Structure–property behaviour of free radical synthesized polydimethylsiloxane–polystyrene multiblock polymers: 1. Effect of the siloxane block length

Daan Feng and Garth L. Wilkes*
Department of Chemical Engineering and Polymer Materials and Interfaces Laboratory, Virginia Polytechnic Institute and State University, Blacksburg, VA 240601-6496, USA

and James V. Crivello
General Electric Corporate Research and Development Center, Schenectady, New York 12301, USA
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The morphological structure and the physical properties of free radical synthesized PDMS–PS multiblock polymers have been studied. The polymers were prepared by free radical copolymerization of PDMS macroinitiators with styrene monomer. The length of the PDMS blocks was basically predetermined by the molecular weight of the PDMS macroinitiators which were cationically prepared. However, the PS blocks were formed during the free radical copolymerization. Therefore, the molecular weight and the molecular weight distribution of the PS blocks varied with the PDMS block length at constant styrene conversion level. Hence, the morphology of these polymers as well as the degree of phase separation was altered by the block length of both components. Specific mechanical properties of these polymers were directly related to their morphological structure.

(Keywords: polydimethylsiloxane–polystyrene (PDMS–PS); multiblock polymers; structure–property behaviour)

INTRODUCTION

Polydimethylsiloxane (PDMS) displays a number of very desirable properties for many applications: it possesses a very low glass transition temperature (–120°C), excellent thermal stability, high oxidative stability, high lubricity, and excellent gas permeability. However, crosslinked PDMS has poor tensile strength and often lacks solvent resistance[1]. Incorporating polydimethylsiloxane with proper vinyl monomers into block polymer materials would, it is hoped, retain many of the advantages of the special properties of polydimethylsiloxane while alleviating some of its shortcomings. Indeed, block polymers utilizing polydimethylsiloxane as the soft segments or blocks have displayed several of the features stated above[2–4]. Another unique feature of block or segmented polymers in general is their ability to achieve a network structure by physical rather than chemical crosslinking. This feature generally allows one to process these materials by methods utilized for thermoplastics[1]. For these reasons, over the past two decades, PDMS block polymers have received a good deal of attention as thermoplastic elastomers. While there are several possible hard blocks that could be utilized in conjunction with PDMS, polystyrene (PS) seems to offer economics suited for potential commercial production[2].

In the synthesis of polydimethylsiloxane–vinyl block polymers, anionic as well as condensation polymerization have been used. The anionic synthesis method has been regarded as the best 'technical' route since it provides a high control on molecular weight and molecular weight distribution of each block and hence a well defined linear structure block polymer can be produced[2–9]. The condensation polymerization of α,ω-hydrogen terminated PDMS with α,ω-vinyl terminated styrene oligomers has been applied to prepare PDMS–PS multiblock polymers by Rempp *et al.*[10].

Free radical addition synthesis has also been used to prepare block polymers as early as the 1960s. In attempting to form block polymers, Tobolsky and Rembaum[11] used polypropylene oxide diisocyanate with t-butyl hydroperoxide to form a diperoxycarbamate macroinitiator, which was then used to initiate free radical polymerization. A major advantage of this system is that it does not require high purity of the species as in the anionic method. Furthermore, by using one macroinitiator, this approach in principle allows one to prepare a large variety of block polymers with a variety of vinyl monomers[12–14]. However, many disadvantages of this route also exist. In general, the free radical synthesis as just described cannot provide good control of the final structure of the block polymers and results in a large variation of the properties of the final products. Of particular importance is that this route has always led to a substantial amount of homopolymer of the second comonomer which often leads to another level of phase separation[15,16].

Recently, Crivello *et al.*[17,18] have developed a unique free radical synthesis method to prepare PDMS–vinyl block polymers. Their method consists of the preparation

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* To whom correspondence should be addressed

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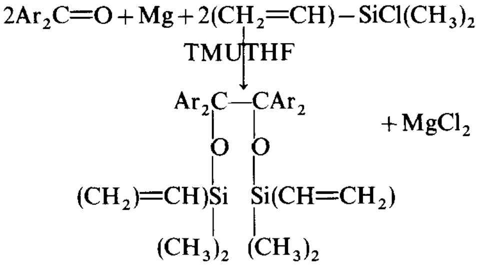
of a bis(silyl pinacolate) initiator; the use of the pinacolate to prepare a high molecular weight polydimethylsiloxane macroinitiator and the use of these macroinitiators in conjunction with proper vinyl monomers to prepare the multiblock polymers by a free radical block polymerization. By using pinacolate initiators, a high blocking efficiency was achieved and the probability of formation of homopolymers is essentially reduced to zero if proper selection of a co-monomer is made.

The silyl pinacolate initiators are prepared by the reduction of diaryl ketones with magnesium metal in the presence of dimethylchlorovinyl silane with THF (tetrahydrofuran) as the solvent and TMU (tetramethylurea) as a promoter (Scheme 1)[17].



Scheme 1

There are two reasons for using the silyl pinacolate as an initiator. First, vinyl silanes are extremely sluggish toward free-radical polymerization even with the most active free radical initiators. Hence, the vinyl double bonds can be retained during the initiator preparation and later serve as sites for attachment of the PDMS blocks under more active conditions. Secondly, the silyl pinacolate initiator can undergo facile thermolysis at low temperatures (60–80°C) to give dimethylvinyl silyl ketyl radicals. However, the 'carbon-centred' free radical which is formed during thermolysis is of low reactivity due to the resonance delocalization due to two neighbouring aromatic rings and the steric hindrance provided by the two aryl groups[18]. The low reactivity of this free radical means a longer life time. During the later free radical block polymerization with vinyl monomers, the steric hindrance of these carbon centre free radicals can reduce the probability of recombination of the macroinitiators.

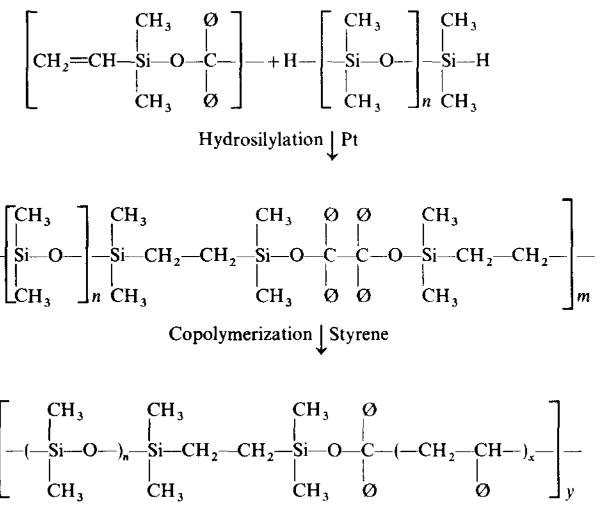
The PDMS macroinitiators are prepared by the hydrosilylation of vinyl containing bis(silyl pinacolates) with α,ω-hydrogen functional polydimethylsiloxane oligomers. These oligomers are prepared by cationic ring-opening polymerization of octamethylcyclotetrasilane (D_4), in the presence of tetramethylsiloxane as a chain stopper. The synthesis of the PDMS oligomers is outlined in Scheme 2. Using this synthesis method, the final molecular weight of the α,ω-hydrogen oligomers can be well controlled.

$$[H\text{—}(CH_3)_2Si\text{—}]_2\text{—}O + n\text{—}[\text{—}(CH_3)_2SiO\text{—}]_4\text{—}$$
$$\downarrow$$
$$H\text{—}[\text{—}(CH_3)_2SiO\text{—}]_{4n+1}\text{—}(CH_3)_2Si\text{—}H$$

Scheme 2

These PDMS macroinitiators can yield a high portion of polydimethylsiloxane macrodiradicals on thermally induced fragmentation. The PDMS diradicals can then undergo chain extension at both ends in the presence of vinyl monomers and form block polymers. The overall reaction is shown in Scheme 3.

Analysis of the products has shown that only block polymers were found in the final polymers by this synthesis just outlined[17,18]. These materials have also displayed evidence of microphase separation due to the development of intense iridescence during the later stages of the styrene reaction. As expected, the mechanical properties of these block systems, utilizing styrene as the vinyl monomer, are highly dependent on the composition of the polymer, and the film casting solvent if solution casting is used. Depending on the block length and the relative portion of the hard polystyrene (PS) and soft (PDMS) segments, either thermoplastic elastomers or rubber-modified thermoplastics can be produced. However, no details of the morphology of these materials have been presented and will be considered as one of the principal topics within this paper.



Scheme 3

In order to develop a better understanding of these new novel systems, a series of these free radical synthesized PDMS–PS block polymers with various PDMS block length and overall conversion levels have been studied. The investigations have concentrated on the effect of block length, overall conversion level, and the influence of film casting solvent on the mechanical and morphological properties. In this paper, the morphological nature, phase separation, and the effect of block length will be discussed. Later papers will describe the effects of styrene conversion level and the influence of the film casting solvent on resulting structure–property behaviour[19].

EXPERIMENTAL

Sample preparation

The composition of the free radical synthesized polydimethylsiloxane-polystyrene block polymers are listed in *Table 1* along with the degree of styrene conversion. The solvent cast polymer sample designation utilized is as follows:

S14—62—M
Casting solvent *m*-methylene chloride
Styrene conversion level %
PDMS block length $M_n/100$

Table 1 Composition of the free radical PDMS–PS block polymers

Sample	PDMS block M_n	PDMS (wt%)	Conversion (%)	M_n (g/mol)
S14-95	1360	37	95	85 400
S26-91	2634	41	91	161 000
S45-95	4520	42	95	148 000
S89-34	8940	49	34	162 100
S99-95	9894	42	95	290 100
S193-95	19300	41	95	310 000

Before film casting, the as received polymers were dried *in vacuo* at 60°C for 24 h. Then 2 g of polymer were dissolved into 20 cc of the selected casting solvent and stirred for 2 h until all polymer was completely dissolved. Films were cast on a Teflon surface at room temperature. The solvent was allowed to slowly evaporate over a period of two to three days. These films were then dried at 80°C for an additional 4 h. The films were further dried *in vacuo* at 80°C for 24 h to remove any last traces of solvent. The prepared sample films were then stored in a vacuum desiccator until used.

Mechanical properties

The tensile stress–strain of these block polymers were performed on an Instron 1122 tester. Dogbone specimens with dimensions of 2.8 mm in width and 10 mm in length were cut from the films. The tensile stress tests were carried out at room temperature (25°C) at a crosshead speed of 5 mm per minute.

Differential scanning calorimetric analysis

The differential scanning calorimetric (d.s.c.) measurements were carried out on Perkin-Elmer DSC-4 and DSC-2 differential scanning calorimeters. The high temperature range (25°–150°C) studies were carried out on the DSC-4 calorimeter. The low temperature measurement range, −150–25°C, were made using the DSC-2 device on some selected samples.

The DSC-4 was calibrated using a standard indium sample. At the scanning rate of 10°C per minute, the temperature deviation was ±0.5°C and the deviation of specific heat was ±0.5%. All samples for the d.s.c. studies weighed 10 ± 0.1 mg and were sealed in an aluminium sample cell. Standard polystyrene samples purchased from Scientific Polymer Products Co., were used for heat capacity analysis. These PS samples have a ratio of $M_w/M_n < 1.06$ and M_w of these PS samples ranged from 1940 to 100 000.

For the high temperature d.s.c. studies, all samples were heated to 140°C for 30 min then quenched to room temperature before d.s.c. data were obtained. After annealing, the d.s.c. measurement was carried out at a heating rate of 10°C per minute and a cooling rate of 320°C per minute under a constant stream of nitrogen. Data were collected during the heating part of the cycle. The glass transition temperature, T_g was defined as the temperature at which the heat capacity of the sample was between that of the glassy and rubbery states (midpoint method).

A few selected samples were run in the low temperature range (−150–25°C) to study the crystallization of the PDMS block. Samples were annealed at 100°C and quenched to room temperature. Then samples were further cooled down to −150°C by liquid nitrogen using a cooling rate of 320°C per minute. The d.s.c. data were collected during heating at a rate of 10°C per minute.

Dynamic mechanical thermal analysis

The dynamic mechanical studies of these PDMS–PS block polymers were performed on an automated dynamic viscoelastometer model Rheovibron DDV-II-C (Imass). The temperature range utilized was from −150–150°C. The sample strips were cut from solvent cast films and cooled to −150°C at a cooling rate of 2–3°C per minute. Then the dynamic measurements were carried out at frequencies of 11 Hz with a heating rate of ca. 2°C per minute. All measurements were performed under a purging dry nitrogen stream.

Thermomechanical analysis (TMA)

The TMA studies of these PDMS–PS block polymers were carried out on a Perkin-Elmer TMS-2 thermomechanical analyser with the penetration probe. The temperature range utilized was from −150–150°C. The loading was 20 g and the heating rate was 10°C per minute.

Small angle X-ray scattering (SAXS)

The microphase structure of the PDMS–PS block polymers was also investigated by using small angle X-ray scattering (SAXS). An automated Kratky small angle X-ray camera was utilized for the SAXS measurements. The X-ray source was a Siemens AG Cu 40/2 tube, operated at 40 kV and 20 MA by a GE XRD-6 generator. A Cu Kα-radiation of wavelength 0.154 nm was obtained by Ni-foil filtering. The scattered intensity was monitored by a one dimensional position sensitive detector (M. Braun-Innovative Technology Inc.).

Transmission electronic microscopy (TEM)

A Philips EM 420 scanning transmission electron microscope (STEM) was used to examine the morphological texture of the PDMS–PS block systems. The STEM was operated in the TEM mode at an accelerating voltage of 100 kV. The ultrathin sections (<50 nm) of a polymer film for the TEM investigations were prepared by cryo-ultramicrotoming on a Reichert-Jung Ultravute system model FC4. The ultramicrotoming temperature was −100°C. The sections were taken from a liquid surface of methanol with copper grids. The ultrathin sections were microtomed in the direction perpendicular to the film surface. Some sections were also prepared parallel to the film surface. However, no major difference was observed in the morphological textures. Due to the high electron density of polydimethylsiloxane compared to polystyrene, sufficient contrast was obtained without the need for selective staining.

The trifluoroacetic acid degradation of PDMS–PS block polymers

To 0.25 g of the block polymer dissolved in 5 ml chloroform there were added 2 drops of trifluoroacetic acid and 30 μl of water. This reaction mixture was refluxed for 5 h to promote the selective chain scission of the block polymer at the pinacolate linkage. The final solution was analysed for the siloxane block molecular weight by g.p.c. with an i.r. detector set at 9.3 μ (SI-O bond) and for the PS blocks using a u.v. detector set at 254 nm. The molecular weights were determined using polystyrene standards. No correction was applied for the molecular weight of the PDMS blocks.

RESULTS AND DISCUSSION

Indication of phase separation

Earlier studies of these PDMS–PS systems[17,18] have shown that only block polymers are formed by this free radical route. This was confirmed by a composite g.p.c. chromatogram using three distinct detectors: a refractive index detector to detect the elution volume of any species, a u.v. detector (at 254 nm) to detect the aromatic rings in the PS block, and an i.r. detector (at 2.9 μm) to detect Si–O–Si groups in the PDMS block[18]. The responses of these three detectors are essentially identical which indicates that the composition of a given PDMS–PS block polymer is homogeneous throughout the entire range of molecular weights. Results from n.m.r. analysis[18] also supported the g.p.c. data regarding only the formation of block polymers. Besides the g.p.c. and n.m.r. results, other indirect evidence for block polymer formation extends from the occurrence of intense iridescence in the later stages of the reaction, solvent dependent mechanical properties, and occurrence of two glass transition regions.

Indeed, results from d.s.c. dynamic mechanical analysis (DMA), TMA and TEM all verify that block polymers are clearly formed by this free radical synthesis and that microphase separation occurs. As one example, *Figure 1* shows the d.s.c. thermograms of these PDMS–PS block polymers. The transition temperatures and other thermal characteristics have been listed in *Table 2*.

The d.s.c. results show that the T_g of the PDMS block decreases as the PDMS block length increases. For example, the T_g of the PDMS blocks is ca. -60°C for S14-95-M and -125°C for S193-95-M (*Figure 1a* and *Table 2*). The latter T_g is almost the same as the T_g of homopolymer PDMS with similar molecular weight[21–24]. For the PDMS homopolymers, the T_g increases from -130°C to -125°C as the number average molecular weight, M_n, increases when the M_n is less than 2460[23]. When the number average molecular weight is greater than 2460, the T_g is around -124°C and only increases very slightly with an increase in molecular weight[23]. Therefore the distinctly higher T_g of the shorter PDMS blocks in these free radical PDMS–PS block polymers is believed due to some degree of polystyrene mixing within the PDMS block phase. It is also possible that since the PDMS blocks would, on the average, be connected to glassy PS blocks, some restriction of mobility at the chain ends would also conceivably slightly enhance the PDMS T_g values. Such postulations have been made by others and have experimental support[25,26]. For example, the T_g of an aminopentyl terminated PDMS oligomer with the M_n of 1550 was -120°C (ref. 25) which was 7°C higher than the T_g of linear PDMS having similar molecular weight[23]. The higher T_g was attributed to the restrictions imposed on the soft PDMS segments by the polar end groups[25].

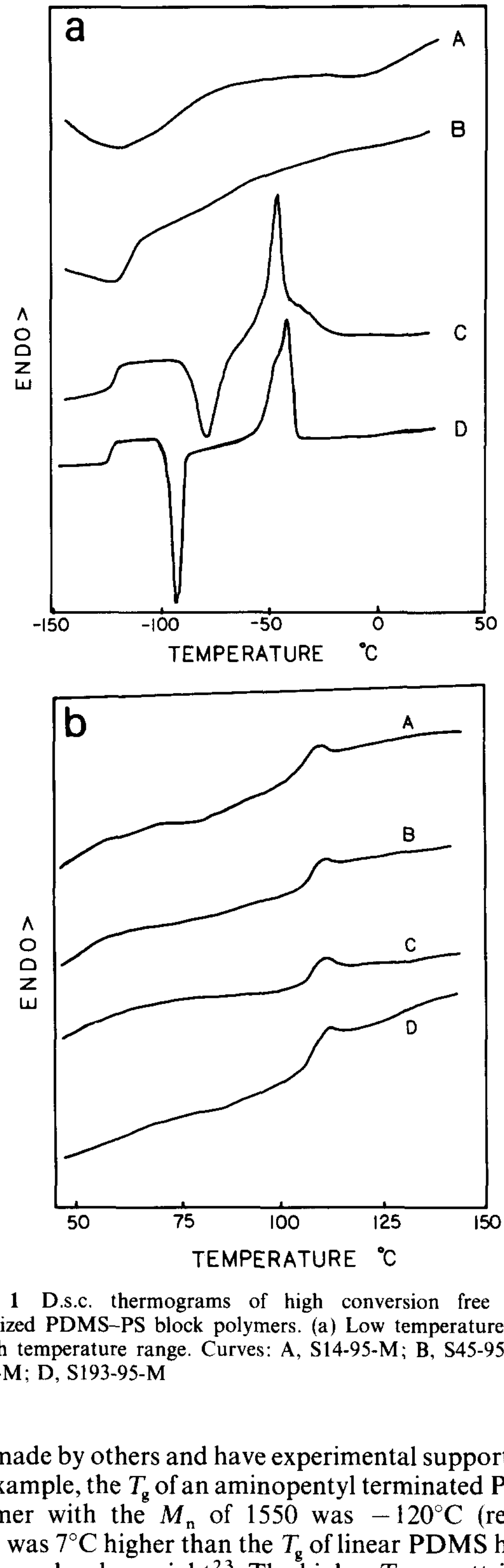


Figure 1 D.s.c. thermograms of high conversion free radical synthesized PDMS–PS block polymers. (a) Low temperature range; (b) high temperature range. Curves: A, S14-95-M; B, S45-95-M; C, S99-95-M; D, S193-95-M

Table 2 Thermal characteristics of the free radical PDMS–PS block polymers

	PDMS Block			PS Block
Sample	T_g °C	T_c °C	T_m °C	T_g °C
S14-95-M	-100	–	–	104
S26-91-M	–	–	–	103
S45-95-M	-116	–	–	104
S89-34-M	-125	-82	-51	101
S99-95-M	-123	-81	-49	107
S193-95-M	-125	-94	-43	107

When the PDMS block length is greater than 4500, both an exothermic peak and an endothermic peak are observed in addition to the glass transitions. The exothermic peak corresponds to the crystallization of PDMS blocks and the endothermic peak is the corresponding crystalline melting peak of these same blocks. The crystallization and melting peaks have not been seen for the shorter PDMS blocks (M_n less than 4500) samples because of the very small length of the siloxane chain involved[25]. Similar observations have been noted in PDMS–PS diblock polymers[27] and in PDMS–urea segmented polymers prepared using oligomeric PDMS species[23,25,28]. While often a dual melting point may be observed in homopolymer PDMS[23,25,28], our results displayed only a single somewhat broadened melting peak. These observations are consistent with earlier results obtained on PDMS–urea segmented copolymers studied within our laboratory[25]. All melting peaks range from −51°C to −43°C and increase with the PDMS block length. As expected the melting temperature of high molecular weight the PDMS blocks is lower than that of pure PDMS homopolymer.

The d.s.c. results also indicate that the glass transition temperatures of the PS blocks for all of these high conversion level polymers is around 105°C (*Table 2*), although there is some difference in the breadth of the T_g dispersion. The T_g values recorded here are higher than the values reported earlier by one of the authors[18]. The lower T_g values presented earlier were caused by the presence of residual solvent in the samples[29]. The polystyrene T_g values (greater than 100°C) for these polymers suggest that a reasonably high molecular weight (greater than 10 000) PS block is formed during the free radical polymerization. The greater breadth of the T_g may result from a broadened molecular weight distribution of the PS block. More detailed discussion on the molecular weight and the molecular weight distribution of the PS blocks will be given in later sections. The d.s.c. results also show that the T_g of the PS phase is not altered with varied PDMS block lengths for these high conversion samples. However, the T_g of the PS phase does change with low levels of styrene conversion. For example, sample S89-34-M displays a distinctly lower T_g for the PS phase and is indeed a real effect which will be a topic of discussion in a later paper where styrene conversion level is considered.

The dynamic mechanical data also clearly confirm that phase separation occurs in these materials. *Figure 2* shows the dynamic mechanical spectra for the high conversion PDMS–PS block polymers. For all samples, two or more transition states are displayed. Two of these transition states correspond to the glass transitions of the two components PDMS and PS respectively. A distinct plateau in the behaviour of E′ also exists between these two transition states but its width is distinctly dependent upon the initial length of the PDMS block. For the polymers containing long PDMS blocks such as S99-95-M and S193-95-M, a small peak also appears at −50°C in the tan δ spectra. This peak corresponds to the crystalline melting region of the PDMS blocks (see *Figure 2*).

The dynamic mechanical results indicate that the PDMS block length has a strong influence on phase mixing. When the block length of the PDMS decreases, the behaviour of tan δ of the PDMS T_g transition is distinctly broadened and shifted to higher temperatures. This shift is believed to be caused by phase mixing of the shorter PS blocks in the PDMS regions. Strong indirect support for this latter statement extends from the work of Hashimoto *et al.*[30] who simulated the dynamic mechanical response of tapered PS–polyisoprene block polymers using a composite model. In particular, their calculations considered the relative effects of two component mixing within domains (phase mixing) and the effects of two components mixing in the boundary regions (interphase mixing) on the dynamic mechanical response. Some of the pertinent results of their simulation are shown in *Figure 3* and distinctly support our own experimental observations. As their results indicate, the E'' peak correlated with T_g of the soft segment is shifted to a higher temperature as the degree of phase mixing of two block components increases (*Figure 3*), while the E'' peak of the hard block is only slightly shifted to lower temperatures. Comparing our data of *Figure 2* with *Figure 3*, one notes that these results are very similar except that we have utilized tan δ instead of E''. This change in variable will result in a somewhat higher transition peak but the general response will be the same. This upward shift of the PDMS T_g in our data is strongly believed to arise from phase mixing of the shorter styrene blocks within the PDMS regions. Note that when the PDMS block is greater than 4500, only a small shift of T_g is observed (recall *Figure 2*).

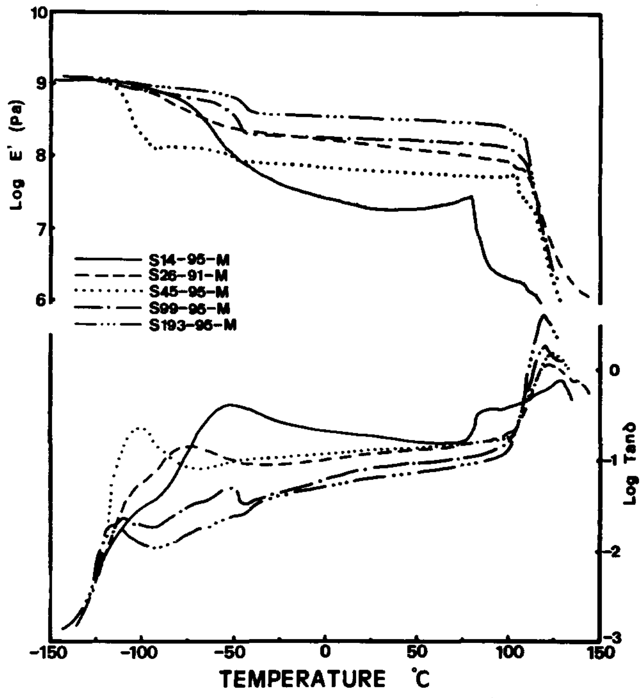


Figure 2 Dynamic mechanical behaviour of the high conversion PDMS–PS block polymers

Interestingly, it is noted that the position of the tan δ peak of the styrene phase is only slightly affected by the PDMS block length. This difference is an important clue and is believed to arise principally from the formation of the more prevalent high molecular weight PS blocks and hence there is at best little mixing of PDMS occurring within the rich PS phase. In *Figure 2*, the E' behaviour of S14-95-M shows an increase with temperature from 25°C to the T_g of the PS blocks. In this specific sample, the PDMS phase is a continuous phase. The increasing modulus with temperature is therefore believed to be caused by the rubber elasticity effect of the PDMS matrix. Another unusual feature of these PDMS–PS polymers is a small but reproducible two-step drop of the storage modulus, E', for the PS glass transition region for most high conversion samples (*Figure 2*). These two step transitions are highly frequency dependent and they may be caused by the incompatibility between the large and the small molecular weight PS blocks which may result

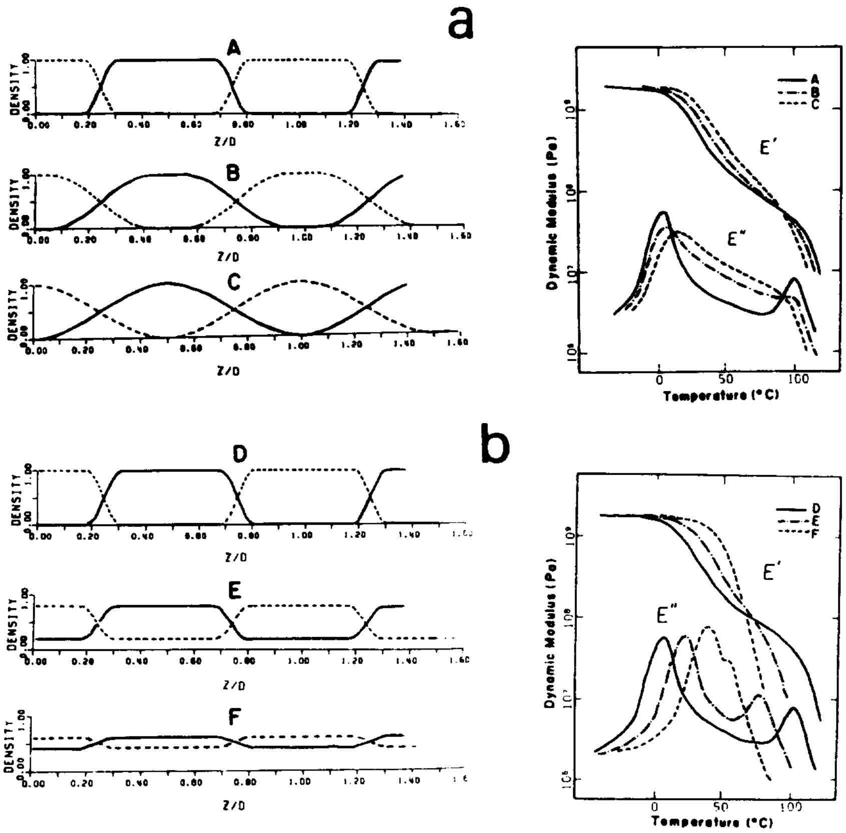


Figure 3 Spatial distribution of PS–BD tapered block polymers and the corresponding computer simulated dynamic mechanical responses at 10 Hz (from ref. 38). (a) Effect of the interphase mixing. The interphase mixing increases in the order from A to C. (b) Effect of the phase mixing. The phase mixing increases in the order from D to F

from the free radical copolymerization (see later discussion).

The TMA results are also in good agreement with dynamic mechanical results. As *Figure 4a* shows, these systems each display two distinct glass transition regions. The T_g of the PDMS phase is shifted to higher temperatures as the PDMS block length decreases. For S193-95-M, the disappearance of the PDMS T_g is caused by the high degree of crystallization of the long PDMS blocks. At temperatures higher than 50°C, a thermal expansion is observed which may be caused by some large PS blocks in this sample. The degree of penetration in the rubbery region (between the two T_g values) also decreases with an increase of the PDMS block length. For all samples, there is a shoulder on the PS softening peak as noted from the derivative curves (*Figure 4b*). These shoulders indicate that the PS glass transition undergoes what appears to be a two step process in these materials. These results are consistent with the results from dynamic mechanical analysis. The changes in the penetration and the step transition in these materials are speculated to be due to the changes in the block length and the molecular weight distribution of the PS blocks resulting from the changes in the PDMS block length. As a result, the morphological texture of these materials would be expected to change. TEM data that will be presented shortly will verify this speculation.

Estimating the level of phase mixing and its dependence on PDMS block length

As is well known, the level of microphase separation of nonpolar or low polarity block and segmented polymers is dependent on the square of the difference in the solubility parameters of the two components[31–33]. However, the block length of each component also affects the degree of phase mixing as does the general nature of certain architectural features such as the number of blocks or junction points per molecule[27]. While at times it is difficult to apply this general solubility parameter consideration in view of more complex interactions caused by polarity or ionic interactions, in the case at hand, the solubility parameter concept seems applicable. In fact, on this basis alone, since PDMS has a solubility parameter of about 7.3 and polystyrene about 9.4 $(\text{cal/cc})^{1/2}$, one would anticipate very good phase separation because generally a difference in solubility parameters of nearly one unit promotes relatively sharp boundary regions at least for higher molecular weight blocks[34]. A means of estimating the nature of phase mixing in a quantitative fashion can be estimated by scattering methods[35] but can also be determined by using calorimetry and, in particular, the measurement of the change in heat capacity over the glass transition region. The latter of these methods will be applied here and in particular to the polystyrene glass transition.

Earlier studies[21,22,36,37] on the block polymer with the PS as the hard segments indicate that the T_g of the PS phase seems to principally depend on the block length of the PS blocks only. In these studies, the soft segments were either isoprene, butadiene, or PDMS. While the T_g of the PS blocks does not seem to change with the chemical nature of the soft segment except when phase separation is lost, the change in the heat capacity over the PS glass transition region (ΔC_p) and the breadth of

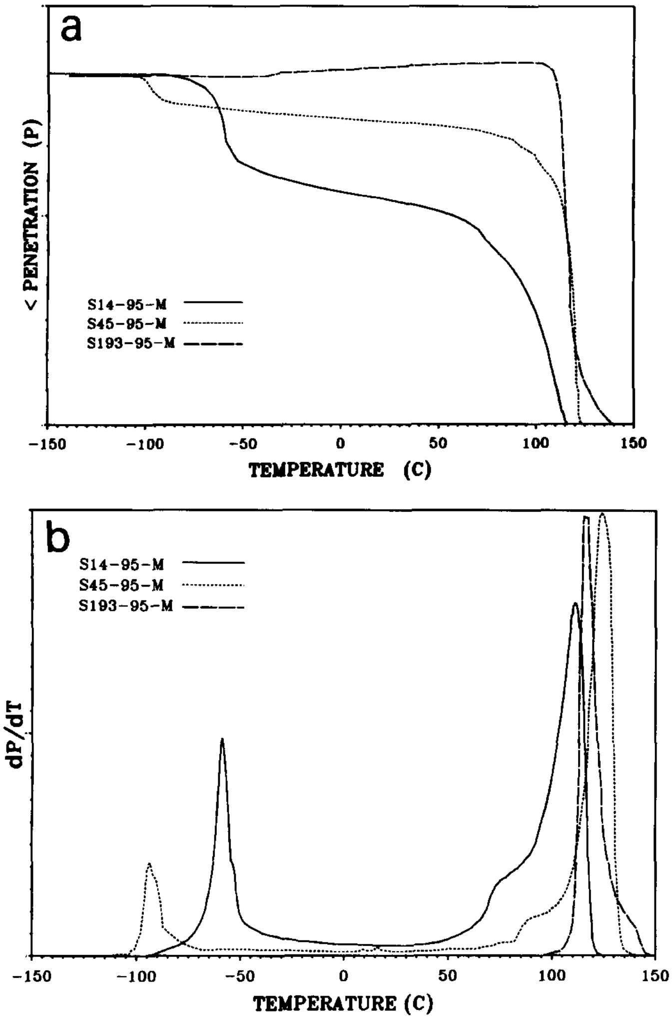


Figure 4 Thermal mechanical responses of high conversion PDMS–PS block polymers. (a) Penetration curves; (b) derivative curves

the T_g have been noted to change with the nature of the soft segment. In block polymers, the ΔC_p of the styrene phase tends to provide lower values than the ΔC_p value of homopolymer styrene. Morese-Sequela *et al.*[36] have reported that the ΔC_p for the polystyrene block in an isoprene–styrene diblock polymer was below that observed for the corresonding styrene homopolymer. In their samples, the PS block molecular weight varied from 1400–4600. Cowie *et al.*[38] have also reported a similar result on the value of ΔC_p for PS blocks of an isoprene–styrene triblock polymer. Krause *et al.*[22] have made related studies of PDMS–PS diblock polymers prepared by anionic synthesis. In their systems, the PS content ranged from 24–88 wt%. The PS block molecular weight ranged from 1400–31 800 and the molecular weight of the PDMS block varied from 2400–23 000. Again, they reported that the ΔC_p of the styrene block was equal or only slightly lower than that of the styrene homopolymer when the block length exceeded 8200. However, when the PS block length was less than this value, the ΔC_p of the PS block was either higher or lower than the homopolymer. The lower ΔC_p value was believed to be caused by the mixing of some of the lower molecular weight PS blocks into the PDMS phase. In contrast, a rise in ΔC_p can only be accounted for on the basis of a mixing of the soft block into the PS phase thereby promoting a greater rise in ΔC_p at the time the styrene transition occurs. This latter case assumes that no PS material has mixed in the PDMS phase. This mixing of the PDMS phase in the hard block however, would only be expected to occur whem the polystyrene block length is low which would help promote a greater solubility of the two components[22].

Inspecting our own d.s.c. data, (recall *Figure 1b*) which indicates that the ΔC_p associated with the PS glass transition gradually increases with an increase of the PDMS block length. Since the T_g of the PS block is around 105°C for all our block polymers (recall *Table 2*) this indicates that the block length of the PS blocks may be well over 10 000 in molecular weight so that partial mixing of PDMS within the styrene phase would have negligible effects on the ΔC_p of the PS component. Hence, any change in ΔC_p of the styrene phase would in turn be indicative of the amount of polystyrene mixed within the PDMS phase. Indeed, one might expect a decrease in the ΔC_p of the PS phase which could then help account for the rise of the PDMS glass transition temperature noted in the shorter PDMS block length containing systems as was observed in the earlier dynamic mechanical spectra as well as the d.s.c. data. Hence, by monitoring the ΔC_p change of each phase, one may be able to estimate the degree of phase mixing quantitatively. In our specific case, the ΔC_p of the PDMS phase is difficult to utilize since as the PDMS block length increases, crystallization can also influence the results thereby making it difficult to separate the effects of phase mixing from that promoted by crystallization. Therefore, only the changes of ΔC_p of the PS glass transition temperature were utilized accordingly since this parameter is not convoluted with any other phenomena such as crystallization.

The ΔC_p method similar to that described by Pascault and Camberlin[31] has been employed to determine or estimate the phase mixing in these PDMS–PS block polymers. *Figure 5a* provides an illustration of the expected results and helps provide definition concerning the parameters utilized to estimate the degree of phase mixing (DPM) which will be defined as follows

$$\mathrm{DPM}=\left[1-\left(\frac{\Delta C''_p}{w''}\right)\Big/\Delta C'_p\right]\times 100\% \qquad (1)$$

In equation (1), $\Delta C'_p$ is the normalized value for homopolymer styrene, $\Delta C''_p$ is the normalized ΔC_p for the block polymer, and w'' is the weight fraction of polystyrene in the block polymer. The value of $\Delta C'_p$ must be obtained from homopolymer polystyrene having comparable molecular wight of the PS blocks in a given block polymer. However, the ΔC_p of homopolymer styrene is almost constant when the molecular wight (M_n) is greater than 10 000 (refs. 22, 39). Considering the large molecular weight and molecular weight distribution of the PS blocks in our PDMS–PS block polymers, the ΔC_p values of the homopolymer styrene with molecular weight of 19 000 has been chosen for the ΔC_p value. Utilizing this approach outlined above, our ΔC_p data provided the results plotted in *Figure 5b*. The results show that the degree of phase mixing (DPM) decreases almost linearly with an increase in PDMS block length. The fact that there is a dependence for the shorter molecular weight PDMS is not surprising but the fact that it extends

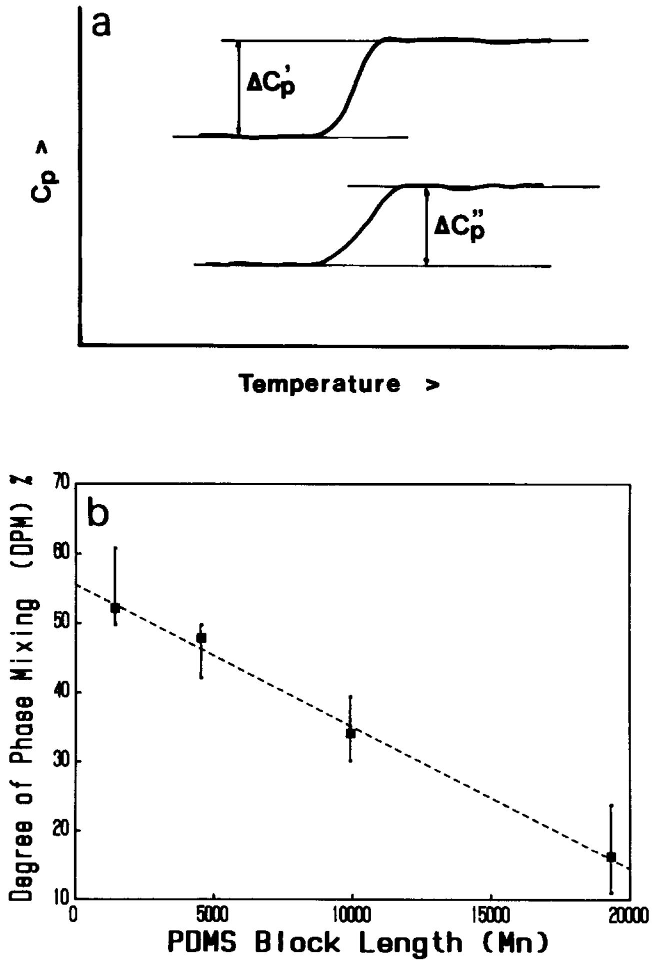


Figure 5 Effect of the PDMS block length on the degree of phase mixing determined by the ΔC_p method. (a) Illustration of the ΔC_p method; (b) effect of the PDMS block length on the degree of phase mixing in the PDMS–PS block polymers

through the complete series where the PDMS block length is nearly 20000 is somewhat unexpected. Certainly as the molecular weight of the PDMS blocks increase, their incompatibility with PS would also increase thereby enhancing phase separation which certainly our d.s.c. results reinforce. It is somewhat surprising to us that the level of phase mixing suggested by these data is as hgh as calculated. But it should be kept in mind that the ΔC_p values would not be influenced to provide an over estimation if PDMS had mixed with the PS phase, i.e., indeed, the results would be the opposite!

Overall, these results are certainly supportive of the earlier observed dynamic mechanical and d.s.c. results, the latter referring to the PDMS transition. That is, it is recalled that the PDMS glass transition observed by either method is shifted upward and broadened as was discussed in terms of the Hashimoto model. In view of the fact that the degree of phase mixing is in the range of 16–50%, therefore, broadening and shifting of the PDMS glass transition response in the dynamic mechanical result is not unreasonable. However, it is important to state again that the cause for this phase mixing within the PDMS component is believed principally due to the shorter styrene blocks, the presence of which will be further confirmed shortly. Interestingly, it is recalled that the upper glass transition for the PS phase shows it to be almost independent of the PDMS block length for both the dynamic mechanical and d.s.c. results. In the case of the dynamic mechanical data, the intensity of this tan δ peak does indeed, however, depend on the PDMS block length. As the PDMS block length increases, the intensity of the PS tan δ peak also rises. This increase clearly suggests an enhancement of the degree of phase separation of the PS component, i.e. a lower degree of phase mixing which is in line with the estimation of phase mixing from the d.s.c. ΔC_p analysis.

Transmission electron microscopy morphological investigations

The results of the indirect methods such as d.s.c. and dynamic mechanical analysis have clearly shown that these PDMS–PS block polymers display phase separation behaviour although the nature of phase mixing varies within the two phases. In order to obtain a better understanding of these implications and the morphological character in general, small angle X-ray scattering studies were initially applied. However, it was immediately found that SAXS did not provide a scattering 'peak' or 'shoulder' indicative of microphase behaviour for all of the higher conversion samples. This lack of a SAXS 'interdomain distance' or correlation peak suggested that the domain structure may be too large to be detected within the resolution limits utilized. Hence, transmission electron microscopy (TEM) investigations were carried out on ultra-thin cryomicrotomed sections of the solvent cast films of these polymers (Note: these films were the same as those used for d.s.c., dynamic mechanical and other characterization studies).

TEM micrographs of these films as cast from methylene chloride (M) are shown in *Figure 6*. The dark regions represent the PDMS phase and the whiter or lighter regions correspond to the PS phase. As mentioned previously, no staining procedures have been utilized nor were necessary to enhance the contrast between the two components. The TEM micrographs clearly show that a rather large styrene domain structure is formed in these block polymers irrelevant of the initial PDMS oligomer molecular weight. Specifically, the average styrene domain size in S14-95-M is about 40 nm and the PS lamellar thickness of sample S193-95-M is about 80 nm (see *Figures 6a* and *6e*). The large PS domain structures exceed the resolution limits initially investigated by SAXS and clarify why a smaller interdomain spacing was not detected. A number of interesting features of these micrographs become readily apparent. The first is that the PDMS component is, in general, the continuous matrix phase for those systems displaying non lamellar morphologies, yet, the PDMS phase seems much lower in volume content than that of the PS component (see *Table 1*). While certainly it is known that the choice of casting solvent can influence the morphology of PDMS–PS block systems[2,40–42], it is somewhat surprising that the lower volume fraction component can be clearly promoted to provide the continuous phase which, as will be illustrated later, distinctly controls the resulting mechanical properties. From these micrographs there is also the observation that rather sharp boundaries are observed between the two phases which might suggest that good phase separation has occurred in these block systems. Recall, the ΔC_p analysis and other related data that suggest that some polystyrene is distinctly mixed within the

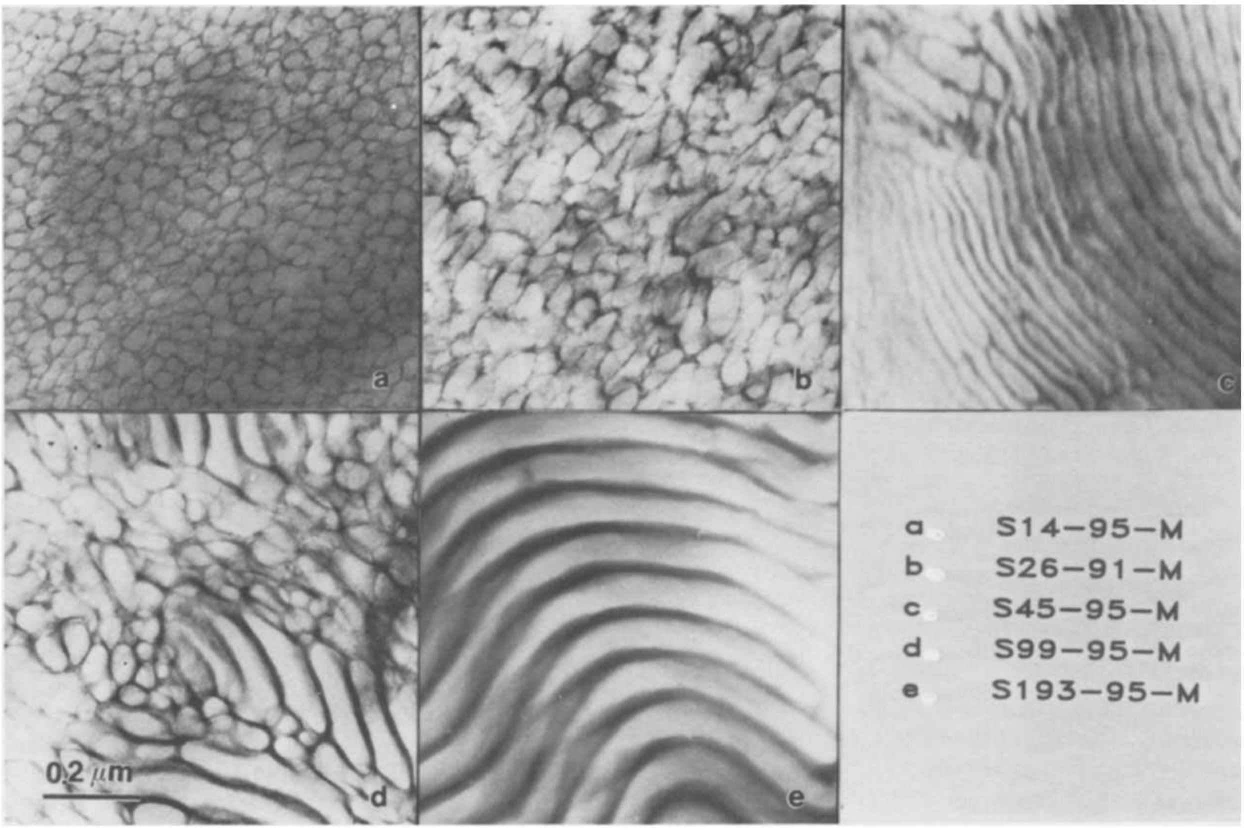


Figure 6 TEM micrographs of high conversion PDMS–PS block polymers. As the PDMS block length increases from A to E, the morphology of these polymers changes from spherical-like to lamellar structure

PDMS phase. This point will be addressed shortly. It might also be surprising that the degree of 'black' PDMS phase appears to be of considerably lower volume content than the 'white' PS phase in view of the fact that the PDMS should occupy the order of 45% by volume (this value will change slightly in view of density differences). However, in the case of where the more sphere-like domain structure exists such as in S14-95-M, one should recall that if a sphere-like morphology exists, the thickness of the outer encapsulating layer will appear much less than the radius, R, of the PS domains, since the volume scales with R^3 while the surface area scales with R^2. A simple calculation shows that the width of the PDMS region sould be equal to one ninth of the diameter of the PS domain on a two dimensional projection for sample S14-95-M. The TEM results are close to this estimation. Caution must be shown, however, in attempting to visualize what volume fraction of each phase should exist in view of composition due to domain boundary overlap and other microscopy considerations. While it will not be discussed here, a topic of a later paper will take into account the effects of casting solvent and how the morphological features can be controlled by utilizing the solubility parameter of the casting solvent accordingly[19].

In considering the effect of the PDMS block length on the morphological textures observed, it is recalled that the PDMS block length is predetermined by the cationic synthesis of the hydrogen-functional PDMS oligomers used to prepare the macroinitiator. Therefore the PDMS block molecular weight distribution is predetermined from the equilibration reaction in generating the species used for the cationic polymerization. This distribution should be of the order of 2.0. In contrast, the PS blocks in these same polymers are produced by the free radical process and hence, its molecular weight and molecular weight distribution may vary depending upon conversion level, size of macroinitiator and other variables. Some of these points will be considered here. Clearly, there is a correlation indeed in view of the PDMS block length and the type of morphology induced as observed in *Figure 6*. Specifically, as the PDMS block length increases, it is noted that the morphological textures for these methylene chloride cast systems changes from sphere-like styrene regions encapsulated within a PDMS matrix to that of the more expected lamellar textures showing continuity of both phases. Observation that the domain structure changes with block length has been also observed by Saam *et al.*[2,40,41] in PDMS–PS diblock polymers prepared by anionic synthesis. In their polymers, the PDMS content was kept constant at 30 weight per cent. By varying the M_n of the polymers, the PDMS block length was varied from 1700 to 17900. As the PDMS block length decreased, the morphological structure is changed from spaghetti-like lamellae to ill defined spherical textures. They suggested that 1700 was the lower block molecular weight limit of PDMS for phase separation to be induced[2].

Another interesting point was the fact that the PDMS phase was always noted to be the continuous phase even though it was the lower volume fraction component. Bajaj and Varshney[42] have also observed spherical PDMS domains in a styrene matrix for PDMS–PS–PDMS triblock polymers having 50 wt% PDMS where the block length of the PDMS was 23400. When the PDMS block length and content was changed to 4700 and 34 wt%

respectively, the rodlike or cylindrical domain structure of styrene was formed. In both samples the PDMS was the centre block with length 17 000 in the former polymer and 11 700 in the latter. These additional observations of others provide some indication that the morphological features were not as predicted as usually implied based on composition ratio. However, there still is a need to account for the dependence upon PDMS block length and the size of the domains observed in our system relative to the usual block systems where domain sizes are often considerably less if one were to assume that the block lengths of the two components being polymerized were comparable.

Some estimation of the expected distance over which a given block traverses can be estimated from considerations of the unperturbed mean square end to end distance of a given chain. This value of the root mean square end to end distance (rms) can be estimated by equation 2 (refs. 44, 45).

$$\mathrm{rms} = (CnL^2)^{1/2} \qquad (2)$$

where C is the characteristic ratio and is 6.3 for PDMS and 10 for polystyrene. Within equation (2), n equals the number of bonds per block. In the case of PDMS, it represents the number of Si–O bonds whereas in the PS block it represents the number of C–C bonds per block. The value of L is the bond length and is equal to 0.164 nm for PDMS and 0.154 nm for PS respectively. It should be realized that in applying equation (2), unperturbed Gaussian behaviour is assumed. While this might be questioned in view of the short block lengths for the PDMS component in particular, this Gaussian approximation has worked quite well in the case of PDMS–urea segmented polymers[25,35] in which the PDMS block length varies from 900 to 3600. This Gaussian approximation has also been used to interpret TEM results on PS–PI–PDMS triblock polymers of a recent work from Malhotra *et al.*[8]. Their triblock polymer was prepared by an anionic method such that a well controlled molecular weight and narrow molecular weight distribution of each block was obtained. In their case, the PS, PI and PDMS blocks had molecular weights (M_n) of 12 400, 11 600 and 18 700 respectively and a lamellar structure was observed. The lamellar thickness measured from TEM micrographs was 10 ± 2 nm, and 8 ± 1.5 nm for the PS and the PDMS blocks. In applying equation (2) to the directly measured PS and PDMS lamella spacings, each result was in very close agreement to Gaussian behaviour, the calculated values being 7.4 nm for the PS block and 9.3 nm for the PDMS block.

In view of the domain structure of block polymers, it should also be pointed out that there have been scaling law relationships developed and tested concerning the domain size and its dependence on molecular weight of the domain forming blocks for diblock systems[46]. Basically, the domain diameter (or width) scales as the 2/3 power of the respective block molecular weight. This law has been confirmed by experimental observations of Hashimoto *et al.* on spherical, cylindrical and lamellar domains of narrow molecular weight distribution styrene isoprene diblock polymers based on SAXS investigations[47]. Recently, York found this same 2/3 power law relationship to fit his TEM and SAXS data obtained on domain forming PDMS–PMMA graft copolymers developed on the basis of macromer synthesis[48]. While we have considered this scaling relationship in view of our own work, it is limited in its application due to the dispersity of block molecular weights particularly in the polystyrene region. Hence, our first approximation to better understand the domain sizes and general morphological textures developed has been to apply the earlier Gaussian approximation to chain dimensions for the specific block species.

Using the TEM micrographs, care was taken to determine the distance across the sharpest black boundary regions (PDMS phase) as well as the white regions (PS phase) and an average value determined accordingly. This was done for the various PDMS block length materials. In addition, equation (2) was utilized to estimate the expected r.m.s. values. The results of the experimentally determined values with their standard deviation (σ) as well as those calculated from equation (2) are provided in *Table 3*. It is noted that for the shorter PDMS block lengths, the measured value is only somewhat greater than that obtained from equation (2). Because the ends of the PDMS segments in the block polymers are somewhat restricted by polystyrene segments and the fact that some degree of mixing of PS is believed to occur in the PDMS phase, it is not surprising that the PDMS r.m.s. value is somewhat enhanced. In addition, the PDMS chains might be expected to be indeed perturbed from their r.m.s. value caused by the restrictions of the PS blocks. One might expect, however, as the PDMS block length increases, the chain would become more flexible and less perturbed as well as the fact that there would be less mixing with the PS component as discerned from the earlier d.s.c. ΔC_p analysis. Hence, a closer approximation of the Gaussian result might occur. The results show just the opposite. For the longer PDMS block containing samples, the block determined length is over twice as long as that obtained from the Gaussian calculation from equation (2). Also the standard deviation (σ) increases with the PDMS segment length. However, the error in the measurements is not so great as to cause this large a discrepancy (*Table 3*). Therefore, these results suggest that exceedingly large PDMS blocks may have been formed during the free radical copolymerization by coupling of two or more of the original PDMS blocks with only a few styrene units, i.e. the observed thicker PDMS lamellae are an effect of the polymerization

Table 3 Domain size or lamellae thickness of the PDMS and PS blocks

	PDMS Domain Size (nm)			
Sample	TEM[a]	σ[b]	rms[c]	TEM/rms
S14-95-M	4.6	1.2	3.6	1.3
S26-91-M	6.6	1.7	4.9	1.4
S45-95-M	7.5	1.8	6.4	1.2
S99-95-M	14.1	4.6	9.5	1.5
S193-95-M	31.8	5.4	13.3	2.4
S14-95-M	47.6	10.7	2.8[d]	17.0
S26-95-M	59.9	18.7	4.3[d]	4.4
S45-95-M	18.8	5.8	4.5[d]	4.2
S99-95-M	52.4	25.9	7.7[d]	3.4
S195-95-M	85.1	9.7	9.6[d]	8.9

[a] Domain size measured from the TEM micrographs
[b] σ is the standard deviation
[c] Root mean square end-to-end distance calculated by equation (2)
[d] Based on the calculated values of M_n for the PS blocks (from ref. 18)

scheme. It should also be noted that the size of the styrene regions, lamellar or sphere-like regions, suggests that the average styrene block length may be considerably larger and therefore explain the observed high T_g of this component. At the same time, it also accounts for why the SAXS technique did not provide an interdomain spacing as would have been expected if the PS block lengths were comparable to those of the corresponding PDMS block in the same polymer.

As stated above, the calculated lamellar thickness of the PDMS block is considerably greater than its Gaussian value as determined from equation (2), at least in those systems with the higher PDMS block lengths. This much higher measured value of the lamella thickness is believed to be explained by the formation of longer PDMS blocks promoted during the free radical process thereby leading essentially to much longer PDMS block lengths. The PS domain size from TEM results and from the Gaussian calculations utilizing equation (2) as based on the calculated average block length initially proposed by Crivello[18] are also listed in *Table 3*. The results indicate that much larger PS blocks clearly have been formed during the free radical polymerization than that based on the calculated block length utilizing composition ratio etc. Clearly, larger average PS block length would certainly account for the much larger PS domains or lamellae as directly observed in *Figure 6*. (It is recalled that the same weight ratio of PDMS macroinitiator to styrene was used in each polymerization[18].) Therefore the formation of larger PDMS blocks might well be expected to lead to the formation of larger PS blocks and hence the number of blocks per chain in the final polymer would be reduced accordingly. This of course assumes that the average molecular weight of the final product of all materials is essentially the same. Indeed, the speculation for the formation of large PS blocks is highly supported by the d.s.c. and dynamic mechanical data (recall *Figures 1b* and *2*). It indicated that the T_g of the styrene block for these high conversion samples is ca. 105°C.

In view of the d.s.c. dynamic mechanical analysis, TMA and TEM studies, the results suggest that this system may have a fairly broad molecular weight distribution of the PS blocks due to the nature of free radical synthesis. As shown in *Figure 6*, the size of the PS domains does clearly vary. The samples, S45-95-M and S99-95-M, also have a mixed morphology of sphere-like domains and lamellae. The variation in the domain size and the mixed morphological structure could be a result of a broad molecular weight distribution. However, this was not suggested directly by d.s.c., probably due to the general breadth of the distribution, although it was strongly suggested on the dynamic mechanical results as well as on the TMA results in the glass transition region of the PS blocks. In view of this, we sought more direct proof to indicate the existence of high PS block molecular weights by applying g.p.c. analysis to the by-products of a trifluoroacidic acid degradation of some of the high conversion samples. This degradation successfully causes selective chain scission at the linking unit (pinacolate unit) connecting the PDMS and PS blocks but causes no further degradation. This latter point was proven by the analysis of the resulting PDMS block lengths of the degraded samples which was directly in line with the hydride difunctional PDMS (di-H-PDMS) precursors utilized prior to the preparation of the macroinitiator (*Table 4*). In carrying out the analysis, the u.v. detector was again set at 254 nm to detect the aromatic groups of the polystyrene or the i.r. detector was placed at 9.2 μm for determining the Si–O bond in the PDMS component. The results of the degradation study were compared with the results from the ^{29}Si n.m.r. and the original g.p.c. data on the silicon hydride difunctional PDMS precursors. The results are given in *Table 4* and *Figure 7* and indicate that complete degradation of these block polymers has been achieved, for the molecular weight of the PDMS degraded material is the same as the PDMS precursor systems (*Table 4*). With this data which establishes the 'cleanness' of the selected degradation, it is then concluded that the g.p.c. trace detections of the polystyrene illustrate that very high molecular weight PS blocks form and that the PS molecular weight distribution varies with initial PDMS block length (see *Figure 7*). Here it is noted that in the S45-95 material, there is a distinct bimodal character to the PS blocks in the final polymer, one region of which illustrates very high molecular weights and another of which is of the order of 10 000 or more. For S99-95 polymer, a trimodal distribution is observed. In this sample, the high molecular weight portion is dominant. There is also a fair amount of lower molecular weight blocks (around 10 000) and a small amount of the lowest molecular weight ($M_n < 1000$) blocks. In the case of S193-95, the bimodal distribution is again obtained. As *Figure 7* shows, the high molecular weight blocks are dominant. The lower molecular weight (around 10 000 or less) blocks are much less numerous as compared to the former systems. It is noted, however, that there is a

Table 4 Results of the selective degradation studies

Polymer	di-H-PDMS M_n[a] ^{29}Si	di-H-PDMS M_n[a] g.p.c.	PDMS Block M_n g.p.c. (after degradation)
S45-95	4 520	5 380	5 970
S99-95	9 890	9 940	10 180
S193-95	19 300	22 500	13 300

[a] di-H-PDMS are the difunctional hydride PDMS precursors which are used to prepare the PDMS macroinitiators

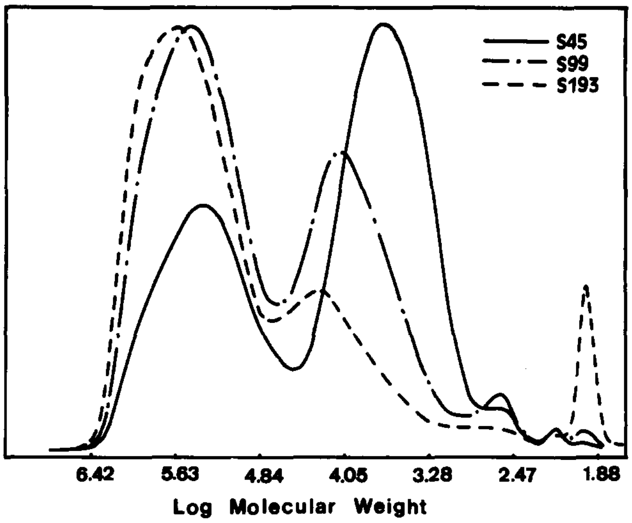


Figure 7 G.p.c. results of the PS blocks after degradation

distribution of low molecular weight styrene blocks that could well be the cause for the fraction that is mixed with the PDMS phase which would account for the rise in PDMS T_g as discussed earlier. Similarly, the presence of the shortest PS block lengths could easily account for the fact that these would serve to couple PDMS chains thereby promoting a much longer PDMS apparent block length which would account for the rise in the lamellar thickness of this particular phase based on calculations utilizing the TEM micrographs.

The bimodal molecular weight distribution of the PS blocks in these PDMS–PS systems can be explained by a hypothesis proposed by Crivello[18] shown in Scheme 4. During thermolysis, the intermediate polymer (shown at the top of the scheme) undergoes cleavage at the strained C–C bond to generate two radical fragments, A and B. The radical species A can either couple with another identical species to form a dead chain D or can add additional styrene monomer units to form species C which can couple with the similar species either A or C to give a dead chain D. The species B which bears the ketyl radical could couple with itself, however, this is a strongly unfavourable process because the temperature is well above the threshold for the dissociation of this bond. Therefore, most of these species will react with styrene monomer units to form species A and eventually form the dead chain. The length of the PS chain formed will depend upon the concentration of both monomer and the radical chain ends present. If the concentration of radicals is high during the polymerization, the PS chain can only grow very little before irreversible termination occurs. If the concentration of monomer is low, and the concentration of radicals is high at the early stage of the polymerization, a great deal of PDMS segments will link together by very short PS chains due to the permanent termination by coupling. As the polymerization proceeds, the concentration of radicals will drop rapidly as they are consumed by the coupling process. In the later stages of the polymerization, the length of the incorporated PS chains will increase dramatically as the probability of coupling decreases. Hence, the PS blocks in the final polymer will have a very unequal molecular weight distribution.

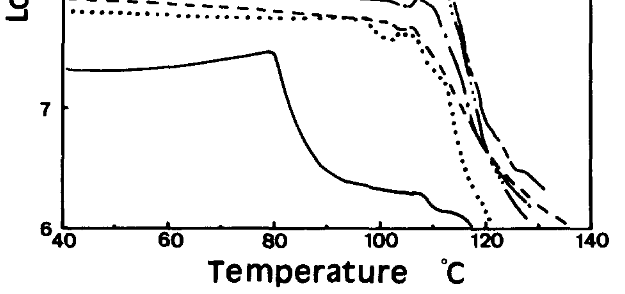
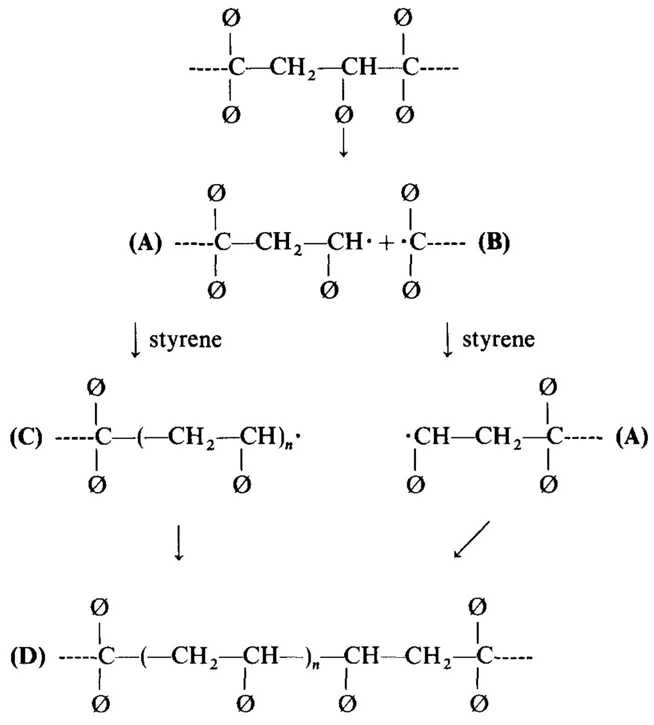


Figure 8 Dynamic mechanical response of free radical PDMS–PS block polymers and the 10k/10k–10k/100k PDMS–PS diblock polymer blend near the PS glass transition range. ——, S14-95-M; ----, S26-91-M; ......, S45-95-M; —.—, S99-95-M; —...—, S193-95-M; – – – blend



Scheme 4

To simulate what we believe to be the occurrence of a mixture of both low and high molecular weight styrene block lengths, a direct blend of two diblock polymers was used. Both diblock polymers contained the same PDMS block length (10K was utilized) but the PS block length varied. The diblock materials were diblocks of PS(10K)–PDMS(10K) as well as a corresponding diblock where the PS was of 100K molecular weight. These systems had been prepared anionically and were well characterized systems[49]. These systems were solvent cast as a blend from methylene chloride using 80 wt% of the 100K/10K diblock to 20 wt% of the 10K/10K diblock. The corresponding film of this blend was then analysed by dynamic mechanical analysis and the TMA. The dynamic mechanical results were shown in *Figure 8*. It is very clear that the dynamic mechanical and the TMA response is exactly analogous to the S99-95-M free radically polymerized block polymer discussed earlier, i.e. a two step transition or softening behaviour is observed which we believe is due to the occurrence of two styrene domain regions. Similar to the result of S99-95-M, the d.s.c. results of this blend did not show two transition peaks, but the breadth of the transition was broad. TEM studies carried out on this blend showed very good phase separation behaviour but no distinct signs from the microscopy that allowed one to judge where the relative blocks of each of the species are located (see *Figure 9*).

Stress-strain results in correlation with morphology

The earlier electron micrographs clearly showed that the morphology for the methylene chloride cast samples changes in a systematic way as the PDMS block length increases. This promoted us to make some initial stress–strain measurements to further illustrate the effect

Table 5 Mechanical properties of high conversion PDMS–PS block polymers

Sample	Modulus (MPa)	Tensile strength (MPa)	Ultimate elongation (%)
S14-95-M	3.1	4.5	102
S26-91-M	28.8	6.7	23
S45-95-M	29.1	3.0	20
S99-95-M	111.9	8.5	140
S193-95-M	170.5	5.9	44

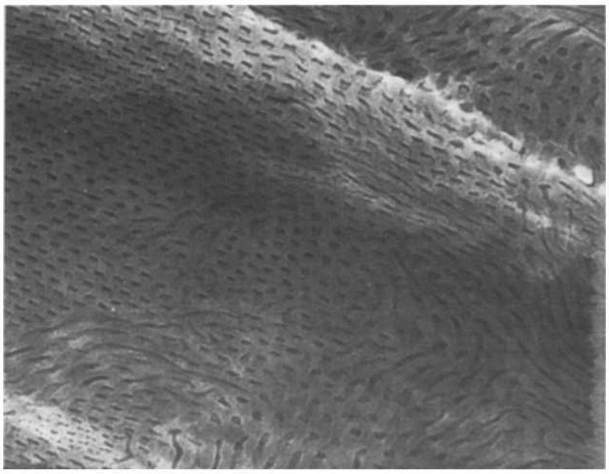


Figure 9 Morphological structure of the 10k/10k–10kz100k PDMS–PS diblock polymer blend cast from methylene chloride

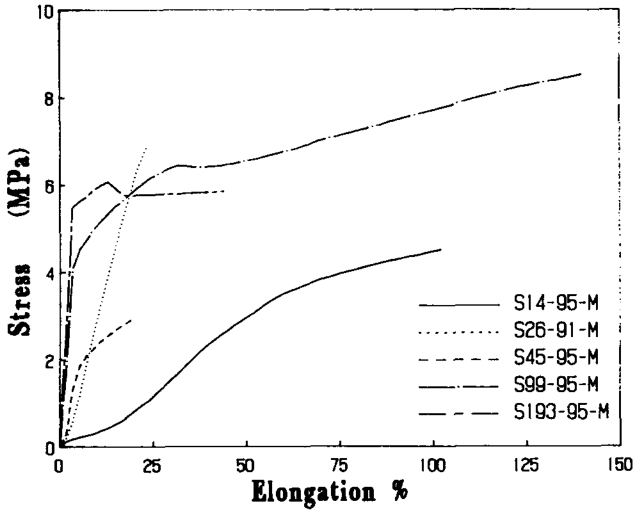


Figure 10 The stress–strain behaviour of high conversion PDMS–PS block polymers

of systematic changes in structure. In particular, it is recalled from *Figure 6a* that the S14-95-M sample illustrated polystyrene domains encapsulated within a rubbery siloxane matrix. While at the other extreme, sample S193-95-M, indicated connectivity of both phases as promoted through a lamellar texture. Hence, while the composition ratio of all of these materials shown in *Figure 6* are very nearly equivalent, the mechanical response with loading would be expected to be quite different. Indeed, as shown in *Figure 10*, the results are exactly in line with the electron micrographs. In particular, sample S14-95-M (the encapsulated polystyrene domain system) illustrates a low modulus as does S26-91-M which also has larger but still encapsulated PS domains. In contrast, the three samples S45-95-M, S99-95-M and S193-95-M materials which possess a greater extent of lamellar texture as the PDMS block length increases clearly show a systematic rise in modulus due to the higher connectivity of the polystyrene glassy phase. While there is a much higher elongation to break for the S99-95-M material (based on several tests), this may arise from the effects of the hard segment size and the number of blocks per chain (N). Earlier studies by Saam *et al.*[2,40,41] did find that the ultimate properties of the PDMS–PS multiblock polymers were strongly dependent on the size of the PS block and the number of blocks per chain. The polymer with larger size PS blocks had higher ultimate stress and longer elongation at break. They also found that the ultimate properties were increased greatly as the N increased when N was less than 8 (ref. 40). When N was greater than 8, only a small improvement was obtained. In our case, the same weight ratio of PDMS macroinitiator to styrene monomer was used. For S45-95-M, S99-95-M, and S193-95-M, the overall molecular weight is in the range from 162 000 to 345 000. Sample S193-95-M, however, has a much larger PS block size than the other two (recall *Table 3* and *Figures 6* and 7). Therefore, fewer blocks per chain for S193-95-M are expected. The shortest break elongation might result from a small value of N.

On the other hand, the PS block size in S45-95-M is much smaller than the other two. Therefore, the ultimate stress for this sample might be expected to be the lowest among these three samples as *Figure 10* shows. The important point is that the general modulus characteristics are indeed reflective of whether or not the PDMS component is the continuous phase or whether the polystyrene material also displays connectivity thereby strongly enhancing the modulus due to its glass-like behaviour at ambient.

CONCLUSIONS

In summary, the results presented here further confirm that only block polymers are produced by this interesting free radical polymerization scheme. In addition, however, we have demonstrated that the resulting chain structure is much more complex than initially thought. Changes in final polystyrene block lengths depend greatly on initial PDMS block length as well as probably upon the reaction conditions or phase separation may be promoted more rapidly due to higher molecular weight PDMS block components; recall that iridescence was observed by Crivello in the stages of styrene polymerization for these higher PDMS containing systems. We have demonstrated that use of ΔC_p analysis can provide an insight into at least an estimate of the degree of phase mixing that occurs but it is principally a mixing of low molecular weight styrene block with the PDMS component, a result that is not only dependent upon the initial chain structure involved but the choice of casting solvent. The latter point will be further confirmed in a later paper. Indeed, as it will be shown at that time, the level of phase mixing for even the low PDMS block lengths can be reduced considerably by using toluene as a casting solvent.

The use of selective degradation of the final polymer into its respective blocks has proven of great assistance in accounting for many of the observations made. Some of these observations have been further confirmed by the use of blending two well defined molecular weight diblock PS–PDMS species together to promote a similar thermal mechanical response. Finally, based on electron microscopy, the anticipated mechanical response in terms of stress–strain behaviour, at least at lower elongations, was verified by carrying out mechanical testing accordingly.

ACKNOWLEDGEMENTS

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