Stereocomplex Formation in Blends of Block Copolymers of Syndiotactic Poly(methyl methacrylate) (PMMA)–Poly(dimethylsiloxane) (PDMS) and Isotactic PMMA. Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Thermal Analysis (DMTA)

H. Deuring, G. O. R. Alberda van Ekenstein, and G. Challa

Laboratory of Polymer Chemistry, State University of Groningen,
Nijenborgh 4, 9747 AG Groningen, The Netherlands

J. P. Mason and T. E. Hogen-Esch*

Loker Hydrocarbon Research Institute and Department of Chemistry,
University of Southern California, Los Angeles, California 90089-1661

Received December 20, 1993; Revised Manuscript Received April 8, 1994®

ABSTRACT: PMMA stereocomplex formation was demonstrated in domains of PMMA–PDMS–PMMA block copolymers having syndiotactic (S) PMMA blocks by mixing a THF solution of the block copolymer and that of isotactic (I) PMMA in the S/I PMMA ratio of 2 followed by precipitation from THF or by forming the same blend by precipitation from chloroform followed by annealing at temperatures in the 100–140 °C range. The various blends and the block copolymer itself were analyzed by DSC and DMTA. The dissociation–melting temperature of the stereocomplexes present in the PMMA domains was shown to increase with increasing annealing temperature. The rate of formation of stereocomplexes in bulk was found to be much slower than that in blends of PMMA homopolymers. Crystallization of PDMS was shown to be hindered by stereocomplex formation. The modulus at temperatures above 100 °C of the blends in which stereocomplex formation occurred was found to be higher than in the same blends in which such a stereocomplex was absent. These results are interpreted by the formation of networks formed by fringed micellar crystallites of PMMA stereocomplexes acting as physical cross-links.

Introduction

Stereocomplex formation of isotactic (I) and syndiotactic (S) poly(methyl methacrylate) (PMMA) has been demonstrated in suitable solvents[1,2] or in the solid state upon annealing.[3] The formation of such complexes involving block copolymers consisting of S-PMMA blocks and an elastomer such as 1,4-polybutadiene (PBD) or poly(dimethylsiloxane) (PDMS) was first reported by Mason et al.,[4] by Helary et al.,[5] and by Kennedy et al.[6] for the case of S-PMMA–polyisobutene block copolymers. In these cases the polymers or block copolymers were mixed with I-PMMA in solvents favoring stereocomplex formation followed by evaporation of the solvent. Alternatively, mixing was carried out in "noncomplexing" solvents such as chloroform[1,2] followed by evaporation of the chloroform. Annealing at temperatures near or above the glass transition temperature of the S-PMMA block leads to I-PMMA–S-PMMA stereocomplex formation.

Block copolymers at high elastomer content usually show a two-phase morphology with the elastomer existing as the continuous phase and with the hard blocks acting as physical cross-links below the T_g of the hard block. The cross-links give such block copolymers useful elastomeric properties. Thus above the T_g of the "hard blocks" such thermoplastic elastomers can be processed or reprocessed.

The presence of I-PMMA–S-PMMA stereocomplexes in PMMA domains is expected to stabilize such domains at temperatures between the T_g of PMMA and the dissociation–"melting" temperature (T_m) of the stereocomplex.[7] PMMA stereocomplexes have been demonstrated to have T_m values between 150 and 200 °C, 30 deg or more above the T_g of the syndiotactic block (T_g = 100–120 °C). Thus stereocomplex formation is expected to lead to better mechanical properties, especially near or above the T_g of the hard block. In the absence of stereocomplex formation, for instance, in nonannealed mixtures of I-PMMA and S-PMMA–PDMS, the mixture will have a hard-block T_g that approximates a weighted average of the T_g's of the I- and S-PMMA. It is expected therefore that the mechanical properties of such systems will depend on the degree of stereocomplex formation in the PMMA domains of S-PMMA–PDMS block copolymers. The degree of stereocomplex formation, in turn, will depend on prior solution or thermal treatments.

In the following we report recent studies on the thermal and thermal-mechanical properties of mixtures of S-PMMA–PDMS–S-PMMA block copolymers with I-PMMA with emphasis on the effects of stereocomplex formation on the DSC and DMTA characteristics of both elastomeric and hard domains. PDMS was chosen as the elastomer because of its very low T_g of about −125 °C. Furthermore, PDMS is known for its excellent resistance to oxidation and UV radiation.[7]

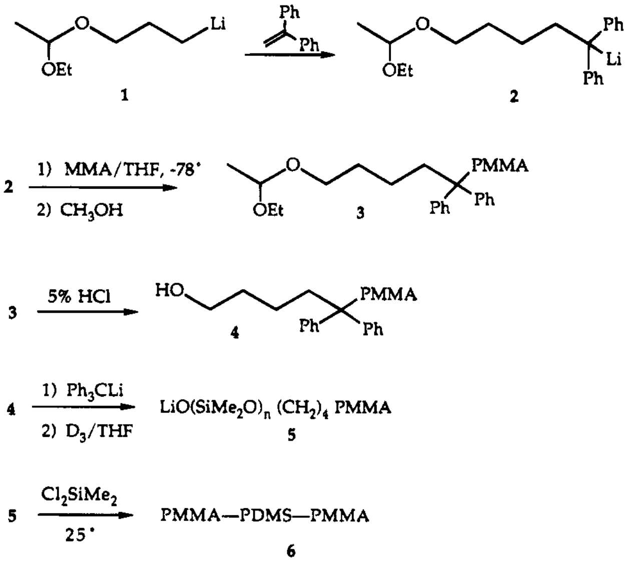
The first part of the study deals with stereocomplex formation in the PMMA domains as a function of parameters such as annealing time and temperature. In the second part the consequences are studied of stereocomplex formation by dynamic mechanical thermal analysis. The influence of stereocomplex formation on the room temperature elasticity of the block copolymer and its blend with I-PMMA was also explored by means of a draw bench.

---

* To whom correspondence should be addressed.

® Abstract published in *Advance ACS Abstracts,* February 1, 1995.

Scheme 1. Synthesis of S-PMMA–PDMS–S-PMMA Block Copolymers



Experimental Methods

Synthesis and Characterization. Isotactic PMMA was synthesized in toluene at 0 °C using phenylmagnesium bromide as initiator.[8] The polymer as prepared had a very wide molecular weight distribution ($D \simeq 25$). In order to remove the low molecular weight (MW) portion, the polymer was dissolved in acetone and precipitated by addition of the solution to excess warm methanol (50 °C). The precipitate was redissolved in acetone, and demineralized water was added until precipitation of the high MW fraction occurred. The solution of the remaining I-PMMA was isolated by filtration and added to excess demineralized water followed by filtration and drying over P_2O_5 in vacuo at 20 °C. The molecular mass of the I-PMMA and its distribution were determined by size-exclusion chromatography (SEC) ($M_w = 113\,000$; $M_w/M_n = 2.7$). The chain was determined by ^{1}H NMR to have a 95% isotactic triad content.

The S-PMMA block of the S-PMMA–PDMS–S-PMMA block copolymer was prepared by anionic initiation of MMA by a (1,1-diphenylalkyl)lithium initiator, **2**, containing an acetal-protected hydroxyl group and termination by CH_3OH (Scheme 1).[4] After hydrolysis (5% HCl) the PMMA containing a terminal OH group, **4**, was dried in vacuo at 50 °C for at least 48 h. A portion of this PMMA was retained for analysis. The remainder was titrated with (triphenylmethyl)lithium until the appearance of a slight reddish color. The desired amount of hexamethylcyclotrisiloxane (D3) was then added, and the polymerization was allowed to proceed for about 2 h. The precursor anion, **5**, was then reacted with Me_2SiCl_2 by slow addition of the needed amount of Me_2SiCl_2 to the polymer solution. The resulting ABA block copolymer was then precipitated in CH_3OH followed by filtration and drying in a vacuum oven at 50 °C for 24 h. The molecular mass was determined by SEC using polystyrene standards ($M_w = 75\,100$, $M_w/M_n = 1.13$). The molecular mass of the PMMA precursor, **4**, was determined independently by SEC ($M_w = 14\,530$, $M_w/M_n = 1.13$) using PMMA standards. The syndiotactic content was found to be 80%.

Proton NMR measurements were carried out on I-PMMA and the isolated PMMA "block" in $CDCl_3$ at 35 °C using 5% solutions. The tacticities were determined from the relative proportions of the α-methyl signals.

Size-exclusion chromatography was carried out using a Waters 150-C ALC/GPC chromatograph with chloform as eluent. Polystyrene standards were used for calibration. The Mark–Houwink constants were $K = 7.16 \times 10^{-5}$ and $K = 4.8 \times 10^{-5}$ for polystyrene and PMMA, respectively, and the a values were 0.76 and 0.80 for polystyrene and PMMA, respectively.[9]

Preparation of blends was carried out by mixing of 1.5–2.0 wt % solutions of I-PMMA and S-PMMA–PDMS–S-PMMA in the desired S-PMMA/I-PMMA ratio of 2/1 (wt/wt) in THF or $CHCl_3$. In the case of THF the mixture was stirred gently for 24 h at 20 °C and precipitated by addition to excess demineralized water. After filtration the blend was dried under vacuum for 3 days in the presence of P_2O_5 at room temperature. For the case of $CHCl_3$ the corresponding solutions of the two polymers were stirred for 2 h and precipitated in excess methanol followed by drying and annealing at various temperatures for various times. Before annealing, the samples were first heated to 200 °C and cooled quickly in order to erase thermal histories.

DSC measurements were performed with a Perkin-Elmer DSC-7 apparatus. Two heating scans, a first scan and a rescan, of each sample were performed from −90 to +230 °C at a heating rate of 10 °C/min. The weight loss of the samples after the first scan was never more than 1.5 wt %. The T_g of the PDMS could not be determined because of limitations of the DSC-7 at low temperatures (≥ -110 °C). DSC measurements on the copolymer samples were carried out in identical fashion.

DMTA measurements on the samples in the presence or absence of stereocomplex formation were performed on a Rheometrics Solids Analyzer Apparatus V (RSA II) and were carried out with a heating rate of 2 °C/min at a constant frequency of 1 Hz (test geometry: tension/compression rectangular) from −145 to about +130 °C or from 25 °C to about 200 °C. Elasticity measurements on the blend or the copolymer were carried out with the draw bench (Instron Corp.) at a sample rate of 20.00 points/s and crosshead speeds between 0.5 and 10 mm/min.

Bars (32 × 4 × 0.5 mm) of the copolymer and its blends were pressed for 3 min at 125 or at 180 °C (393 ton/m^2) and cooled with water. Subsequently, some bars were annealed at 125 or 140 °C for 24 h or longer. Only the blends obtained in chloroform were used in these studies since the blends obtained in THF did not stick to the press matrix. This is possibly connected with the immobilization of the PDMS chains caused by the formation of the stereocomplex in THF (see Results and Discussion).

Wide-angle X-ray scattering (WAXS) of the copolymer blend was analyzed using a Statton photographic X-ray camera using Cu Kα radiation ($\lambda = 0.154$ nm).

Results and Discussion

DSC Studies. Figure 1 shows the first scan (A) and the rescan (B) of the I-PMMA/S-PMMA–PDMS–S-PMMA blend prepared in THF (Experimental Methods). Thermogram A shows a very small endotherm with a maximum at −45 °C and a large endotherm with a maximum at 198 °C. The small endotherm corresponds to the melting of crystalline PDMS whereas the large endotherm corresponds to the dissociation–melting of the stereocomplex. The large endotherm at −45 °C in the rescan (B) indicates extensive crystallization of PDMS during the cooling of the sample after scan A. Rescan B shows a T_g at about 110 °C of the PMMA blend and a small transition at about 60 °C corresponding to the T_g of I-PMMA (see below). In this case there is no clear indication for the presence of the stereocomplex.

For comparison I-PMMA and the block copolymer were also precipitated by addition of the corresponding THF solutions to demineralized water (Experimental Methods). The corresponding thermograms showed no endotherms above 150 °C so that the endotherm observed at 198 °C for the copolymer blend cannot be due to solvent evaporation or to melting of I-PMMA crystals. However, the thermogram of the copolymer showed the same large endotherm at −45 °C as observed in Figure 1B, and the ΔH_m value was also found to be identical.

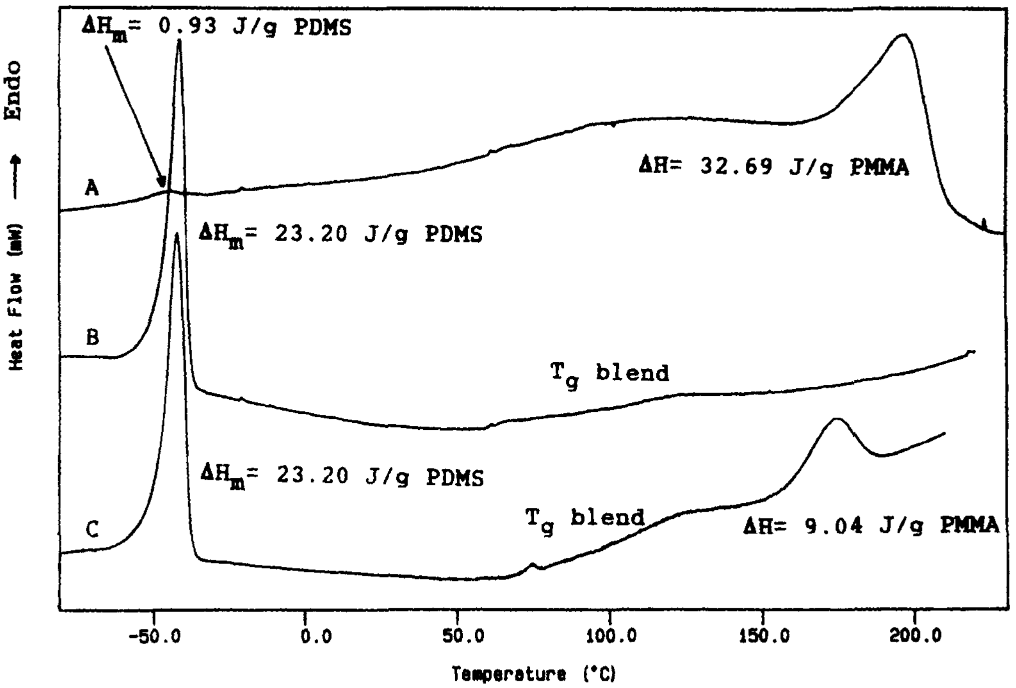


Figure 1. DSC thermograms of the blend I-PMMA/S-PMMA–PDMS–S-PMMA (S/I = 2) formed in THF (1.5 wt %): (A) in the presence of stereocomplex; (B) rescan without stereocomplex; (C) after 65 h at 125 °C. Heating rate: 10 °C/min.

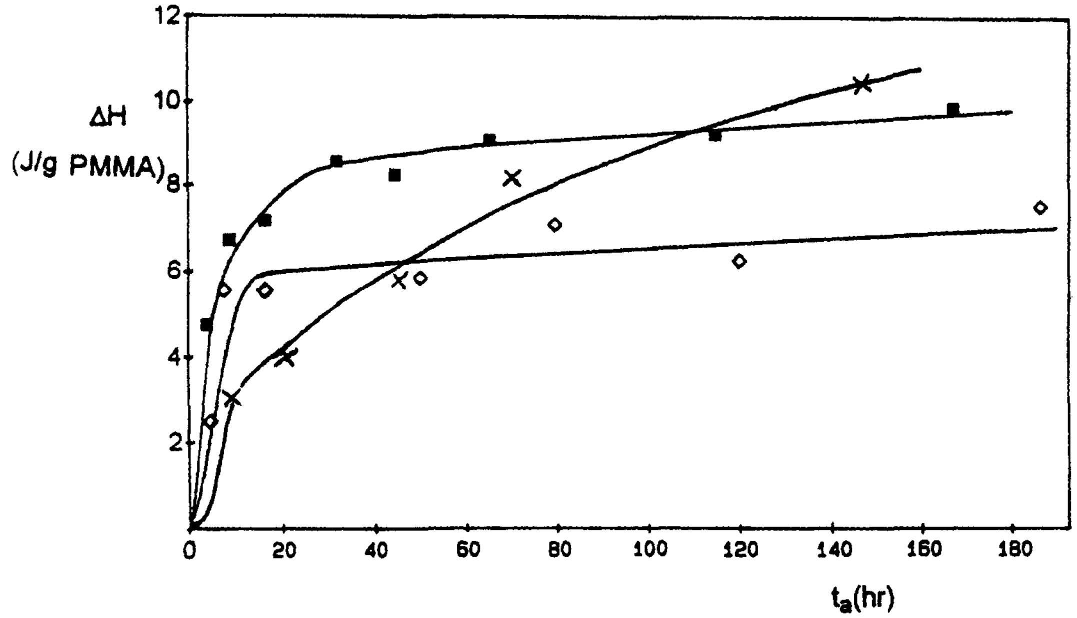


Figure 2. Heat of stereocomplex decomposition–melting $(\Delta H)_m$ as a function of annealing time t_a and annealing temperatures for the band I-PMMA/S-PMMA–PDMS–S-PMMA (I/S = 1/2) (heating rate: 10 °C/min). Annealing temperatures: 110 °C (◇); 125 °C (■); 140 °C (×).

The absence of a large endotherm at −45 °C in scan A is of interest. The presence of stereocomplexes appears to effectively prevent PDMS crystallization, presumably by immobilization of the PMMA blocks attached to the central PDMS block. The formation of PMMA stereocomplexes in THF (scan A) is also indicated by rapid viscosity increases observed on mixing the THF solution of I-PMMA and that of the block copolymer in the same ratio (S-PMMA/I-PMMA = 2).[9,10] Such increases are not unexpected since stereocomplex formation in such a case leads to bridging of the block copolymers by I-PMMA. Similar viscosity increases have been observed in the case of THF mixtures of S-PMMA–PBD–S-PMMA and I-PMMA (PBD = 1,4-polybutadiene).[5,10]

The rapid formation of stereocomplexes for the polymer blends in THF (Figure 1, scan A) is expected to lead to extensive immobilization so that much reorganization and formation of large crystals of stereocomplexes are not probable. Branching from fringed micellar crystals is more plausible in this case. The presence of a small transition at 60 °C in Figure 1 (scan B) is noteworthy since mixing of I-PMMA with the S-PMMA blocks of the copolymer would be expected to lead to the observation of a single T_g corresponding to homogeneous domains of I-PMMA and S-PMMA blocks. Perhaps the presence of this apparently phase-separated I-PMMA is due to incomplete mixing with the S-PMMA blocks which are attached to the large PDMS chain in the surrounding matrix. The presence of I-PMMA in the blend (scan B)

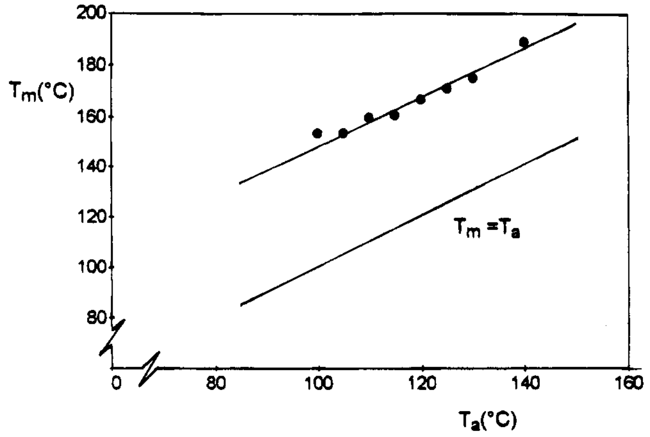


Figure 3. Decomplexation–melting temperature (T_m) as a function of annealing temperature (T_a) for stereocomplex formed in the bulk of the blend I-PMMA/S-PMMA–PDMS–S-PMMA (I/S = 1/2) (heating rate: 10 °C/min).

apparently had no substantial effect on the heat of PDMS melting since this was essentially the same for the copolymer blend and the copolymer itself.

Figure 1 also shows the thermogram (C) of the same I-PMMA/S-PMMA–PDMS–S-PMMA blend that was heated to 200 °C to erase thermal history followed by annealing at 125 °C for 65 h. The thermogram also shows a large endotherm at −45 °C corresponding to the melting of the PDMS block, a T_g at about 110 °C due to the PMMA blend, and an endotherm at 170 °C. Apparently, annealing at 125 °C allows for PMMA stereocomplex formation without adversely affecting PDMS crystallization during subsequent cooling since the ΔH_m for the PDMS block is identical to that of scan B. This is not unreasonable since in this case the slow formation of the PMMA stereocomplex allows adjustments allowing PDMS crystallization upon cooling. The amount of the stereocomplex is another matter, however, since the heat of melting is lower (9.04 J/g of PMMA vs 32.69 J/g of PMMA) than for the blend prepared in THF (scan A). Furthermore, the dissociation–melting temperature is lower as well (170 vs 198 °C). Apparently, in solution more and higher melting stereocomplex is formed than by annealing in bulk. This was also demonstrated by Challa and co-workers.[3,11] The mobility of the PMMA chains and chain segments is greater in solution, allowing the formation of more and "more perfect" stereocomplexes.

The effects of time and temperature on stereocomplex formation are illustrated in Figure 2. The heat of stereocomplex dissociation–melting (ΔH_m) of the block copolymer blend is shown to increase with annealing time (t_a) at annealing temperatures of 110, 125, and 140 °C. At 110 and 125 °C there is a substantial increase in ΔH_m over a period of about 20 h followed by a much smaller and slower increase over the next 160 h. However, at 140 °C the increase is somewhat slower initially but ΔH_m at longer annealing times eventually exceeds that at lower annealing temperatures. Furthermore, in all of these cases stereocomplex formation was slow initially since no clear endotherm for the stereocomplex was found for up to 30 min of annealing. In contrast, stereocomplex formation for I–S PMMA homopolymer blends is rapid, being detectable after annealing at comparable temperatures for only a few minutes.[3] Stereocomplex formation in the case of the block copolymer is apparently hindered substantially by the presence of the PDMS chain attached to the S-PMMA blocks and perhaps by the lower syndiotactic content of these blocks.

At the lower annealing temperatures, 110 and 125 °C, the heat of stereocomplex dissociation–melting increases faster as a function of t_a and reaches a lower limiting value earlier than at 140 °C. At 145 °C no endotherm could be detected, indicating a lack of stability of stereocomplexes at that temperature. At the lower temperatures the critical sequence length for stereocomplex formation is smaller than at higher annealing temperatures so that nucleation occurs faster

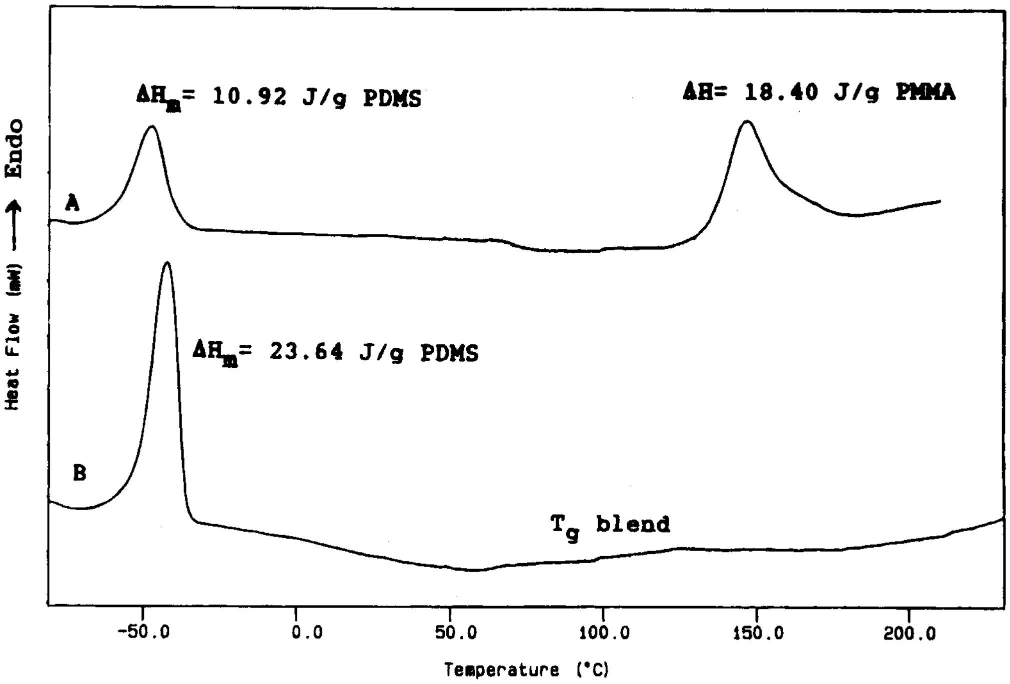


Figure 4. DSC thermograms of the blend I-PMMA/S-PMMA–PDMS–S-PMMA (I/S = 1/2). The blend was obtained by precipitation from a 2 wt % chloroform solution in methanol. First scan (A) and rescan (B). Heating rate: 10 °C/min.

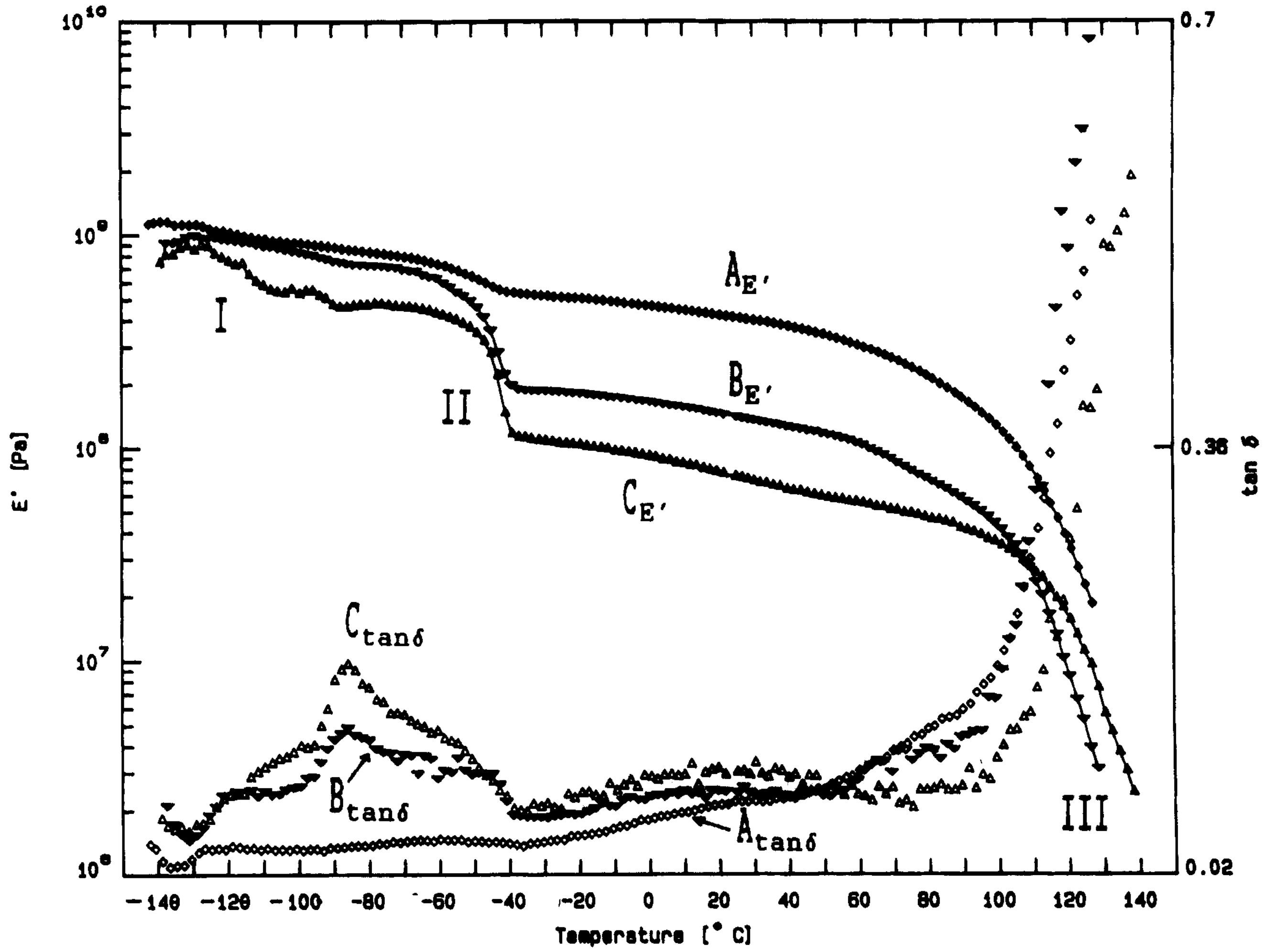


Figure 5. Storage modulus and loss tangent as a function of temperature (frequency: 1 Hz; heating rate: 2 °C/min) for the blend I-PMMA/S-PMMA–PDMS–S-PMMA (I/S = 1/2). The blend was obtained by precipitation from a 2 wt % chloroform solution in methanol. The blend was pressed at 125 °C (A) and 180 °C (B). The copolymer pressed at 180 °C is shown for comparison (C).

at lower temperatures and more "short" complexes are formed. As a result, immobilization resulting in network formation occurs faster and this slows down further complex formation and crystallization. At 140 °C the sequence length required for complex formation is longer so that a longer induction period is observed. However, the degree of perfection and length of the PMMA sequences involved in stereocomplex formation at 140 °C is higher, resulting in higher T_m values. This is illustrated in Figure 3, showing an approximately linear relationship between annealing temperature (T_a) and T_m in so-called Hoffman–Weeks plot.[12] The slope of approximately one is indicative of nonlamellar microcrystallites. This result is in accord with that of Schomaker et al. for annealed homopolymer blends of I- and S-PMMA.[13] On the basis of their mechanism, the endotherms shown in Figures 1 and 2 due to the stereocomplex "melting" may be ascribed to the presence of microcrystallites consisting of fringed micellar clusters of complexes. Apparently, both the short length of the S-PMMA block (M_w = 14 530) and the hindering by the elastomeric block in the copolymer prevent the formation of larger lamellar-type crystals, at least by annealing in bulk. Similar results, i.e., the linear correlation of T_m and T_a for PMMA stereocomplex formation in block copolymers, were demonstrated by Helary et al. for blends of AB block copolymers of S-PMMA–PBD with I-PMMA.[5] It was also observed that T_m increased a few degrees with annealing time both at 110 and 125 °C and became constant after about 16 h. At 140 °C it took more time before T_m became constant as complex formation proceeded more slowly at that temperature. Again these increases in T_m may be ascribed to rearrangements of imperfectly formed stereocomplexes or of poorly crystallized micellar clusters. However, Helary et al. found no dependence of T_m on T_a for stereocomplex formation in the case of S-PMMA–PDB block copolymers. It is possible that this is due to the shorter block length of S-PMMA in that case ($M_w \simeq$ 5000).

Figure 4 shows the scan (A) and rescan (B) of an I-PMMA/S-PMMA–PDMS–S-PMMA (I/S = 1/2 wt/wt) blend obtained by precipitation from a "noncomplexing" solvent chloroform by addition of the chloroform solution to methanol (Experimental Methods). The PDMS melting endotherm (A) is much lower than in the rescan, probably as a result of extensive but incomplete stereocomplex formation (see above). Thus, stereocomplex formation and its subsequent crystallization interferes with PDMS crystallization as shown above. The involvement of stereocomplex formation in this case is indicated by the fact that the DSC of the block copolymer sample obtained by precipitation under identical conditions gives no endotherm besides that of PDMS. The appreciable formation of stereocomplexes is of interest and indicates significant complex formation during precipitation and drying. However, the T_m of the stereocomplex is rather low (~145 °C), indicating

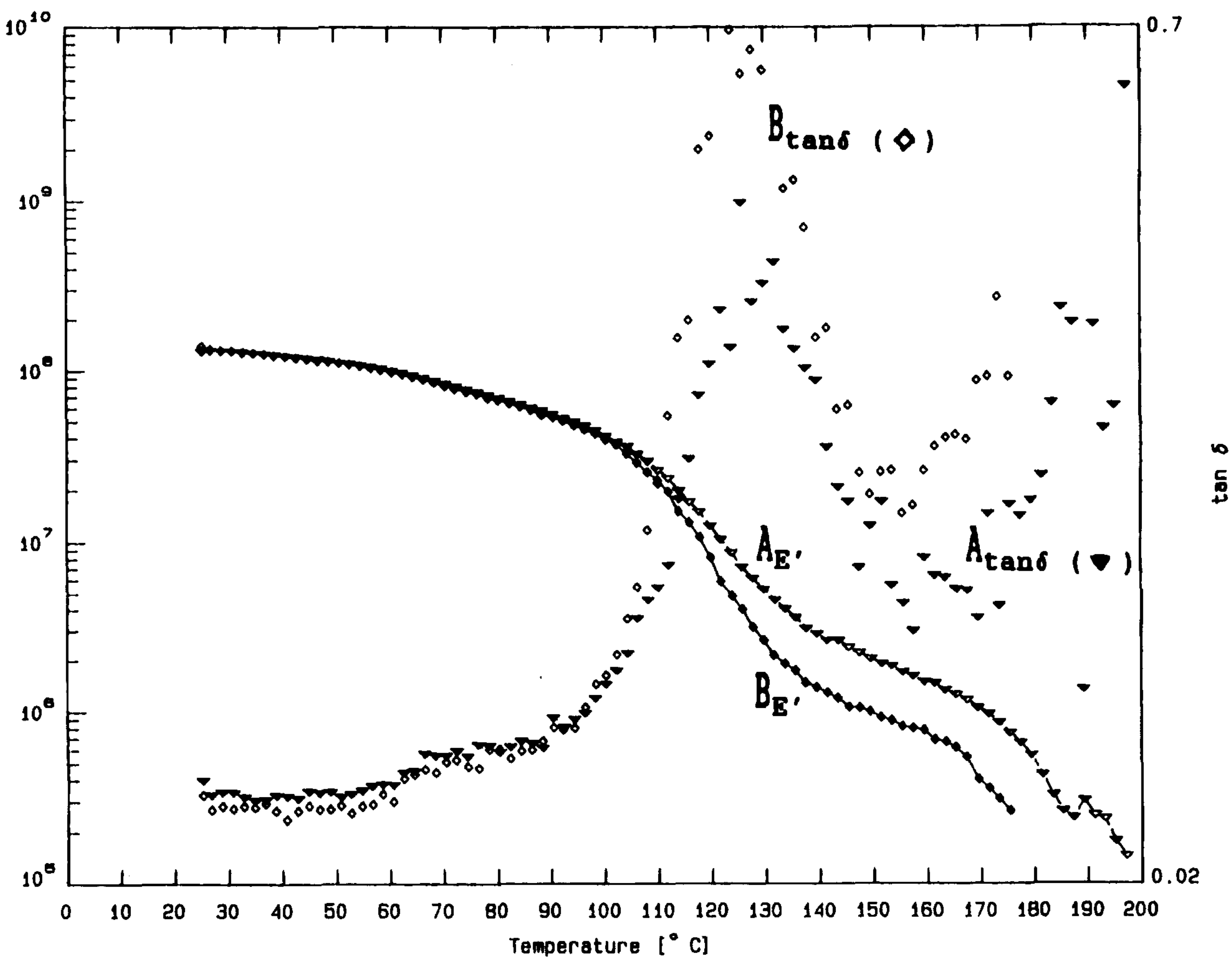


Figure 6. Storage modulus and loss tangent as a function of temperature (frequency: 1 Hz; heating rate: 2 °C/min) for the blend I-PMMA/S-PMMA–PDMS–S-PMMA (I/S = 1/2) annealed at 140 °C for 3.5 days (A) and without annealing (B). Both samples were pressed at 180 °C.

the formation of much less perfectly formed stereocomplexes compared to similar blends formed in THF (Figure 1). Furthermore, the ΔH_m of stereocomplex dissociation–melting is only about 55% of that of the blend formed in THF. The rescan B shows again the absence of stereocomplex and the presence of a much larger PDMS melting endotherm. An X-ray diagram (WAXS) of sample A showed two reflections at $2\theta = 12$ and 16°. These angles are nearly the same as were found by de Boer et al. for S-/I-PMMA blends containing stereocomplexes formed in solution,[14] indicating again that stereocomplex formation is probably involved.

DMTA Measurements. Stereocomplex formation in I-PMMA/S-PMMA–PDMS–S-PMMA blends is expected to stabilize the PMMA domains, especially at temperatures between the T_g of the PMMA domains and the T_m of the stereocomplexes. This is expected, at least in principle, to result in better mechanical properties of the annealed blends. Therefore the dynamic mechanical thermal analysis (DMTA) of the copolymers and their blends with I-PMMA is of obvious interest.

The DMTA scans of the blend of Figure 4 are shown in Figure 5 for samples pressed at 125 (A) and 180 °C (B). Both runs show three thermomechanical transitions. The weak transition at about −120 °C (I) corresponds to the T_g of PDMS. The transitions at −45 °C (II) and at about 110 °C (III) correspond to the melting of crystallized PDMS and the T_g of the blended PMMA domains, respectively. The storage modulus, E', of sample A is decreased less compared to sample B at the PDMS melting transition near −45 °C. Stereocomplex formation in sample A would be expected to be similar to that of sample A in Figure 4, whereas stereocomplex formation in sample B is much lower as a result of pressing this sample at 180 °C followed by rapid cooling as demonstrated by the absence of the stereocomplex in the rescan B in Figure 4. Thus in this sample (Figure 5, B) the melting transition at −45 °C leads to an approximately fourfold decrease in the modulus E' as a result of the melting of crystalline PDMS. For sample A the decrease is less, first since the fraction of crystalline PDMS is much lower (Figure 4) and also because stereocomplex formation serves to anchor the S-PMMA end blocks into a network. The difference in modulus between samples A and B remains intact over the −40 to +130 °C range and even increases slightly at the higher temperatures.

Figure 5 also shows the corresponding DMTA behavior of the copolymer itself pressed at 180 °C (scan C). Like the two other samples this one shows all three thermal transitions. The modulus is lower than that of scan B by about a factor of 2 over the −120 to +100 °C range. Presumably, this is the result of the lower PMMA content of this sample compared to that of B (39 vs 49%). Since the latter sample has domains containing both I- and S-PMMA, however, the T_g of these domains is lower than that of pure S-PMMA domains in sample C, which is in accord with the more rapidly decreasing modulus of sample B around 110 °C.

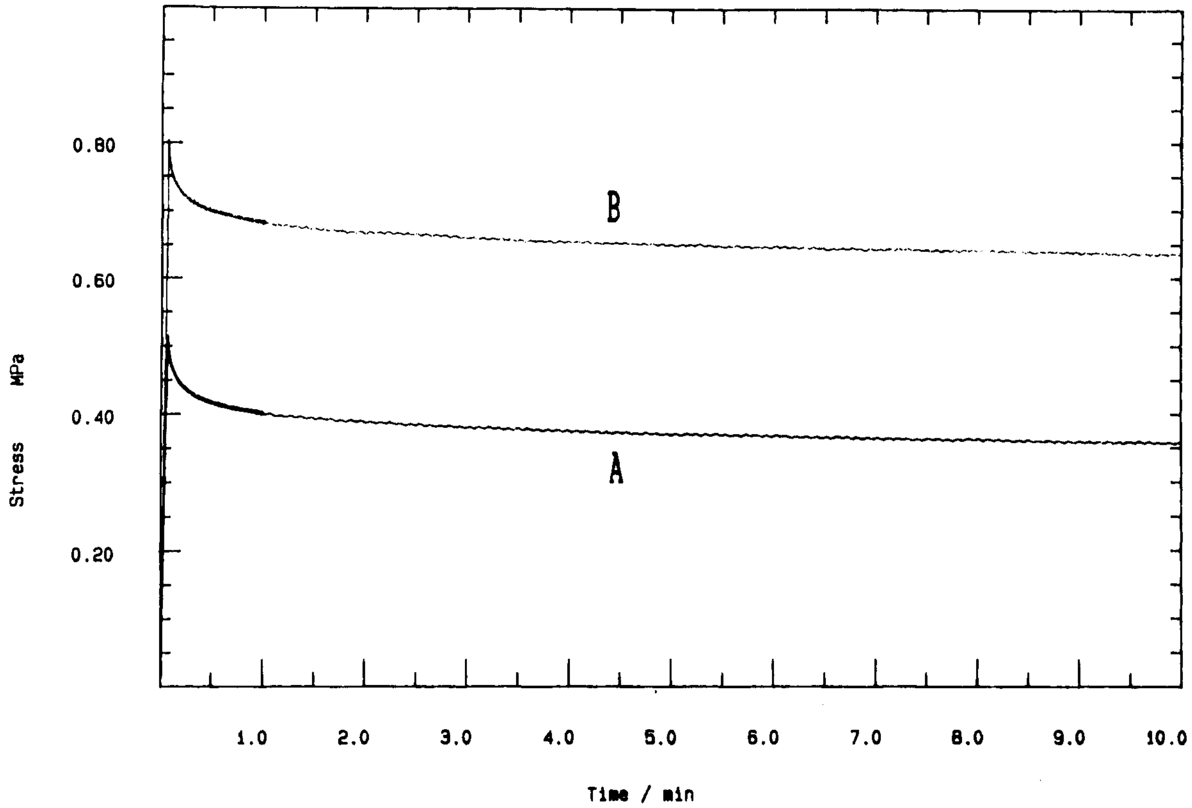


Figure 7. Stress relaxation at room temperature of the blend I-PMMA/S-PMMA–PDMS–S-PMMA (I/S = 1/2) (A) and the copolymer (B) after respectively 3.1 and 2.5% strain (crosshead speed: 10.0 mm/min). The blend and the copolymer were annealed for 24 h at 125 °C.

Figure 6 shows two DMTA scans of the copolymer blend without (B) and with (A) annealing for 84 h at 140 °C. An annealing temperature of 140 °C was chosen because this was shown to lead to stereocomplexes with the highest "melting" temperatures. The blend without stereocomplex formation is identical to scan B in Figure 5. The blend (A) has a lower storage modulus than blend A in Figure 5 in the same temperature region because annealing in bulk at 140 °C yields far less stereocomplex than precipitation and drying (see Figure 4A). Above 100 °C the difference in modulus gradually increases, and a differential of about a factor of 2 is maintained starting at about 120 °C until at least 180 °C. The annealed blend could even be heated to 200 °C without strong deformation of the bar. The loss tangent of the annealed blends shows somewhat lower values above 100 °C compared with the unannealed sample, indicating a stiffer material. These data clearly indicate that stereocomplex formation plays a significant role in the mechanical properties of the blends even at temperatures approaching the melting temperature (T_m) of the stereocomplex with very high T_m.

In addition, the cyclic stress–strain behavior of the copolymer and the copolymer blend was tested with a draw bench at room temperature after annealing both samples at 125 °C for 24 h. Both the blend and the copolymer showed recoverable strain and a slight hysteresis indicative of an elastic network with S-PMMA or blended PMMA domains acting as physical cross-links.

Finally, the stress relaxation of the annealed blend and the copolymer was determined after 2.5 or 3.1% strain as a function of time at room temperature (Figure 7). After a short time (~1 min) with about 20% stress relaxation, the stress again appears to become more or less constant in both cases, as should be the case for a stable network. The stress appears to be higher for the copolymer, presumably as a result of greater (elastic) PDMS content in the case of the copolymer.

Acknowledgment. T.E.H. wishes to acknowledge support by the DOD/Army Research Office, by the NSF/NBTM, and by the NSF-DMR Polymers Program.

References and Notes

(1) Challa, G.; De Boer, A.; Tan, Y. Y. *Int. J. Polym. Mater.* **1976**, *4*, 239.
(2) Katime, I. A.; Quintana, J. R. *Makromol. Chem.* **1986**, *187*, 1441.
(3) Feitsma, E. L.; De Boer, A.; Challa, G. *Polymer* **1975**, *16*, 515.
(4) Hogen-Esch, T. E.; Ladd, B. J.; Mason, J. P.; Helary, J.; Belorgey, G. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1990**, *31*(1), 405. Mason, J. P.; Hogen-Esch, T. E. *Ibid.* **1990**, *31*(1), 510.
(5) Helary, G.; Belorgey, G.; Hogen-Esch, T. E. *Polymer* **1992**, *33*(9), 1953.
(6) Kennedy, J. P.; Price, J. L.; Koshimura, K. *Macromolecules* **1991**, *24*, 6567.
(7) Mason, J. P. Ph.D. Thesis, University of Southern California, 1989.
(8) Goode, W. E.; Owens, F. H.; Feldmann, R. P.; Snijder, W. H.; Moore, J. H. *J. Polym. Sci.* **1960**, *46*, 317.
(9) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989.
(10) Hogen-Esch, T. E.; Mason, J. R.; Ladd, B. J.; Helary, G.; Belorgey, G. *Contemporary Topics in Polymer Science*; *Advances in New Materials*, Riffle, J., Salamone, J. C., Eds.; Plenum Press: New York, 1992; Vol. 7, p 339.
(11) Vorenkamp, E. J.; Bosscher, F.; Challa, G. *Polymer* **1979**, *20*, 59.
(12) Hoffman, J. D. *SPE Trans.* **1964**, *4*, 315.
(13) Schomaker, E.; Challa, G. *Macromolecules* **1988**, *21*, 2195.
(14) De Boer, A.; Challa, G. *Polymer* **1976**, *17*, 633.

MA941288D