Synthesis and characterization of linear and three-arm star radial poly(styrene-*b*-isobutylene-*b*-styrene) block copolymers using blocked dicumyl chloride or tricumyl chloride/$TiCl_4$/pyridine initiating system

Robson F. Storey*, Bret J. Chisholm and Youngkwan Lee
Department of Polymer Science, University of Southern Mississippi, Hattiesburg, MS 39406-0076, USA
(Received 29 October 1992; revised 29 January 1993)

Linear and three-arm star styrene-*b*-isobutylene-*b*-styrene block copolymers were synthesized by living cationic polymerization using ring-substituted di- or tricumyl chloride, respectively, as initiator, $TiCl_4$ as coinitiator, pyridine as an electron donor and 2,6-di-tert-butylpyridine as a proton trap in a 60/40 (v/v) methylcyclohexane/methyl chloride solvent mixture at $-80°C$. The polymers had equivalent compositions and segmental molecular weights allowing the effect of molecular geometry on sample morphology and physical properties to be determined. The samples exhibited a dual-phase morphology consisting of cylindrical polystyrene domains dispersed within a matrix of polyisobutylene; polymer geometry was found to have a significant effect on the tensile properties, with the three-arm star sample displaying a tensile strength twice that of the linear sample. In addition, the three-arm star block copolymer was found to have a higher rubbery plateau modulus than the linear block copolymer. Due to their perfectly saturated mid-block, polyisobutylene-based block copolymers were found to be much more thermally stable than the closely related styrene-*b*-(ethylene-*co*-1-butene)-*b*-styrene block copolymers (hydrogenated polybutadiene centre block).

(Keywords: block copolymers; synthesis; characterization)

INTRODUCTION

There is great interest in well defined A–B–A block copolymers due to their unique properties in the bulk state. The result of linking immiscible polymer segments by covalent bonds is the formation of a dual-phase morphology in which the minor block forms microdomains in a continuous phase of the major block. When an A–B–A block copolymer is designed with the inner block as the major component and rubbery in nature and the outer block as the minor component and glassy in nature, a high-strength rubber is produced which does not require vulcanization and displays thermal reversibility between the solid–elastic and melt states. Block copolymers of this type have been termed thermoplastic elastomers (TPEs). An example of commercially available TPEs is Shell's Kraton® rubbers, which are synthesized by living anionic polymerization and consist of a rubbery diene-based mid-block and glassy polystyrene (PS) outer blocks. The advent of living cationic polymerization has enabled the synthesis of TPEs with a totally saturated mid-block, namely polyisobutylene (PIB). TPEs based on PIB offer greater oxidative and thermal stability over their corresponding butadiene counterparts due to the lack of unsaturation in the polymer backbone. Kennedy and co-workers[1,2] have thoroughly characterized the polymerization of isobutylene and have produced various TPEs by living cationic polymerization and sequential monomer addition techniques.

In addition to linear A–B–A block copolymers, radial star-block copolymers, possessing glassy outer and elastomeric inner blocks, have also been found to exhibit a dual-phase morphology and elastomeric properties. For samples of equivalent composition and segmental molecular weight, tensile tests have shown that star-block copolymers display greater tensile strengths and slightly lower extension ratios than linear block copolymers[3]. The higher tensile strength of star-block copolymers is attributed to the permanent covalent junction point, represented by the hub of the star, within the elastomeric domain.

The purpose of this article is to report the synthesis and characterization of linear and three-arm star radial PS–PIB–PS block copolymers having equivalent compositions via living carbocationic polymerization, using cumyl chloride-type initiators and pyridine as electron donor. This particular initiating system has been well characterized in our laboratory[4] and previously applied to the synthesis of telechelic PIB ionomers with narrow polydispersity[5]. By producing linear and three-arm star block copolymers with equivalent compositions on a per arm basis, the effect of molecular geometry on physical properties may be determined.

---

*To whom correspondence should be addressed

0032-3861/93/204330–06

EXPERIMENTAL

Materials

Methylcyclohexane (Aldrich) was distilled from calcium hydride under a nitrogen atmosphere just prior to use. Isobutylene and methyl chloride (Linde Division, Union Carbide Corp.) were dried by passing the gaseous material through a column packed with BaO and $CaCl_2$. Styrene (Aldrich) was distilled from calcium hydride under vacuum and stored under nitrogen for no longer than 1 day before use. Titanium tetrachloride, pyridine, 2,6-di-tert-butylpyridine (DtBuP), anhydrous methanol, methyl ethyl ketone (MEK) and pentane were used as received from Aldrich.

1,3-Di(2-chloro-2-propyl)-5-tert-butylbenzene (m-tBuDCC) was synthesized from 1,3-dicarboxyl-5-tert-butylbenzene by first producing 5-tert-butyl-1,3-dicumylalcohol (m-tBuDCA) as described by Wang *et al.*[6], and then converting the latter to the corresponding dichloride (m-tBuDCC) by reaction with gaseous HCl, as described previously[4]. 1,3,5-Tri(2-chloro-2-propyl)benzene (TCC) was prepared from 1,3,5-triisopropylbenzene (Aldrich) using a modification of the procedure of Santos *et al.*[7], which has been described previously[4].

Preparation of linear and three-arm star PS-b-*PIB*-b-*PS*

The synthesis of linear and three-arm star PS-*b*-PIB-*b*-PS block copolymers having equivalent arm and block molecular weights (*Figure 1*) was accomplished using a modification of the procedure of Kaszas *et al.*[8]. The reagents used to synthesize these block copolymers are listed in *Table 1* along with their corresponding concentrations. Arm and block molecular weights were kept constant for both polymers by maintaining the same molar ratio of monomer to initiator functionality, and by carrying each blocking step (isobutylene and styrene) to the same fractional conversion for each polymer.

Polymerizations were carried out at −80°C in a glove box under a dry nitrogen atmosphere using dry 2000 ml, three-necked, round-bottom flasks equipped with mechanical stirrers. The first step of the block copolymer synthesis was the living cationic polymerization of isobutylene to moderately high monomer conversion. This was accomplished by adding pre-chilled $TiCl_4$ to a methylcyclohexane/methyl chloride (60/40, v/v) solution of isobutylene, pyridine, DtBuP and the appropriate initiator, and allowing the reaction mixture to polymerize for 1 h. The second step of the polymerization was the formation of PS blocks by the addition of neat styrene to the living PIB chains formed in the first step and allowing polymerization to continue for an additional hour at which time it was stopped by the addition of 30 ml of pre-chilled methanol.

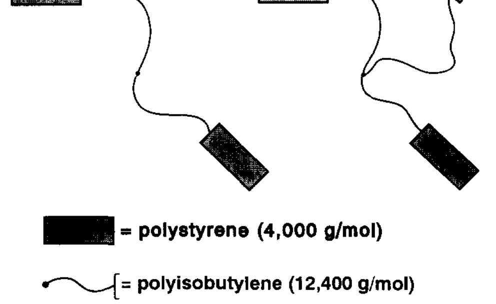

Figure 1 Illustration of the block copolymers synthesized

Table 1 Concentration of reagents used in the synthesis of the linear and three-arm star PS–PIB–PS block copolymers

Reagent	Concentration (M)
Linear PS–PIB–PS	
m-tBuDCC	0.0016
Pyridine	0.0033
DtBuP	0.0046
Isobutylene	0.78
$TiCl_4$	0.035
Styrene	0.17
Three-arm star radial PS–PIB–PS	
TCC	0.0011

Throughout the course of the block copolymerization, small aliquots of the polymerization mixture were removed and quenched with methanol so that the molecular weight of growing polymer chains could be monitored as a function of reaction time. Once quenched, the reaction mixture was allowed to warm to room temperature, causing the methyl chloride to volatilize, and washed three times with a 5% aqueous HCl solution, three times with distilled water, and then precipitated into 3000 ml of rapidly stirring methanol. The polymer, once isolated, was dissolved in toluene, dried over magnesium sulfate and reprecipitated into methanol.

Homopolymer extraction

Determination of the amount of sample contamination by homopolymers or diblock materials was attempted by selective solvent extraction using a Soxhlet extractor. Approximately 20 g of material was placed in a cellulose thimble and extracted with refluxing MEK for 3 days and then with refluxing pentane for 3 days. Extracts were isolated by solvent evaporation, dried under vacuum, weighed and analysed by gel permeation chromatography (g.p.c.) and ^1H n.m.r. spectroscopy.

Instrumentation

Molecular weights were determined by g.p.c. using an instrument composed of a Waters high-pressure 6000A pump, four Waters Ultra-Styragel columns of pore sizes 10^5, 10^4, 10^3 and 10^2 Å, and a Waters differential refractometer (model 410). A PIB calibration curve was constructed using standards obtained from American Polymer Standards Corp.

Differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.) were conducted using a DuPont 9900 thermal analyser. D.s.c. thermograms were obtained with a 910 differential scanning calorimetry cell using a heating rate of 10°C min^{-1} and 8–12 mg samples, while t.g.a. thermograms were obtained using a 951 Thermogravimetric Analyzer module, 10–20 mg samples, and a heating rate of 20°C min^{-1} under a nitrogen atmosphere.

Tensile properties were determined at room temperature with a strain rate of 5 cm min^{-1} using a calibrated Instron tensile tester (model 1130) equipped with a 5000 g load cell on 4 cm × 0.5 cm × 0.05 cm micro-dumb-bell test specimens.

Dynamic mechanical properties of dogbone-shaped samples (20 mm × 2 mm × 0.5 mm) were determined from −100 to 210°C with a heating rate of approximately

1°C min^{-1} using an Imass dynamic mechanical instrument equipped with a Rheovibron model DDV-IIC assembly.

Domain morphology was analysed by transmission electron microscopy (TEM) with a Jeol 100CX instrument on 800–1000 Å thick microtomed samples stained with RuO_4.

^1H n.m.r. spectra were obtained using a 200 MHz Bruker ACE-200 n.m.r. spectrophotometer.

Film preparation

Samples for tensile testing and d.m.a. were prepared by compression moulding at 120°C for 30 min at 34.5 MPa.

RESULTS AND DISCUSSION

Block copolymerization

The bulk properties of an A–B–A block copolymer (thermoplastic elastomer) depend strongly on the morphological order of the two-phase system; thus, a synthetic method that allows control over sequence architecture, segment length and polydispersity, while eliminating homopolymer formation, is highly desirable. Living polymerization in conjunction with sequential monomer addition has proven to be the most effective method of synthesis of well defined block copolymers. In our laboratory, we have developed a system for living cationic polymerization of isobutylene which enables the production of linear and three-arm star polymers with very narrow molecular weight distributions (MWDs) (1.10–1.13) and controlled molecular weights. This system, which employs cumyl chloride-type initiators (*Figure 2*), $TiCl_4$ as coinitiator and pyridine as moderator of cation reactivity, often referred to as an electron donor, has been described previously[4]. The application of this system to the synthesis of linear and three-arm star PS-*b*-PIB-*b*-PS block copolymers has been accomplished by utilizing developments of Kaszas *et al.*[8], which involve a change in solvent from a 60/40 hexanes/methyl chloride system to a 60/40 methylcyclohexane/methyl chloride system and the addition of a proton trap, DtBuP. The substitution of methylcyclohexane for hexanes follows from the greater solubility of the block copolymer in methylcyclohexane/ methyl chloride than hexanes/ methyl chloride, while the addition of DtBuP to the reaction mixture serves to lessen the formation of homo-PS caused by protic initiation.

The most critical aspect of the synthesis of the block copolymers under investigation was the timing of the styrene addition. Styrene had to be added late enough in the isobutylene polymerization to ensure a sharp crossover from the PIB block to the PS blocks, yet early enough to prevent the formation of block copolymers with an A–B block architecture and/or PIB or styrene homopolymer caused by chain transfer reactions which become significant at high monomer conversions. To determine the proper time of styrene addition in order that blocking efficiency could be maximized, number-average molecular weight (M_n) and MWD were monitored as a function of time for the living polymerization of isobutylene using the system m-tBuDCC/$TiCl_4$/pyridine at −80°C. As can be seen from *Figure 3*, the M_n of growing PIB chains increased rapidly during the early stages of the polymerization, and the MWD remained narrow at approximately 1.12–1.13; however, after the M_n levelled off, indicating nearly complete conversion of isobutylene, the M_n decreased due to a broadening of the MWD caused by chain transfer. These results show that it is imperative that styrene be added just prior to the complete consumption of isobutylene to ensure adequate blocking efficiency.

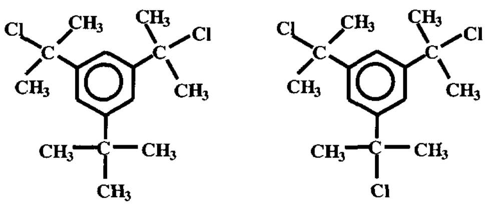

Figure 2 Di- and tricumyl chloride initiators

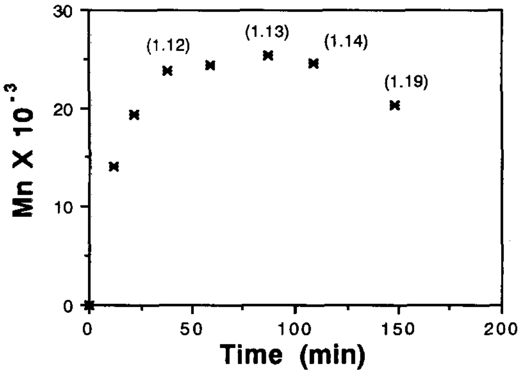

Figure 3 Build-up of M_n with reaction time for the living polymerization of isobutylene

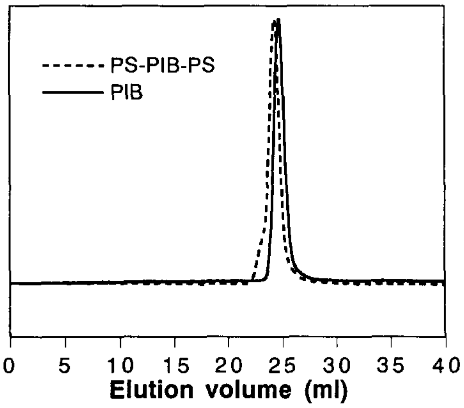

Figure 4 G.p.c. traces of PIB mid-block (——) and linear PS–PIB–PS block copolymer (– – –)

Successful block formation was demonstrated by periodically removing aliquots from the block copolymerization reaction mixture, quenching the aliquots with methanol, and determining the molecular weight of polymers formed by g.p.c. *Figure 4* displays g.p.c. traces for PIB obtained from a reaction mixture aliquot taken just before the addition of styrene and for the final block copolymer obtained. The shift of the polymer peak position to a shorter elution time upon the addition of styrene without the appearance of a new peak indicates that styrene was added to living PIB chains and that styrene homopolymerization was negligible. The slight shoulder on the high molecular weight side of the block copolymer peak is probably due to intermolecular ring alkylation, as suggested by Kaszas *et al.*[8]. *Figure 5* plots g.p.c. M_n (relative to PIB standards) as a function of time throughout the entire block copolymerization. Rapid molecular weight increase after styrene addition also

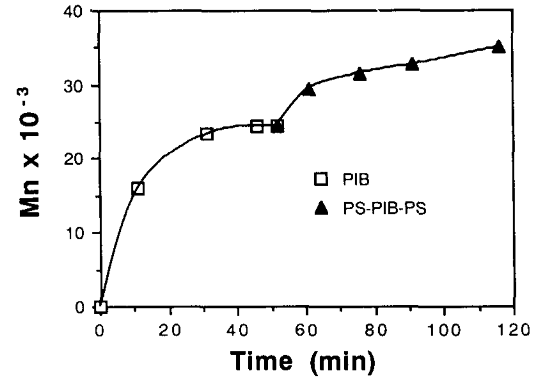

Figure 5 Build-up of M_n with reaction time for the block copolymerization of isobutylene and styrene

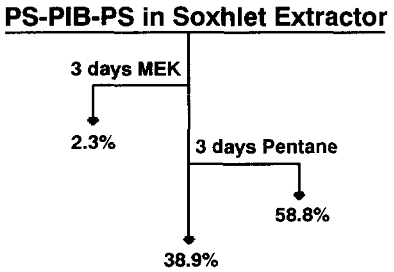

Figure 6 Results of extraction study conducted on the linear block copolymer

clearly indicates that the addition of styrene results in block formation.

To ensure quantitative blocking efficiency and the absence of homopolymer contamination, the linear block copolymer was extracted with MEK to remove any homo-PS and subsequently with pentane to remove any homo-PIB or diblock copolymers. As illustrated in *Figure 6*, MEK extraction resulted in a 2.3% weight loss while pentane extraction resulted in a 59% weight loss. The high fraction of pentane extractables was unexpected; however after characterizing the pentane extract by ^{1}H n.m.r. spectroscopy, g.p.c. and tensile testing, it was found that the pentane extract had the same composition as the pentane-insoluble material, and thus it was concluded that the A–B–A block copolymer is partially soluble in refluxing pentane. G.p.c. characterization of the MEK extract indicated the presence of two polymer fractions, as shown in *Figure 7*, one with low molecular weight and broad MWD and the other with higher molecular weight and narrow MWD. The g.p.c. trace of the higher molecular weight, narrow MWD fraction was identical to the g.p.c. trace of MEK-insoluble material, indicating that the block copolymer was very slightly soluble in refluxing MEK. The low molecular weight, broad MWD fraction, however, was believed to be homo-PS, the amount of which was determined to be 1.7 wt% of the total sample by integrating the area under the g.p.c. trace.

The linear and three-arm star block copolymers produced in this study were designed to have equivalent block lengths on a per-arm basis so that the effect of polymer geometry on bulk properties could be determined. This was accomplished by keeping constant the ratio of moles of initiator functionality to moles of monomer for the synthesis of both the linear block copolymer and the three-arm star block copolymer, and by running isobutylene and styrene conversions to the same extent for both the linear and star block copolymer syntheses.

The molecular weight and MWD of PIB inner blocks were determined from g.p.c. traces of aliquots taken from reaction mixtures just prior to styrene addition, and are displayed in *Table 2*. Assuming 100% initiation efficiency, the conversion of isobutylene prior to styrene addition was about 90% for both the linear and three-arm star samples. The molecular weight of styrene blocks was determined using ^{1}H n.m.r. by integrating the aromatic proton resonance peaks and the aliphatic proton resonance peaks of the extracted material, and are also displayed in *Table 2*. The percentage conversion of styrene for these polymers, assuming 100% blocking efficiency, was determined to be 72% for the linear sample and 78% for the three-arm star polymer. The overall composition of the block copolymers is displayed in *Figure 1*.

Sample morphology

The morphology of block copolymer samples was examined using TEM, as shown in *Figures 8* and *9* for the linear block copolymer and the three-arm star block copolymer, respectively. To enhance the contrast between the phases, the aromatic rings of the PS blocks were stained with RuO_4. It can be clearly seen that these block copolymers possess a heterogeneous morphology consisting of cylindrical PS domains (dark) dispersed within a matrix of PIB (light). The cylindrical PS domains are aligned with their long axes parallel to one another, and form a regular array when viewed in the direction of their long dimension, as can be seen in *Figures 8* and *9*.

The two block copolymer samples under investigation have nearly the same composition, and in fact the size and shape of the domains appear to be independent of molecular geometry; however, they would be expected to be strongly dependent on the volume fraction of PS in the block copolymer.

Physical characterization

As discussed previously, the two block copolymer samples under investigation have virtually equivalent arm lengths and block lengths. This allows the two molecular

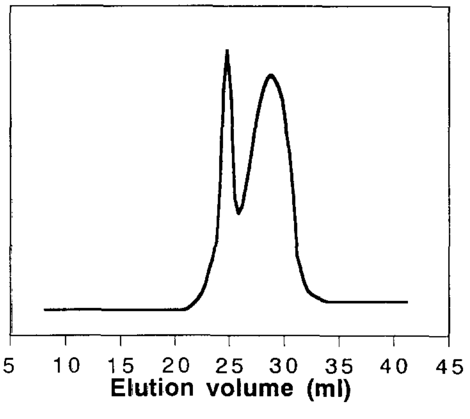

Figure 7 G.p.c. trace of material extracted from the linear block copolymer using MEK

Table 2 PIB and PS block molecular weights for the block copolymers

	Linear PS–PIB–PS	Three-arm star PS–PIB–PS
M_n of PIB by g.p.c. (g mol^{-1})	24 600	37 400
MWD of PIB	1.14	1.17
M_n of PS by ^{1}H n.m.r. (g mol^{-1})	4000	4200

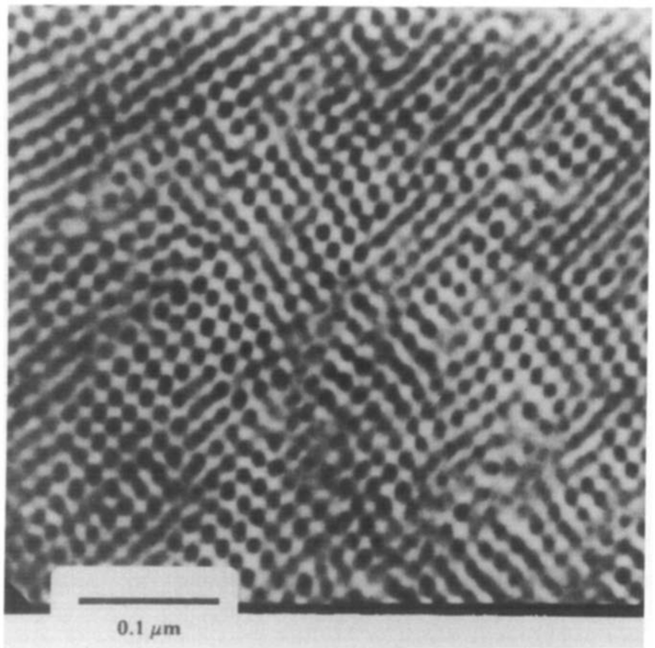

Figure 8 Scanning tunnelling electron micrograph of the linear block copolymer

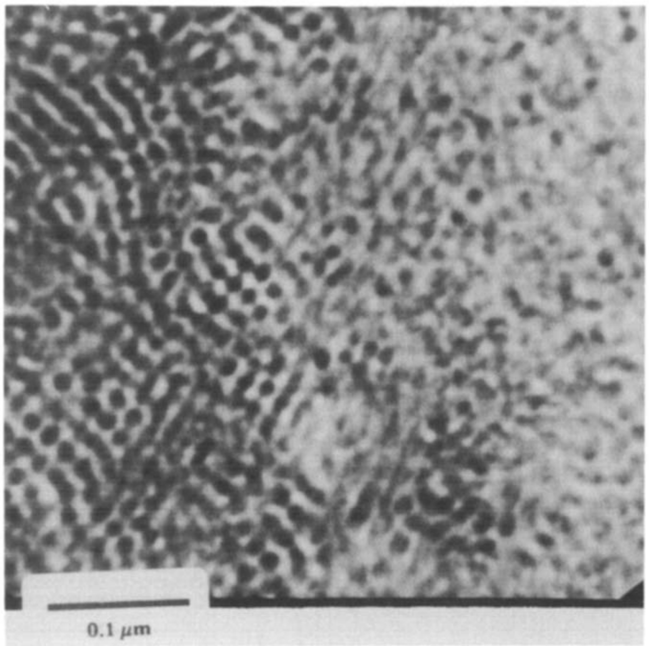

Figure 9 Scanning tunnelling electron micrograph of the three-arm star block copolymer

architectures to possess equivalent compositions, i.e. the volume fraction of PS blocks is the same in either sample. It also provides a constant molecular weight for the rubbery segment which connects two PS blocks; in either case, this was roughly 25 000 or the sum of the molecular weight of two arms.

The effect of sample geometry (linear *versus* three-arm star) on stress–strain behaviour is shown in *Figure 10.* The three-arm star block copolymer showed much higher engineering stresses compared to the linear block copolymer at any given elongation; in fact the tensile strength of the three-arm star block copolymer (16 MPa) was observed to be roughly twice that of the linear block copolymer. Interestingly, however, the two samples displayed nearly the same elongation at break. Apparently, this property is affected most strongly by the span length of the polymer molecules, i.e. the length of two arms, which is the same for both samples. The stress–strain curves also exhibit a rapid upturn at 400–700% elongation, and the effect is more pronounced with the three-arm star block copolymer. This strengthening at high elongations is common for PIB rubbery segments and has been shown to be due to strain-induced crystallization[9].

Dynamic mechanical analysis (d.m.a.) was performed on both the linear and three-arm star block copolymers, and their dynamic responses are plotted as a function of temperature in *Figures 11* and *12*, respectively. Typically for dual-phase systems, these polymers exhibit two glass transition temperatures, the first occurring at −55°C due to the PIB phase and the second at about 100–110°C, characteristic of the PS phase. In regard to the effect of molecular geometry on dynamic response, the rubbery plateau modulus of the three-arm star block copolymer was found to be slightly higher than that of the linear block copolymer.

Thermal properties

D.s.c. thermograms (not shown) of both the linear and the three-arm star block copolymer suggest segregation of the PIB and PS phases as indicated by the observation of two glass transition temperatures, the first at −60°C corresponding to the PIB continuous phase and the second at 80°C corresponding to PS domains. The latter was almost undetectable due to the relatively short PS block length of these polymers.

The thermal stability of block copolymers was measured using t.g.a. under a constant nitrogen blanket;

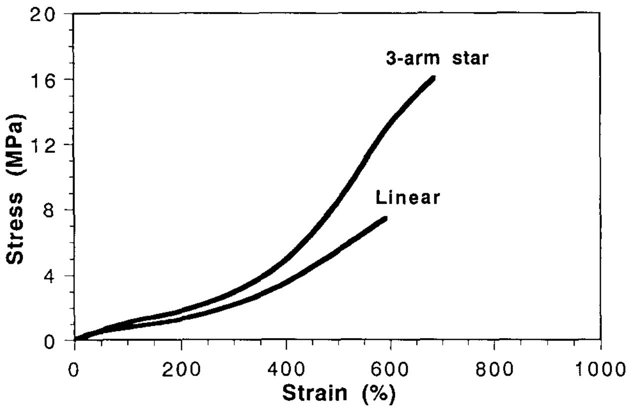

Figure 10 Stress–strain behaviour of the linear and three-arm star block copolymers

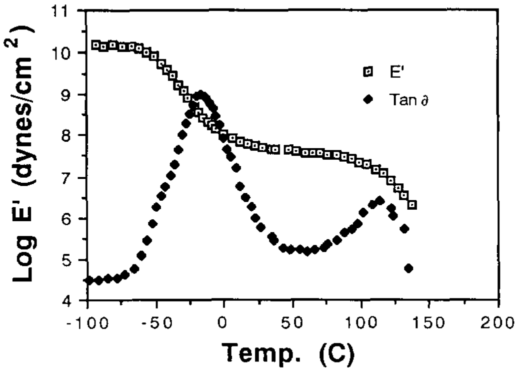

Figure 11 D.m.a. of the linear block copolymer

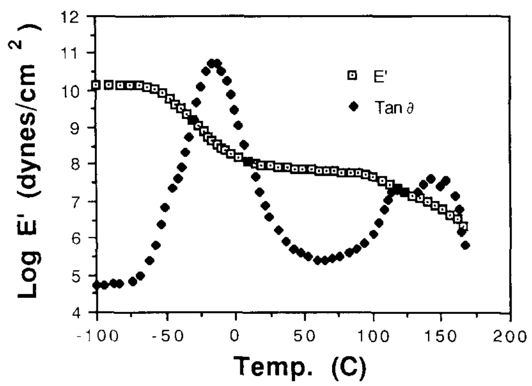

Figure 12 D.m.a. of the three-arm star block copolymer

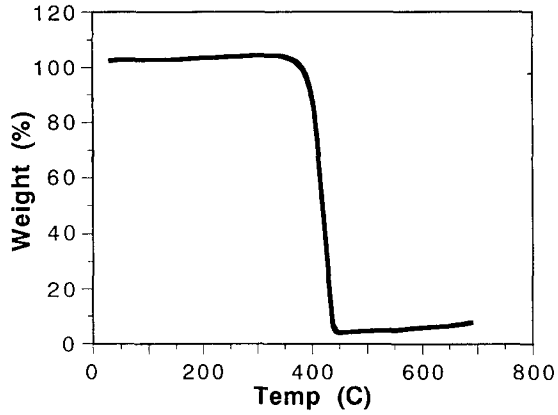

Figure 13 T.g.a. of the linear block copolymer

a representative thermogram is shown in *Figure 13*. The mid-point of the major mass loss process is observed at 417°C, which is considerably higher (~100°C) than the hydrogenated version of poly(styrene-*b*-butadiene-*b*-styrene) (Kraton®G) observed by Weiss *et al.*[10]. The superior thermal stability of PS–PIB–PS block copolymers as compared to poly(styrene-*b*-butadiene-*b*-styrene) is obviously due its fully saturated mid-block as opposed to the butadiene mid-block which retains some unsaturation even after hydrogenation.

CONCLUSIONS

Linear and three-arm star PS–PIB–PS block copolymers possessing narrow MWDs and minimal homo-PS contamination were successfully synthesized using blocked dicumyl chloride or tricumyl chloride/$TiCl_4$/pyridine initiating system in methylcyclohexane/methyl chloride (60/40, v/v) with a small concentration of DtBuP added as a proton trap. The most critical aspect of the block copolymer synthesis was the timing of the styrene addition. The results showed that styrene must be added late enough in the polymerization to ensure a sharp crossover from the PIB block to the PS block, yet early enough to prevent the formation of homo-PS resulting from chain transfer reactions, which become significant in the limit of high isobutylene conversion.

The linear and three-arm star block copolymers were designed to possess equivalent block lengths on a per-arm basis, allowing the effect of polymer geometry on physical properties to be determined. TEM indicated that these samples possess a heterogeneous morphology consisting of cylindrical PS domains dispersed within a matrix of PIB. In addition, it was found that the size and shape of the PS domains is independent of molecular geometry. The production of a dual-phase morphology was further confirmed by the observation of two endotherms in d.s.c. thermograms, one at low temperature (−60°C) corresponding to the glass transition temperature of PIB and the other at high temperature (80°C) corresponding to the glass transition temperature of PS.

Tensile studies showed that the three-arm star block copolymer yields much higher engineering stresses compared to the linear block copolymer at any elongation; however, both polymers show essentially the same elongation at break and both were found to undergo strain-induced crystallization at high elongation.

The dynamic mechanical responses of these materials determined as a function of temperature displayed typical dual-phase behaviour with the production of two peaks in the tan δ, the first occurring at −55°C due to the PIB phase and the second at about 100–110°C, characteristic of the PS phase. In addition, the rubbery plateau modulus of the three-arm star polymer was found to be higher than that of the linear polymer.

The thermal stabilities of these polymers determined by t.g.a. were found to be about 100°C higher than hydrogenated poly(styrene-*b*-butadiene-*b*-styrene), with the mid-point of the major loss process occurring at 417°C.

ACKNOWLEDGEMENTS

Acknowledgement is made to Shell Development Company for the partial support of this research. The authors also acknowledge Drs Michael Massey, Dale Handlin and Donn DuBois of the Shell Development Company for the TEM and d.m.a. and for helpful discussions. Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.

REFERENCES

1 Kaszas, G., Puskas, J. E. and Kennedy, J. P. *J. Appl. Polym. Sci.* 1990, **39**, 119
2 Puskas, J. E., Kaszas, G., Kennedy, J. P. and Hager, W. G. *J. Polym. Sci., Polym. Chem. Edn* 1992, **30**, 41
3 Bi, L. K., Fetters, L. J. and Morton, M. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* 1974, **15**, 157
4 Storey, R. F. and Lee, Y. K. *J. Mater. Sci., Pure Appl. Chem.* 1992, **A29**(11), 1017
5 Loveday, D., Wilkes, G. L., Lee, Y. and Storey, R. F. *Am. Chem. Soc. Div. Polym. Chem., Polym. Prepr.* 1992, **33**(2), 288
6 Wang, B., Mishra, M. K. and Kennedy, J. P. *Polym. Bull.* 1987, **17**, 205
7 Santos, R., Kennedy, J. P. and Walters, M. *Polym. Bull.* 1984, **11**, 261
8 Kaszas, G., Puskas, J. E., Kennedy, J. P. and Hager, W. G. *J. Polym. Sci., Polym. Chem. Edn* 1991, **29**, 427
9 Mohajer, Y., Bagrodia, S., Wilkes, G. L., Storey, R. F. and Kennedy, J. P. *J. Appl. Polym. Sci.* 1984, **29**, 1943
10 Weiss, R. A., Sen, A., Willis, C. L. and Pottick, L. A. *Polymer* 1991, **32**, 1867