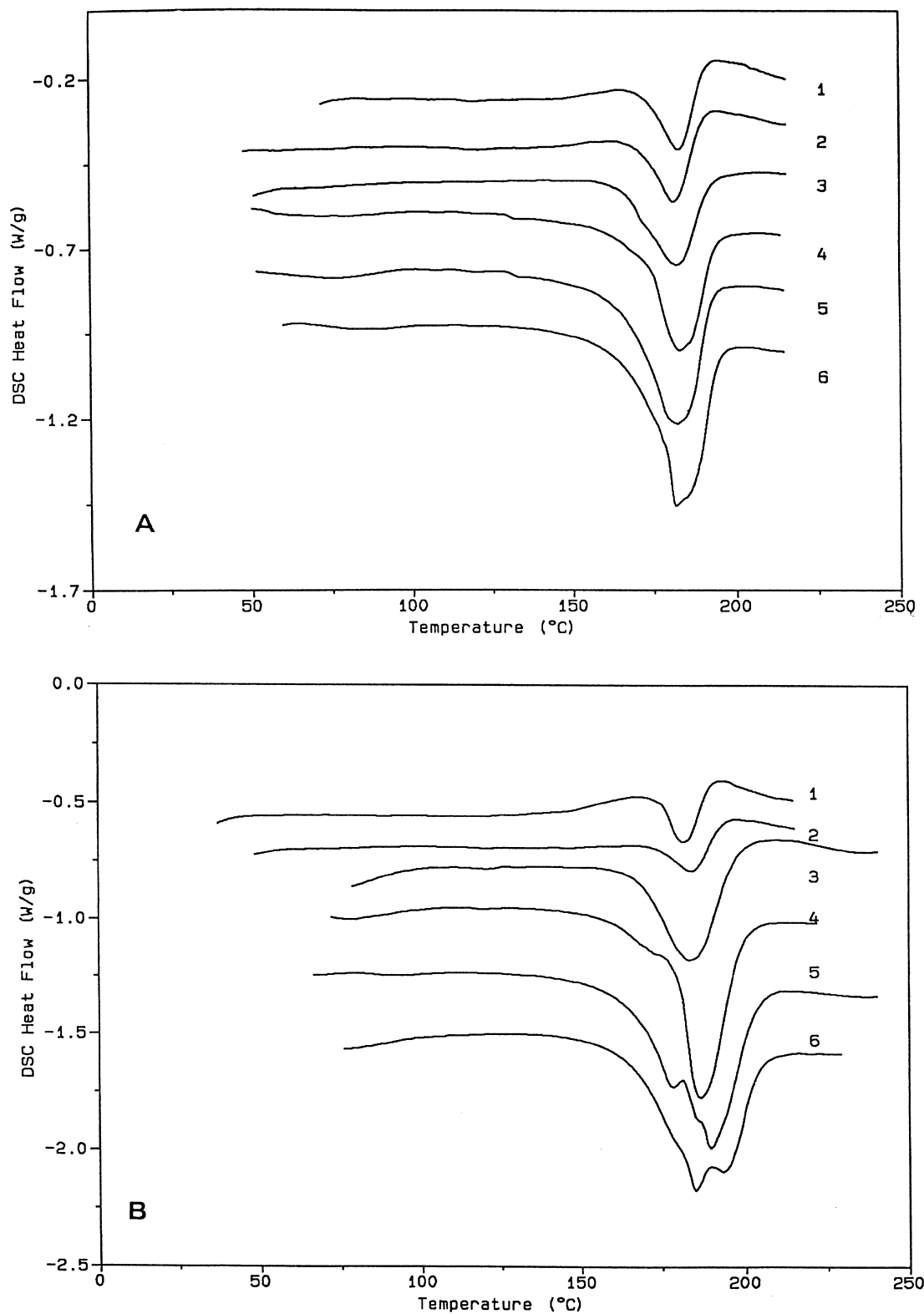


Figure 1 D.s.c. thermograms for blends (see Table 3) of iPMMA (I2 sample) with MBM triblock copolymers of a constant PBD block ($\bar{M}_n = 36\,000$) and sPMMA blocks of various molecular weights (Table 1) in a 2/1 s/i mixing ratio: (1) C1; (2) C2; (3) C3; (4) C4; (5) C5; (6) C6. (A) Heating rate of 20°C/min. (B) Heating rate of 40°C/min. Samples were dried at 40°C for 2 days

Figure 4). It is worth noting that the melting region of these blends is generally broad (Figure 4), since it extends from 130°C to 210°C, except for sample C8 which melts over a narrower temperature range (from 160°C to 200°C). Note that the sPMMA block and iPMMA have a comparable molecular weight in this sample C8. The broader melting region in samples C7, C9 and C10 suggests a larger

distribution for the size and perfection of the crystallites which is, however, improved by annealing at 140°C for 15 h as shown for sample C10 in Figure 4 (traces 4 and 5).

Effect of the \bar{M}_n iPMMA/ \bar{M}_n sPMMA ratio

Kennedy *et al.*¹¹ have reported that a large dissimilarity between the \bar{M}_n iPMMA and \bar{M}_n sPMMA resulted in a

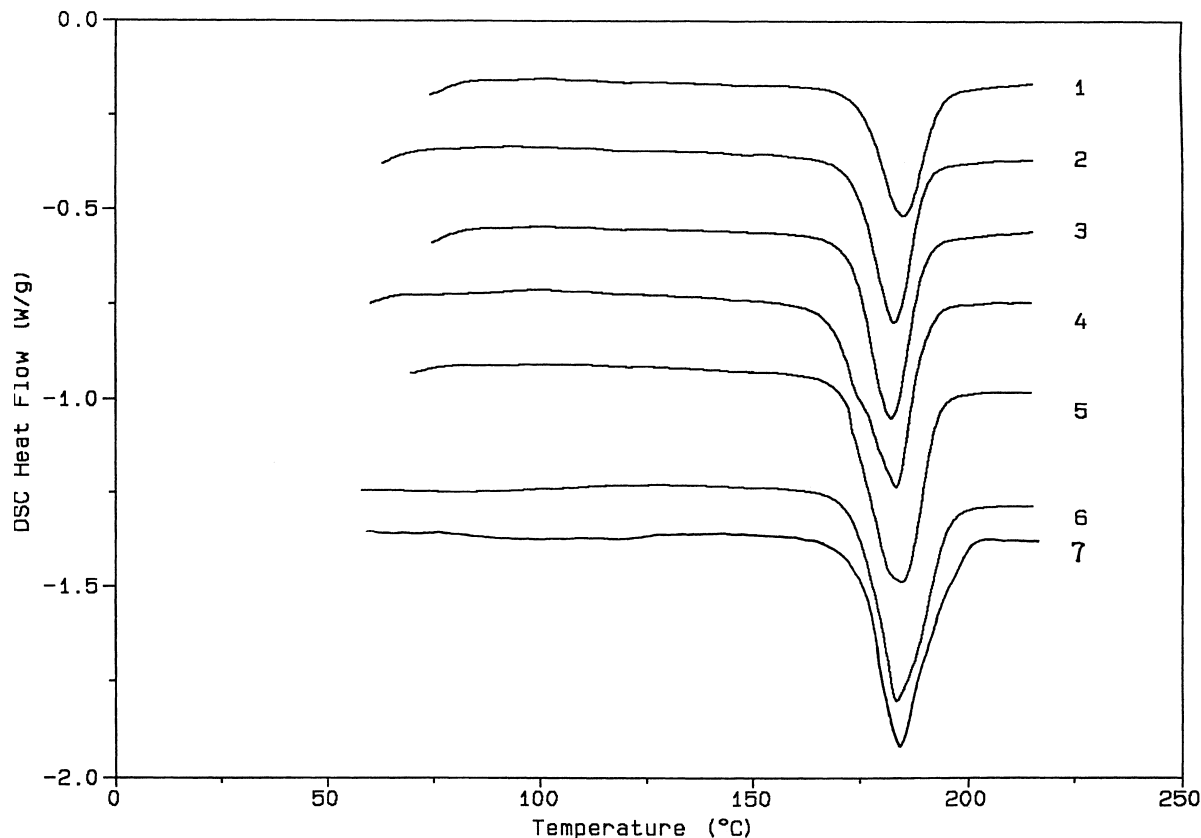


Figure 2 D.s.c. thermograms for the same samples as in Figure 1, but annealed at 140°C for 15 h. (1) C1; (2) C2; (3) C3; (4) C4; (5) C5; (6) C6. The heating rate is 20°C/min for all these samples. (7) Sample C6 scanned at a heating rate of 40°C/min

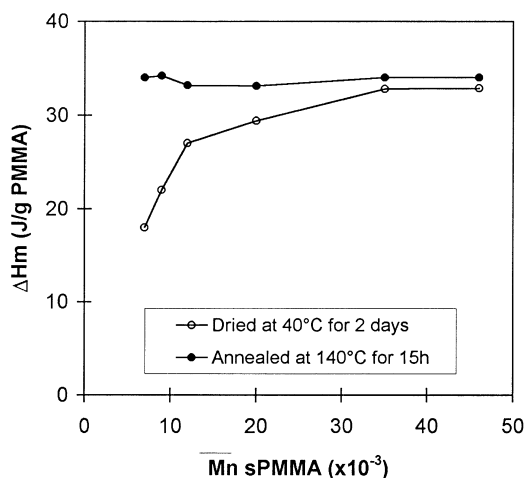


Figure 3 Melting enthalpy for blends of iPMMA (I2 sample) with MBM triblock copolymers containing the same PBD block ($\bar{M}_n = 36\,000$) as function of molecular weight of the sPMMA block

difficult stereocomplexation in solvent (Toluene/THF mixture) cast blends of sPMMA–polyisobutylene–sPMMA triblocks with iPMMA even after annealing. In order to check whether this behaviour also prevails for blends of iPMMA with triblock copolymers containing a polybutadiene instead of a polyisobutylene midblock, three blends C11–C13 have been prepared (Table 3). C11 combines a low \bar{M}_n sPMMA block (6000) with a high \bar{M}_n iPMMA (74 000). C12 is the reverse combination of a high \bar{M}_n sPMMA (50 000) with a low \bar{M}_n iPMMA (5000), and C13 is a combination comparable to C12, except for a still higher M_n sPMMA (84 000). The d.s.c. thermograms

of these samples are shown in Figure 5. One endotherm is clearly observed for sample C11. In contrast, samples C12 and C13 show overlapping of at least two endotherms, which becomes less extensive at a higher heating rate (comparison of traces 3 and 4 in Figure 5). Thus, in agreement with previous observations, high enough \bar{M}_n sPMMA is at the origin of more than one endotherm for the melting of the stereocomplexes. It is worth noting that an increase in \bar{M}_n of the PBD block [from 36 000 (C6) to 100 000 (C12)] has also an effect on the PMMA chain mobility, since two endotherms are observed at the lower heating rate (20°C/min) for sample C12 (trace 2, Figure 5) compared with sample C6 (trace 6, Figure 1A and Figure 1B), which only shows these endotherms at a higher heating rate (40°C/min). Compared with blend C8 in which \bar{M}_n sPMMA and \bar{M}_n iPMMA are comparable, melting temperature and melting enthalpy of C11 are slightly decreased, in contrast to C12 and C13 samples that have quite comparable thermal characteristics.

DYNAMIC MECHANICAL ANALYSIS

The thermal dependence of the dynamic shear storage modulus (G') and loss $\tan \delta$ ($= G''/G'$) has been analyzed in the temperature range from -100 to 200 °C at the 1 Hz frequency for the T7 triblock copolymer and the blends with iPMMA of various molecular weights from 5000 to 74 000 (samples C7, C8 and C10, Table 3). Figure 6 shows that all these materials are microphase separated, since two transitions are clearly observed, which are characteristic of the glass transition of the PBD soft phase at the lower temperature of *ca.* 60°C (T_{g1}) and the

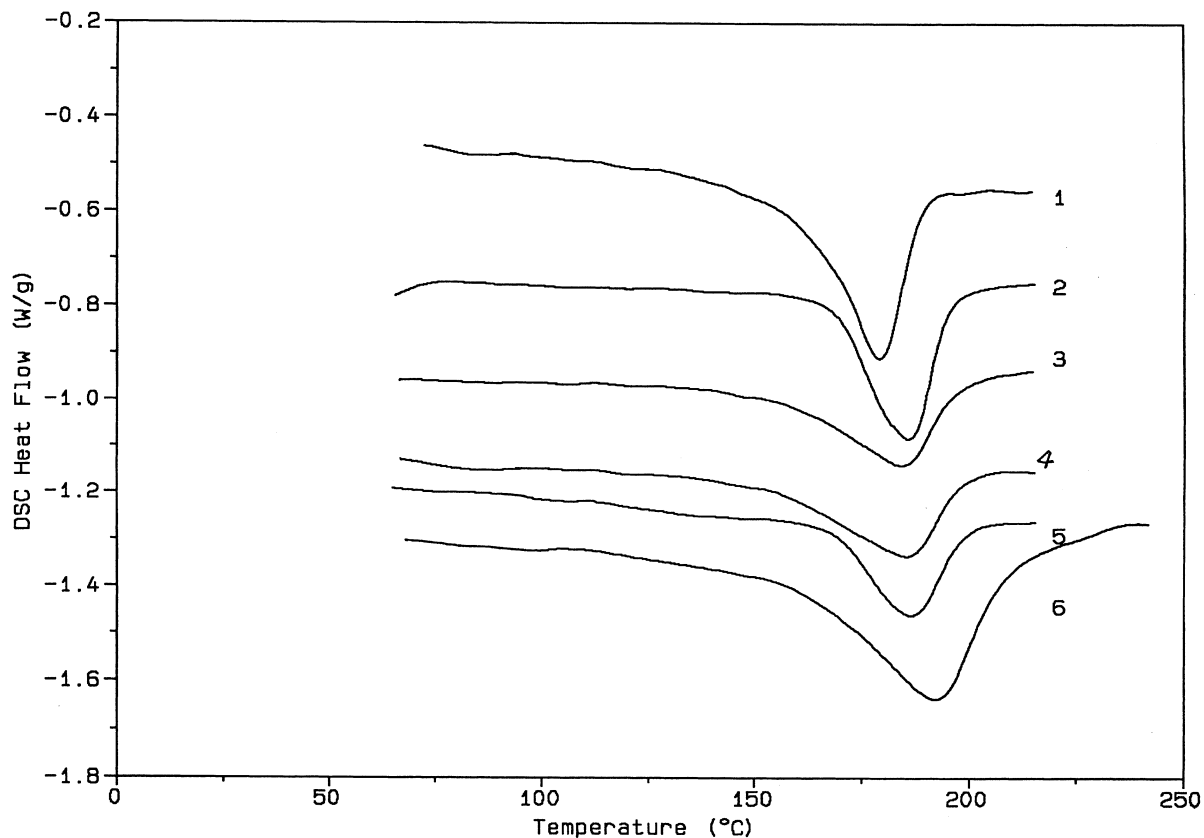


Figure 4 D.s.c. thermograms for blends of MBM triblock copolymer T7 (Table 1) with iPMMMA of different molecular weight in a 2/1 s/i mixing ratio: (1) C7, (2) C8, (3) C9, (4) C10. The samples (Table 3) were dried at 40°C for 2 days and scanned at a heating rate of 20°C/min. (5) C10 annealed at 140°C for 15 h, and scanned at 20°C/min; (6) C10 dried at 40°C for 2 days and scanned at a heating rate of 40°C/min

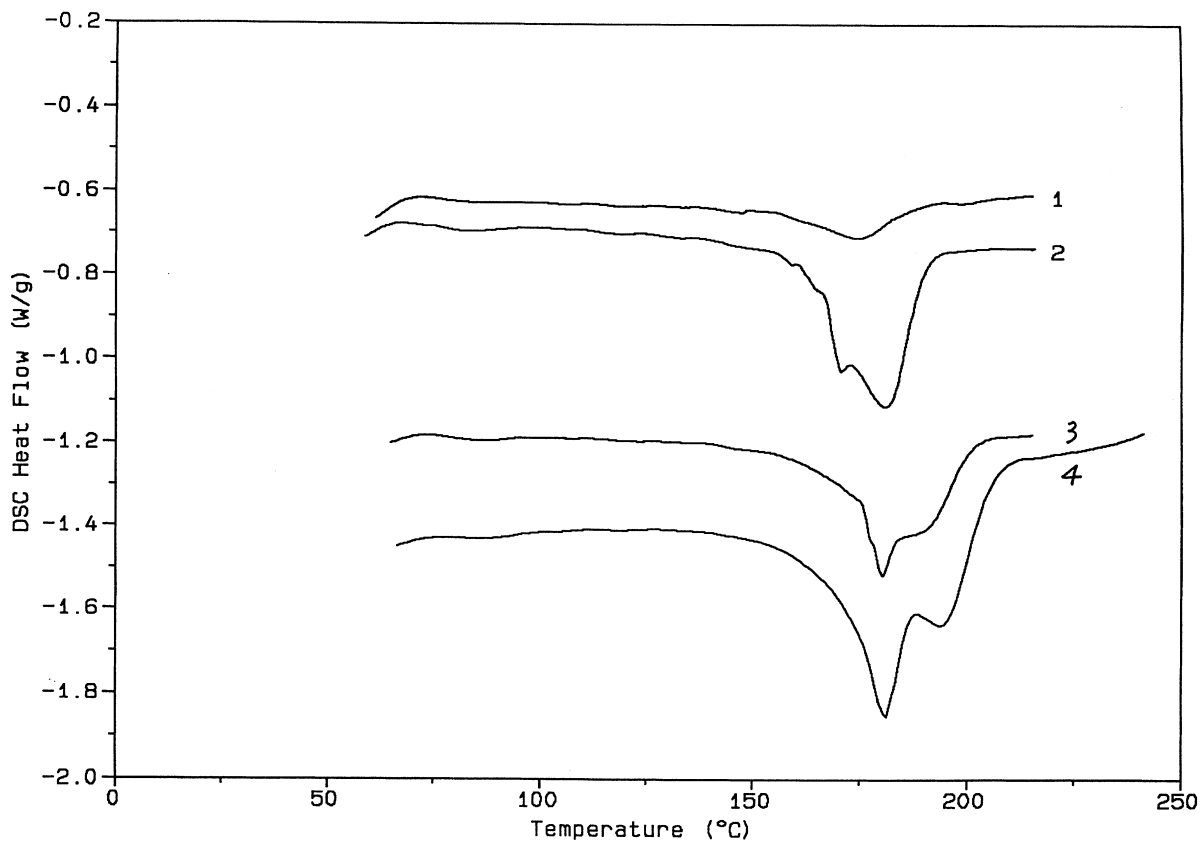


Figure 5 D.s.c. thermograms for blends of MBM triblock copolymer with iPMMMA in a 2/1 s/i mixing ratio (Table 3): (1) C11, (2) C12, (3) C13 (heating rate of 20°C/min); (4) C13 (heating rate of 40°C/min). All the samples were dried at 40°C for 2 days

transition of the hard phase at a higher temperature (T_g2) of ca. 135°C for the triblock copolymer and higher for the stereocomplexes. The storage modulus G' in the glassy and the rubbery regions is systematically higher for the stereocomplexes compared with the parent T7 triblock copolymer (Figure 6A), in a possible relation with a higher PMMA content and partial crystallization of the stereocomplex. This storage modulus G' of the stereocomplexes is, however, essentially independent of \bar{M}_n iPMMA up to ca. 90°C. At higher temperature, G' rapidly decreases for samples C7 and C10 which consist of the lowest and the highest \bar{M}_n iPMMA (5000 and 74 000), whereas G' of sample C8 only decreases sharply above 150°C. This observation is consistent with d.s.c. that has previously shown the earlier melting of samples C7 and C10 compared with sample C8 (Figure 4).

Figure 6B shows that T_g1 and thus the PBD chains are unaffected by stereocomplexation of the outer sPMMA blocks with iPMMA. The damping at T_g1 is, however, much smaller for the stereocomplexes compared with the parent copolymer (Figure 6B), which at least partly reflects the decrease in the weight content of the soft phase when iPMMA is blended with the triblock. In agreement with G' in the high temperature range, the second tan peak is observed at 135°C for the unmodified triblock, at a temperature higher than 150°C for the C7 and C10 stereocomplexes and above 165°C for the C8 stereocomplex that consists of iPMMA and sPMMA components of a comparable \bar{M}_n .

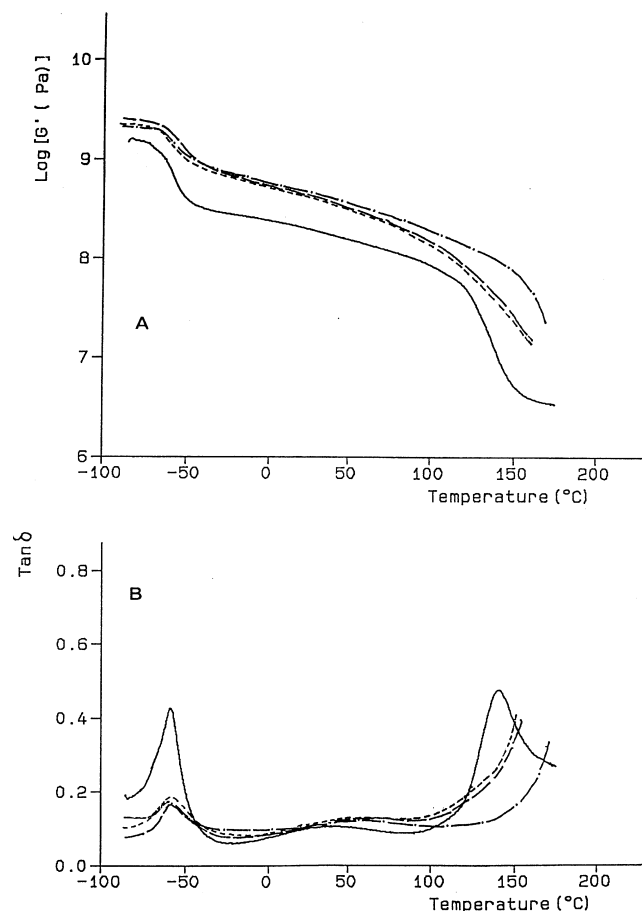


Figure 6 Temperature dependence of the shear storage modulus (G') (A) and loss $\tan \delta$ ($= G''/G'$) (B) at 1 Hz for the T7 MBM triblock (—), and stereocomplexes with iPMMA of $\bar{M}_n = 5000$ (C7, ···), 30 000 (C8, - - -) and 74 000 (C10, — · — ·). Heating rate: 5°C/min

TENSILE PROPERTIES

Effect of \bar{M}_n sPMMA

Kennedy *et al.*¹¹ have reported an increase in the tensile strength of sPMMA–polyisobutylene–sPMMA triblocks upon stereocomplexation with iPMMA. The previous paper of this series has shown that the effect of stereocomplexation on the tensile strength of MBM copolymers was dependent on the copolymer composition and the s/i mixing ratio²³. Table 4 compares the tensile properties of MBM triblock copolymers containing the same PBD midblock ($\bar{M}_n = 36\,000$) and blended with iPMMA. The ultimate tensile strength, σ_b , and the elongation at break, ϵ_b , are significantly increased for sample C1 of the lowest \bar{M}_n sPMMA (7000) compared with the original copolymer T1. In sharp contrast, the ultimate tensile properties remain unchanged upon stereocomplexation when \bar{M}_n of the sPMMA blocks is increased from 7000 (C1) to 9000 (C2). The C1 and C2 samples show a yield point which is not seen for the parent triblock copolymers, indicating formation of a semi-continuous hard phase upon addition of iPMMA. Finally, when the sPMMA block is longer ($\bar{M}_n > 12\,000$), blending with iPMMA substantially decreases both σ_b and ϵ_b , in contrast to the yield stress which increases. It is worth noting that stereocomplexation with iPMMA increases the PMMA content of the original MBM triblock, as indicated in Table 4.

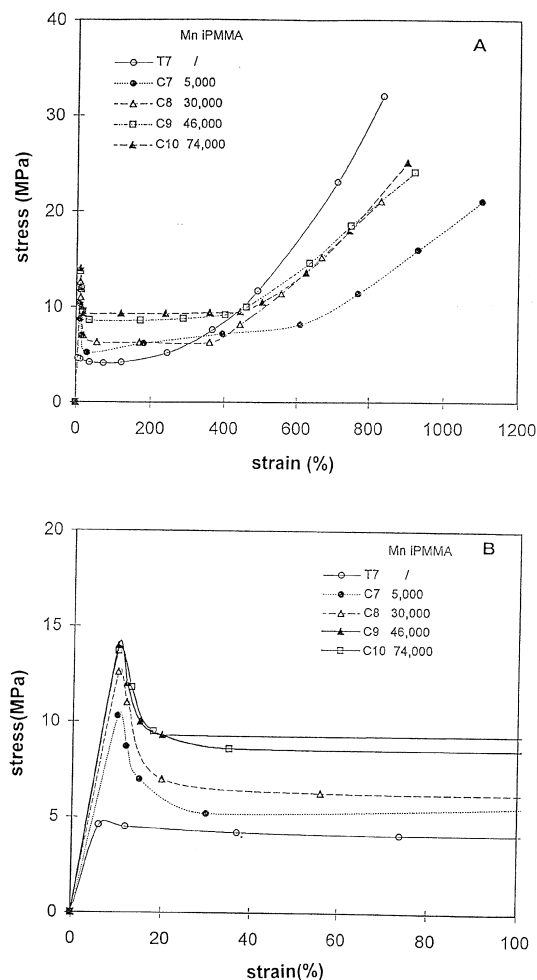


Figure 7 Stress–strain curves at room temperature for the MBM triblock copolymer T7 and blends with iPMMA of different molecular weight. Full curves (A) and partial curves (B) in the small strain range

Table 4 Mechanical properties of blends of MBM triblock copolymers with iPMMMA

Sample	PMMA (%) ^a	Yield stress (MPa) ^a	Ultimate tensile strength σ_b (MPa) ^a	Elongation at break ε_b (%) ^a
C1	37 (28)	5.0 ± 0.6 (-)	7.0 ± 0.6 (2.0 ± 0.5)	500 ± 20 (320 ± 20)
C2	42 (33)	8.0 ± 0.6 (-)	13.0 ± 1.0 (11.0 ± 1.0)	800 ± 30 (800 ± 30)
C3	50 (40)	11.0 ± 0.7 (3.0 ± 0.7)	22.0 ± 1.4 (31.0 ± 1.5)	650 ± 20 (850 ± 30)
C4	63 (53)	26.0 ± 1.3 (11.0 ± 0.8)	18.0 ± 1.1 (33.0 ± 1.6)	100 ± 10 (650 ± 30)
T7	39	5.0 ± 0.8	32.0 ± 1.0	840 ± 30
C7	48	10.0 ± 0.7	21.0 ± 1.5	1100 ± 50
C8	48	13.0 ± 1.0	21.0 ± 1.0	830 ± 40
C9	48	14.0 ± 1.0	25.0 ± 1.4	900 ± 50
C10	48	14.0 ± 1.0	24.0 ± 1.0	920 ± 30

^aValues in parentheses are for the original MBM triblock copolymers

Effect of \overline{M}_n iPMMMA

Figure 7 compares the stress–strain curves for the T7 MBM triblock copolymer and the stereocomplexes with iPMMMA of molecular weight varying from 5000 to 74 000 (samples C7 to C10, Table 3). Yield stress, ultimate tensile strength (σ_b) and elongation at break (ε_b) are listed in Table 4. For all these samples, a yield point is observed followed by necking and then an increase in stress at higher strain (Figure 7A), which is a typical tensile behaviour of semi-crystalline polymers and thermoplastic elastomers of a high content of hard blocks. The original triblock copolymer T7 has a relatively low yield stress, necking occurs over a comparatively small strain range, and the ultimate tensile strength σ_b (32 MPa) is higher compared with the stereocomplexes C7 to C10. The stereocomplex C7 formed with the smaller \overline{M}_n iPMMMA (5000) has a lower yield stress and initial modulus (Figure 7B) than the other blends, which is consistent with a lower melting enthalpy (ΔH_m) as observed by d.s.c. The stereocomplexes (C9 and C10) formed with iPMMMA of the higher \overline{M}_n (46 000 and 74 000, respectively) show a slightly higher σ_b and yield stress. It is thus clear that the length of the sPMMA blocks and their propensity of forming stable stereocomplexes with iPMMMA are most important for the tensile properties of the MBM/iPMMMA blends.

CONCLUSION

Stereocomplexation of sPMMA–PBD–sPMMA triblock copolymers with isotactic PMMA (iPMMMA) at a constant 2/1 s/i mixing ratio has been investigated as a function of molecular weight of both the sPMMA blocks and iPMMMA.

Melting temperature of the stereocomplexes is not affected by the sPMMA molecular weight (\overline{M}_n sPMMA) in the studied range from 7000 to 46 000, although the melting enthalpy increases with increasing \overline{M}_n sPMMA. This effect is erased by annealing the samples at 140°C for 15 h, since a melting enthalpy of ca. 33 J/g total PMMA is then observed whatever \overline{M}_n sPMMA. Molecular weight of iPMMMA has no significant effect on the melting temperature and melting enthalpy of the stereocomplexes.

One melting endotherm is commonly observed by d.s.c. for stereocomplexes formed by MBM containing short sPMMA blocks ($\overline{M}_n < 40 000$) and scanned at a low heating rate (20°/min). Two major melting endotherms are, however, observed when \overline{M}_n sPMMA is higher (> 50 000) and the samples scanned at the heating rate of 20°C/min or when intermediate \overline{M}_n sPMMA (> 20 000) together with a higher

heating rate (40°C/min) are considered. This behaviour is essentially independent of \overline{M}_n iPMMMA in the range of 5000 to 74 000.

At constant molecular weight for the PBD midblock (36 000) and iPMMMA, stereocomplexation results in higher tensile properties for the MBM copolymer with the shortest sPMMA block (\overline{M}_n : 7000). This effect is reversed in the case of the MBM copolymer consisting of longer sPMMA block (12 000). Finally, an increase in the total molecular weight of MBM at a constant composition (26 000–80 000–26 000) generally decreases the ultimate tensile strength and elongation at break and increases the initial modulus and yield stress of the complexed material. The effect of stereocomplexation on the ultimate tensile properties is not significantly affected by the iPMMMA molecular weight in the studied range from 5000 to 74 000.

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REFERENCES

- Fetters, L. J. and Morton, M., *Macromolecules*, 1969, **2**(5), 453.
- Morton, M. and Mikesell, S. L., *J. Macromol. Sci-Chem.*, 1993, **A7**(7), 1391.
- Morton, M., in *Thermoplastic Elastomers*, ed. N. R. Legge, G. Holden and H. E. Schroeder. Hanser Publishers, Munich, Vienna, New York, 1987, p. 67.
- Weiss, R. A., Sen, A., Potlick, L. A. and Willis, C. L., *Polym. Commun.*, 1990, **31**, 220.
- Weiss, R. A., Sen, A., Willis, C. L. and Potlick, L. A., *Polymer*, 1991, **32**(10), 1867.
- Patent, Wo-A-8800603.
- Long, T. E., Broske, A. D., Bradley, D. J. and McGrath, J. E., *J. Polym. Sci. Chem. Ed.*, 1989, **27**, 4001.
- DePorter, C. D., Ferrence, G. M. and McGrath, J. E., *Polym. Prepr.*, 1993, **34**(2), 574.
- Loveday, D., Wikes, G. L., DePorter, D. D. and McGrath, J. E., *Macromolecules*, 1995, **28**, 7822.

10. Kennedy, J. P. and Price, J. L., *Polym. Mater. Sci. Eng.*, 1991, **64**, 40–41.
11. Kennedy, J. P., Price, J. L. and Koshimura, K., *Macromolecules*, 1991, **24**, 6567.
12. Ladd, B. J. and Hogen-Esch, T. E., *Polym. Prepr.*, 1989, **30**(11), 261.
13. Yu, Y., Jerome, R., Fayt, R. and Teyssie, Ph., *Macromolecules*, 1994, **27**, 5957.
14. Yu, J. M., Dubois, Ph., Teyssie, Ph. and Jerome, R., *Macromolecules*, 1996, **29**, 6090.
15. Fox, T. F., Garrett, B. S., Goode, W. E., Gratch, S., Rincaid, J. F., Spell, A. and Stroupe, J. D., *J. Am. Chem. Soc.*, 1958, **80**, 1768.
16. Spevacek, J. and Schneider, B., *Adv. Colloid. Interface Sci.*, 1987, **27**, 81.
17. Feitsma, E. L., DeBoer, A. and Challa, G., *Polymer*, 1975, **16**, 515.
18. Schomaker, E. and Challa, G., *Macromolecules*, 1988, **21**, 2195, 3506.
19. Lemieux, E., thesis, University Laval, Quebec, 1988.
20. Helary, G., Belorgey, G. and Hogen-Esch, T. E., *Polymer*, 1992, **33**(9), 1953.
21. Berkoukchi, M. P., Hélyary, G., Bêlorgey, G. and Hogen-Esch, T. E., *Polym. Bull.*, 1994, **32**, 297.
22. Deuring, H., Alberda Van Ekenstein, G. O. R., Challa, G., Mason, J. P. and Hogen-Esch, T. E., *Macromolecules*, 1992, **25**, 28.
23. Yu, J. M., Yu, Y., Dubois, Ph., Teyssie, Ph. and Jerome, R., *Polymer*, 1997, **38**, 2143.
24. Hatada, K., Ute, K., Tanaka, K., Kitayama, T. and Okamoto, Y., *Polym. J.*, 1985, **17**(8), 977.
25. de Boer, A. and Challa, G., *Polymer*, 1976, **17**, 633.
26. Katime, I., Quintana, J. R. and Veguilas, J., *Polymer*, 1983, **24**, 903.