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Poly(styrene-*b*-isobutylene-*b*-styrene) block copolymers produced by living cationic polymerization

I. Compositional analysis

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Abstract

Poly(styrene-*b*-isobutylene-*b*-styrene) block copolymers made through controlled–living cationic polymerization using the ^{t}Bu-*m*-DCC–$TiCl_4$ initiating system in 60/40 (v/v) hexane–methyl chloride cosolvents were analyzed using curve-resolution software in conjunction with high-resolution g.p.c. Fractional precipitation and selective solvent extraction were applied to a representative sample in order to confirm the identity of contaminating species. The block copolymers were found to consist of 70–75 wt% of the target molecule, and about 20 wt% of coupled (and higher linked) block copolymers formed by intermolecular electrophilic aromatic substitution linking reactions occurring during the styrene polymerization. Minor contaminants were identified as diblock copolymer and low molecular weight polystyrene homopolymer. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Living cationic polymerization; High-resolution g.p.c.; Selective solvent extraction

1. Introduction

There is a great deal of interest in A-B-A block copolymers due to their useful properties which are a result of their unique phase-separated morphology. A-B-A block copolymers of special interest are the so-called thermoplastic elastomers (TPEs) which are composed of glassy outer blocks and rubbery inner blocks. Due to phase separation of the glassy blocks into discrete domains, these materials behave as crosslinked rubbers at low temperatures, but can be processed as thermoplastics at higher temperatures. An important commercial example is the poly(styrene-diene-styrene) block copolymers which are made by living anionic polymerization, yielding well-defined polymers with narrow molecular weight distributions. These materials are typically composed of 20–40% polystyrene (PS) block segments, which exist in discontinuous, phase-separated domains. These domains act as physical crosslinks which can be weakened by heating to temperatures above the T_g of PS.

Recently, poly(styrene-*b*-isobutylene-*b*-styrene) (PS-PIB-PS) block copolymers have become available [1–5] through the process of living cationic polymerization. PS-PIB-PS block copolymers have the advantage of a completely saturated mid-block, which yields superior thermal and oxidative stability which are required for some applications. To obtain comparable properties from diene-based materials, one must resort to expensive post-polymerization hydrogenation. PS-PIB-PS copolymers may have other specific advantages in certain applications due to the superior dampening and barrier properties of polyisobutylene. In addition, using PIB as the elastomeric segment yields a softer TPE for a given PS content due to the much higher molecular weight between entanglements (M_e) of PIB as compared with poly(ethylene-*co*-butylene) and other diene based elastomer segments [6]. Another potential advantage of PS-PIB-PS block copolymers, which are grown from the center outward using a difunctional cationic initiator, is the minimization of contamination by diblock copolymer which results from incomplete linking reactions in the anionic process. These contaminants may exist at levels up to 20% in commercial triblock copolymers, and have a detrimental effect on mechanical properties such as tensile strength.

In a three-part series of papers we have rigorously investigated the composition, morphology, and properties of several PS-PIB-PS triblock copolymers with similar PIB center block and varying PS outer blocks. The research

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Table 1
Reaction conditions and reagent concentrations for linear PS-PIB-PS block copolymer syntheses

PS outer blocks	BCP01	BCP02	BCP03	BCP04	BCP05	8907
Styrene added (mol)[a]	1.39	1.39	1.39	0.96	0.78	1.39
Styrene pzn. time (min.)	20	30	30	30	20	45

PIB inner block: hexane (ml) 1524; methyl chloride (ml) 1016; IB @ 0 min (ml) 215 (2.73 mol); IB @ 20 min (ml) 98 (1.24 mol); ^{t}Bu-*m*-DCC (g) 1.35 (4.70×10^{-3} mol); pyridine (ml) 0.83 (1.0×10^{-2} mol); DTBP (ml) 0.61 (2.7×10^{-3} mol); $TiCl_4$ (ml) 10.5 (9.6×10^{-2} mol); Total pzn. time (min) 130

[a] Added as 50% (v/v) solution in hexane–MeCl.

described in this, the first paper of the series, arose from recent investigations in our laboratories that showed that PS-PIB-PS block copolymers often contain significant levels of polymeric contaminants [2]. The purpose of this work was to analyze the composition of linear PS-PIB-PS triblock copolymers by comparing curve-resolved high-resolution gel permeation chromatograms (HRg.p.c.) of the PIB center block, sampled just prior to the addition of the styrene, to those of the final block copolymer. Proton n.m.r. was utilized to determine the overall PS content of each sample, and this value was compared with the PS content determined from the PIB inner block and final block copolymer molecular weights obtained by g.p.c. To confirm the identity of certain low molecular weight contaminants, ^{1}H n.m.r. and g.p.c. were utilized to determine the compositions of samples obtained by fractional precipitation of a representative block copolymer sample.

2. Experimental

2.1. Materials

Hexane (Aldrich Chemical Co.) was distilled from calcium hydride just prior to use. Isobutylene (IB) and methyl chloride (MeCl) (Linde Div., Union Carbide Corp.) were dried by passing the gaseous material through a BaO–$CaCl_2$ column. Styrene (Aldrich) was distilled from calcium hydride under vacuum and stored at -80°C under nitrogen until use. Titanium tetrachloride, pyridine, 2,6-di-*tert*-butylpyridine (DTBP), and anhydrous methanol (all Aldrich) were used as received.

The preparation of 1,3-bis(2-chloro-2-propyl)-5-*tert*-butylbenzene (^{t}Bu-*m*-DCC) has been described [2,7].

2.2. Synthesis of PS-PIB-PS block copolymers

Linear PS-PIB-PS block copolymers were synthesized using a ^{t}Bu-*m*-DCC–$TiCl_4$ initiating system employing pyridine as an externally added electron donor and DTBP as a proton trap in 60/40 (v/v) hexane–methyl chloride cosolvents at −80°C. Polymerizations were conducted within a stainless steel glove-box, equipped with an integral cold temperature bath, under a dry nitrogen atmosphere. Specific reaction conditions and reagent concentrations are listed in Table 1.

All linear copolymers were designed with identical PIB inner blocks possessing a target number average molecular weight, M_n, of 48 000 g mol^{-1}. The living difunctional PIB block was formed by adding neat $TiCl_4$ to a hexane–methyl chloride solution of IB, initiator, and pyridine. At a polymerization time of 20 min, a second portion of IB was added. At a polymerization time of 130 min, DTBP was added, followed by a hexane–methyl chloride (60/40) solution of styrene (50 vol% styrene). At a pre-determined time, the polymerization was stopped by the addition of excess pre-chilled methanol to the reaction mixture. The molar ratio of styrene to living PIB chains and time of styrene polymerization were used to vary the molecular weight of the PS blocks.

A representative polymerization procedure used to synthesize a linear block copolymer was as follows: to a chilled 5 l two-necked round-bottomed flask, equipped with mechanical stirrer were added sequentially 1524 ml of hexane, 1016 ml of methyl chloride, 215 ml IB (2.73 mol), 1.35 g ^{t}Bu-*m*-DCC (4.70×10^{-3} mol), 0.83 ml pyridine (1.0×10^{-2} mol), and 0.61 ml DTBP (2.7×10^{-3} mol). Methyl chloride and IB were condensed into, and hexane was pre-cooled in chilled graduated cylinders before addition to the flask. The mixture was stirred 0.5 h; then, with rapid stirring, neat $TiCl_4$ (10.5 ml, 9.6×10^{-2} mol, unchilled) was injected using a syringe to commence polymerization. After 20 min, 98 ml (1.24 mol) isobutylene was added to the polymerization mixture. After 130 min, a small aliquot was withdrawn from the polymerization mixture by pipette and precipitated into methanol. Immediately following the withdrawal of the aliquot, a pre-chilled solution of styrene in hexane–methyl chloride [160 ml (1.39 mol) styrene–96 ml hexane–64 ml methyl chloride] was added to the polymerization mixture to commence the polymerization of the styrene outer blocks. After 20 additional min, the polymerization was terminated by the injection of 160 ml (4 mol) of pre-chilled methanol. The terminated polymerization mixture was then allowed to warm to room temperature overnight with constant stirring. Hexane and methylene chloride were added, as necessary, for good dissolution of the polymer, and the solution was slowly precipitated with vigorous stirring into a large excess of ethanol. The precipitate was collected by decantation and filtration, dried, and redissolved for a second precipitation into ethanol. The washed polymer was then dried in vacuo at 80°C for 3 days.

2.3. Fractionation

A representative block copolymer was purified by fractional precipitation. This was done by first preparing a 1 wt% solution of the block copolymer in toluene. The solution was transferred to a 4 l separatory funnel, and methanol was then added in small increments, with mixing, until two cloudy layers formed upon standing. The separatory funnel was then placed into a warm water bath (40°C–50°C) until the contents were clear and homogeneous. The water bath was then allowed to slowly cool (~10 h) to room temperature, resulting in the formation of two layers. The bottom layer was removed completely and the top layer was sampled. After analysis of both layers by g.p.c., additional fractionation was performed either by adding methanol to the remaining top layer in order to get another fraction, or by redissolving the bottom layer in toluene and repeating the process. After several steps, choosing the best fraction each time, the sample was freed of most high and low molecular weight contaminants.

2.4. Selective solvent extraction

Selective solvent extraction was performed on the block copolymers using methyl ethyl ketone (MEK), a selective solvent for polystyrene. A Soxhlet extraction apparatus equipped with a cellulose thimble was used. Extraction with MEK was carried out for 7 days, after which the thimble and remaining polymer were carefully dried and weighed. The non-MEK soluble polymer was then recovered by extraction with methylene chloride for 24 h. This solution was dried at 50°C under a stream of dry nitrogen. The hot polymer solution was protected from the effects of u.v. light by covering the entire apparatus with aluminum foil during the extraction.

2.5. Proton magnetic resonance spectroscopy (^{1}H n.m.r.)

Proton n.m.r. was used to determine block copolymer composition in terms of wt% PS by comparing the integrated areas of the aliphatic and aromatic regions of the spectra. Spectra were obtained using either a 200 MHz Bruker ACE-200 or a 300 MHz Bruker ACE-300 n.m.r. spectrometer. Samples were analyzed as 5% (w/v) solutions in $CDCl_3$, and reported against an internal reference (0 ppm) of tetramethylsilane (TMS).

2.6. High-resolution g.p.c.

High-resolution g.p.c. (HRg.p.c.) was performed using a Shell Development Co. proprietary system which employed a THF mobile phase at 50°C and dual refractive index (RI) and ultraviolet (u.v.) detectors. All molecular weights were referenced to PS standards.

2.7. Curve resolution

Curve resolution of the chromatograms was performed using Peakfit software by Jandel Scientific. Each PIB inner block was fitted with three peaks while each final block copolymer was fitted with five peaks. For ease of discussion, the peaks were numbered from left to right (high to low molecular weight) and referred to by their numbers. All fitted component peaks were Gaussian with the exception of peak 2 in the PIB samples and peak 3 in the block copolymer samples. These peaks represented the main component in both cases and were fitted using the Haarhoff–Van der Linde function (HVL) [8], which was designed to fit the skewed peaks characteristic of chromatographic data. Like the Gaussian function, the HVL function has area, center, and width parameters. In addition, the HVL function contains a distortion parameter which allows the peak to be skewed in either direction. The HVL function is identical to the Gaussian when the distortion or skewing factor is zero. In all cases, the distortion factor used ranged from 0.0095 to 0.0017; therefore, the peaks are very nearly Gaussian.

3. Results and discussion

Fig. 1 shows the RI and u.v. HRg.p.c. chromatograms of a typical block copolymer. The major peak represents the target block copolymer. The principal contaminants are seen as a small high molecular weight peak with a molecular weight twice that of the target molecule and a low molecular weight tail, which appears to be rich in PS due to the stronger response of the u.v. detector in this region. The high molecular weight peak represents a PS-PIB-PS-PIB-PS pentablock copolymer, which is thought to arise from a coupling reaction in which one carbocationic growing chain end attaches to the polystyrene segment of another by electrophilic aromatic substitution (EAS). There is also a long, high M_w tail that appears to be due to successively higher orders of this reaction, i.e. three, four, or more molecules linked together.

The origin of the low molecular weight contaminants is less clear, but they were found to consist at least partially of low M_w PS, as indicated by ^{1}H n.m.r. analysis of the low molecular weight fractions obtained by fractional precipitation and by comparing the RI and u.v. detector responses in the low molecular weight regions of the chromatograms.

In the following paragraphs is presented a detailed discussion of the curve fitting process applied to these chromatograms. We also discuss in more detail the evidence supporting the identities of the various components mentioned earlier.

In Fig. 2, curve-resolved chromatograms are shown with

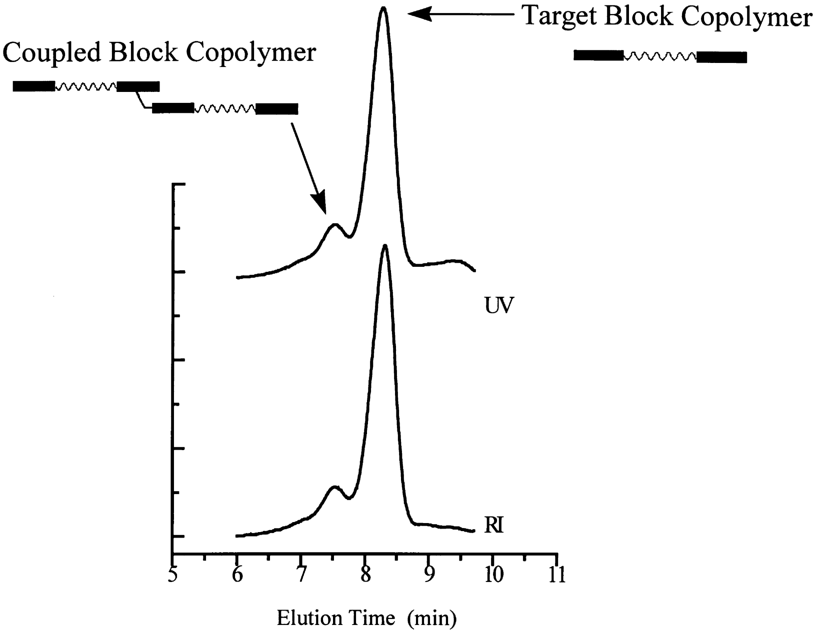

Fig. 1. Typical high-resolution gel permeation chromatograms (HRg.p.c.) (u.v. and RI detectors) of PS-PIB-PS block copolymers.

the actual chromatogram, the component peaks, and the sum of the component peaks all plotted on the same scale; Table 2 lists the integrated percent areas for the component peaks. With properly fitted data, the actual chromatogram and the sum of the component peak curves overlap and appear as a single line. The center chromatogram in Fig. 2 (five Gaussians) purposefully illustrates a poor fit; two separate lines can be seen in the region where the fit is poor.

As previously mentioned, each block copolymer chromatogram was resolved into five peaks, four Gaussian and one HVL function. Initially it was found that six Gaussian peaks produced a very good fit (top of Fig. 2); however, the small peak immediately to the left of the main peak (peak*) is of questionable legitimacy considering the mechanism of block copolymer formation. The center chromatogram illustrates the effect of simply removing this small Gaussian peak. The bottom chromatogram illustrates the use of a slightly distorted HVL function for the main component (peak 3) in place of two Gaussian peaks (peaks* and three in the top set of curves); it can be seen that the fit is excellent with the HVL function. Thus it is proposed that peak* represents a slight distortion of the main peak rather

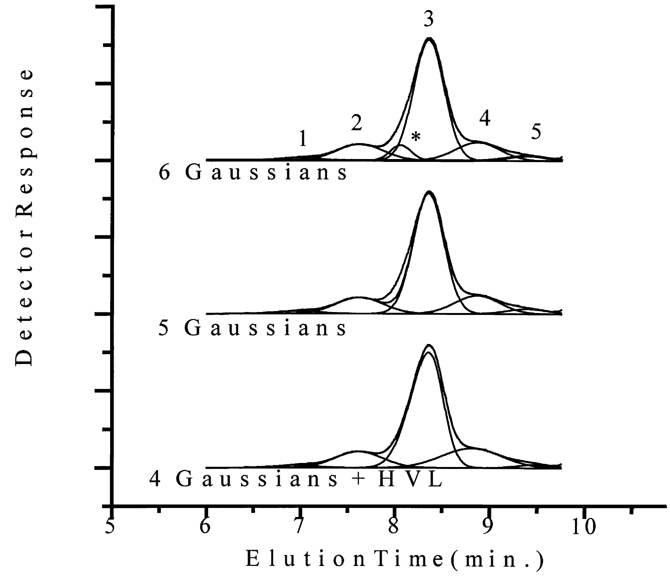

Fig. 2. Comparison of curve-resolved HRg.p.c. chromatogram (RI detector) of block copolymer 8907 using different types of component peaks. Peak 1, three or more PS-PIB-PS linked by EAS; peak 2, two PS-PIB-PS coupled by EAS; peak*, Gaussian peak accounting for chromatographic distortion of peak 3; peak 3, target PS-PIB-PS triblock copolymer; peak 4, diblock copolymer with molecular weight equal to $^1/_2$ that of target triblock; and peak 5, homo-polystyrene.

Table 2
Component peak percent areas for the three curve-resolved spectra shown in Fig. 2

Curve	Peak 1	Peak 2	Peak*	Peak 3	Peak 4	Peak 5	Fit (r^2)
Six Gaussians	1.83	12.94	5.43	62.93	13.82	3.04	0.99974
Five Gaussians	1.94	13.69		66.54	14.62	3.22	0.98577
Four Gaussian + HVL	1.64	13.01		64.21	19.48	1.65	0.99982

The sample is block copolymer 8907 and peaks are numbered from left to right.

than an actual component of the polymer sample. Such distortion is most likely inherent to the chromatographic process, but is evident in the largest peak only. The same distortions may be present in all component peaks, but are undetectable due to the small magnitude of these peaks. Fits were also attempted using distortions on the low molecular weight side of peak 2, however, none of these resulted in a satisfactory fit and all involved very long, low molecular weight tails, or large amounts of distortion.

The resolved chromatogram shown at the bottom of Fig. 2 is in most respects typical of the block copolymers analyzed, except that this particular sample (8907) displayed an abnormally large peak 4 component fraction, about 3.4 times the average found in the other samples. In most cases, the ratio of the molecular weight of each peak to that of the target block copolymer was 3–4, 2, 1, and 0.5 for peaks 1–4, respectively. Thus, the high molecular weight fraction (HMWF) corresponding to peak 1 was attributed to very large molecules consisting of three or more primary PS-PIB-PS triblocks that were linked together through EAS reactions. Likewise, peak 2 was attributed to coupled (dimeric) triblocks produced by this same process. Peak 3 was assigned to the target triblock copolymer. Peak 4, with molecular weight equal to 0.5 of the target molecule, was of particular interest. The chromatograms of the parent PIB middle blocks (Fig. 3 is typical) also exhibited a component with half the molecular weight of the main component; therefore, it is possible that a small fraction of the difunctional initiator molecules was effectively monofunctional and that these PIB chains added styrene at the same rate as the difunctional chains, resulting in a small amount of diblock copolymer in the final product. This diblock copolymer would have the same composition or PIB–PS ratio as the triblock, but it would be expected to adversely affect the mechanical properties of the material. Polymer 8907 contains nearly 20% of this component while all other samples contain from 4 to 7.5%.

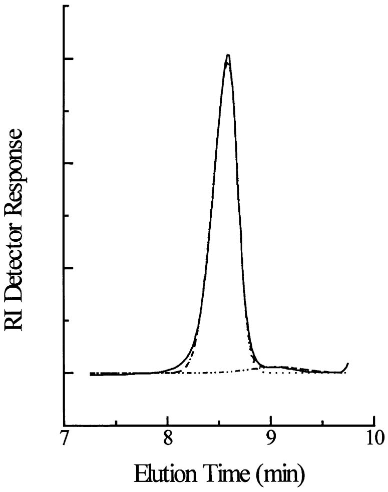

Fig. 3. Typical HRg.p.c. chromatogram (RI detector) of a PIB inner block.

The low molecular weight fraction (LMWF), represented by peak 5, was identified as homo-polystyrene. It had no corresponding component in the parent PIB chromatogram, and its UV detector response was much stronger than its RI response. Evidence supporting the proposed identity of the low molecular weight fraction (LMWF) as polystyrene was obtained by determining the styrene content of LMWF-rich fractions obtained by fractional precipitation. Polystyrene contents of several fractions were compared using proton n.m.r., which affords a very accurate method of determining the overall PS content of these polymer samples. Fig. 4 shows g.p.c. chromatograms of the block copolymer starting material (top chromatogram) and of two samples rich in the LMWF along with their PS contents determined by proton n.m.r. Clearly, when the LMWF was isolated from the target molecule, analysis showed it to be virtually 100% homo-PS.

Table 3 summarizes the results of RI chromatogram deconvolution for all samples. The values shown in each column are the percentage area represented by each peak. For a homopolymer or a copolymer with constant composition throughout its entire molecular weight range, these values would represent the weight percentage of the corresponding component in the sample. A small correction could be applied to account for the difference in RI detector response toward PS versus PIB. The HRg.p.c. PS/PIB response factor ratio was found to be 1.4. This correction would primarily affect the value for peak 5, which is homo-PS. In practice, however, peak 5 is so small in these samples that this correction was not considered worthwhile. It is simply noted that the uncorrected data in Table 3 overstate the real fraction of homo-PS contamination.

Fig. 5 shows RI g.p.c. chromatograms of a typical block copolymer (BCP02) before and after Soxhlet extraction using MEK, a selective solvent for PS, as well as a chromatogram of the MEK soluble fraction. The latter has a M_n of 10 000 g mol^{-1} and a polydispersity index (PDI = M_w/M_n) of 2.7, although, it should be noted that this fraction contains a small amount of the block copolymer which tends to

Table 3
Results of RI chromatogram curve-resolution showing approximate (not corrected for RI detector response factors of PS and PIB) weight fractions of each component and overall molecular weight distributions for each polymer sample

Sample	% Target	% Coupled	% Diblock	% HMWF	% LMWF	M_w/M_n
BCP01	71.0	15.9	7.5	3.6	2.1	1.48
BCP02	73.5	15.5	4.9	4.6	1.6	1.43
Fract. 02	80.7	13.3	4.1	1.8	0.0	1.20
BCP03	70.5	15.8	6.9	5.1	1.8	1.50
BCP04	74.9	15.1	4.0	4.5	1.5	1.33
BCP05	77.0	13.2	7.0	1.6	1.3	1.31
8907	64.2	13.0	19.5	1.6	1.7	1.41

inflate these numbers slightly. Nonetheless, these values are in excellent agreement with the results of the HRg.p.c. deconvolution; the corresponding peak (peak 5) in the deconvoluted HRg.p.c. chromatogram for this block copolymer had $M_n = 9900\ \mathrm{g\ mol^{-1}}$ and PDI = 1.31. They also agree very well with the measured molecular weight and PDI of the LMWF obtained by fractional precipitation (bottom chromatogram in Fig. 4), as listed in Table 4.

The weight percent PS in each block copolymer was determined using ^{1}H n.m.r. by comparing the integrated areas of the aromatic (6–8 ppm) and aliphatic (0.5–2.5 ppm) regions of the spectra, denoted A_{arom} and A_{aliph}, respectively. Each isobutylene unit contains eight aliphatic protons while each styrene unit contains three aliphatic protons and five aromatic protons. Thus, the following equation was used to calculate weight percent PS by n.m.r. ($W_{\mathrm{PS,\,n.m.r.}}$) from the integrated areas:

$$W_{\mathrm{PS,\,n.m.r.}} = \frac{M_{\mathrm{S}} \cdot A_{\mathrm{arom}}}{M_{\mathrm{S}} \cdot A_{\mathrm{arom}} + M_{\mathrm{IB}}(5A_{\mathrm{aliph}} - 3A_{\mathrm{arom}})/8} \cdot 100\% \qquad (1)$$

where, M_{S} and M_{IB} represent the molecular weights of styrene and isobutylene repeat units, respectively. The weight percent PS was also calculated from g.p.c. data ($W_{\mathrm{PS,\,g.p.c.}}$) by simply measuring the difference in molecular weight between the final block copolymer and the PIB inner block as shown in Eq. (2):

$$W_{\mathrm{PS,\,g.p.c.}} = M_{\mathrm{p,\,BCP}} - \frac{M_{\mathrm{p,\,PIB}}}{M_{\mathrm{p,\,BCP}}} \cdot 100\% \qquad (2)$$

where, $M_{\mathrm{p,BCP}}$ and $M_{\mathrm{p,PIB}}$ are the peak molecular weights of the final block copolymer and PIB inner block, respectively. Peak molecular weights (M_p) were used in these calculations because the polymer component which comprises the majority (≈75%) of the sample is in all cases nearly monodisperse; therefore, $M_p \approx M_w \approx M_n$ for this component. Using number or weight average molecular weights would result in significant errors in the calculated composition of the primary component (the target molecule), due to inclusion of low and high molecular weight species into these averages. Therefore, M_p provides the most accurate and meaningful characterization of the samples in this investigation.

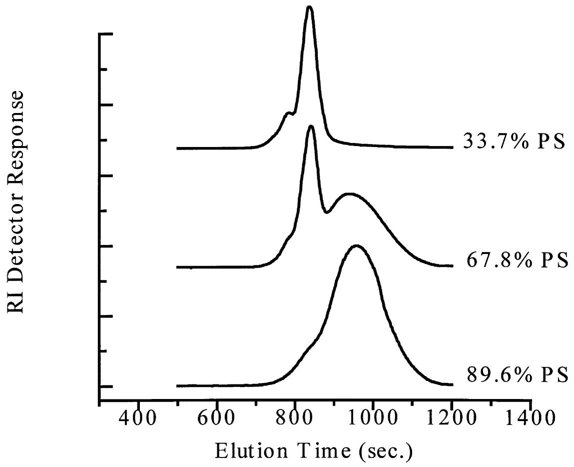

Fig. 4. Gel permeation chromatograms of BCP02 (top) and two low molecular weight fractions with their corresponding PS contents as determined by proton n.m.r.

The PS block molecular weight (M_{PS}) was calculated, based either on the wt% PS determined by n.m.r. and the PIB inner block molecular weight as determined by g.p.c. Eq. (3), or from the difference in peak molecular weight of the final block copolymer and the PIB inner block Eq. (4).

$$M_{\mathrm{PS}}(\mathrm{n.m.r.}) = M_{\mathrm{p,\,PIB}} \cdot \frac{W_{\mathrm{PS,\,n.m.r.}}}{2(100 - W_{\mathrm{PS,\,n.m.r.}})} \qquad (3)$$

$$M_{\mathrm{PS}}(\mathrm{g.p.c.}) = \frac{M_{\mathrm{p,\,BCP}} - M_{\mathrm{p,\,PIB}}}{2} \qquad (4)$$

Table 5 shows $W_{\mathrm{PS,\,n.m.r.}}$ and $W_{\mathrm{PS,\,g.p.c.}}$, as well as PS block sizes calculated based on these values, and the data allow comparison of the different methods of determining copolymer composition. Clearly, the existence of small amounts of homo-PS should result in higher values for $W_{\mathrm{PS,\,n.m.r.}}$ compared with $W_{\mathrm{PS,\,g.p.c.}}$; however, the two samples

Table 4
Molecular weight and molecular weight distribution data for low molecular weight fractions of BCP02 shown in Fig. 4

wt% PS (n.m.r.)	M_n	M_w	PDI
33.7	65 200	101 000	1.55
67.8	15 800	50 400	3.19
89.6	11 200	27 300	2.43

Table 5
Comparison of weight percentage polystyrene (W_{PS}) in PS-PIB-PS block copolymers determined by n.m.r. and g.p.c., and PS block molecular weights calculated based on n.m.r. and g.p.c. data as described in the text

Sample	$W_{PS,\ n.m.r.}$	$W_{PS,\ g.p.c.}$	$M_{p,\ PIB}$ (g mol^{-1} × 10^{-3})	$M_{p,BCP}$ (g mol^{-1} × 10^{-3})	M_{PS} (n.m.r.) (g mol^{-1} × 10^{-3})	M_{PS} (g.p.c.) (g mol^{-1} × 10^{-3})
BCP01	25.5	21.5	53.0	67.5	9.1	7.3
BCP02	33.7	28.4	51.7	72.2	13.1	10.3
BCP03	33.5	29.9	53.8	76.7	13.6	11.5
BCP04	19.2	21.4	51.9	66.0	6.2	7.1
BCP05	12.7	20.3	49.9	62.6	3.6	6.4
8907	32.4	23.8	51.8	68.0	12.4	8.1

with smallest PS blocks (BCP04 and BCP05) yielded the opposite result. This is probably because all molecular weights were reported relative to PS standards and block copolymers may have significantly different elution times for a given molecular weight. Thus, the PS block molecular weights are only approximate; however, the values determined by n.m.r. are probably more accurate since the amount of homo-PS contamination is very low.

4. Conclusion

PS-PIB-PS triblock copolymers were rigorously characterized to obtain a better understanding of their characteristic composition and the origin of various polymeric reaction byproducts. It was shown that these block copolymers consist primarily of the target molecule (70–75 wt%), with significant amounts of coupled (and higher linked) block copolymers (~20 wt% combined). Diblock copolymer and homo-PS were detected as minor contaminants. The linked species were proposed to result from electrophilic aromatic substitution of growing PS chain ends onto pendent phenyl rings of other polymer molecules. The coupled species was observed to possess a molecular weight approximately twice that of the target molecule. It is probable that the amount of linked species produced in these systems is related to the choice of non-polar cosolvent. Hexane is a non-solvent for PS, which might cause aggregation of the growing triblocks after the PS block molecular weight reaches some critical value. This would raise the effective concentration of phenyl rings in the vicinity of the growing carbocations and promote EAS. An alternative solvent which is good for PS, methylcyclohexane, has been utilized in conjunction with MeCl for PS-PIB-PS block copolymer synthesis by several researchers [1–4]; however, coupling was still observed at least in one case [1]. Recent investigations have confirmed that coupling also occurs in methylcyclohexane–MeCl (60/40, v/v), although to a lesser extent than in hexane–MeCl (60/40, v/v) [9].

Diblock copolymer, with a molecular weight approximately one half that of the target molecule, could be produced by difunctional initiator molecules that fail to initiate from one side, although the reason for this failure is obscure. Standard precautions were taken to utilize highly purified

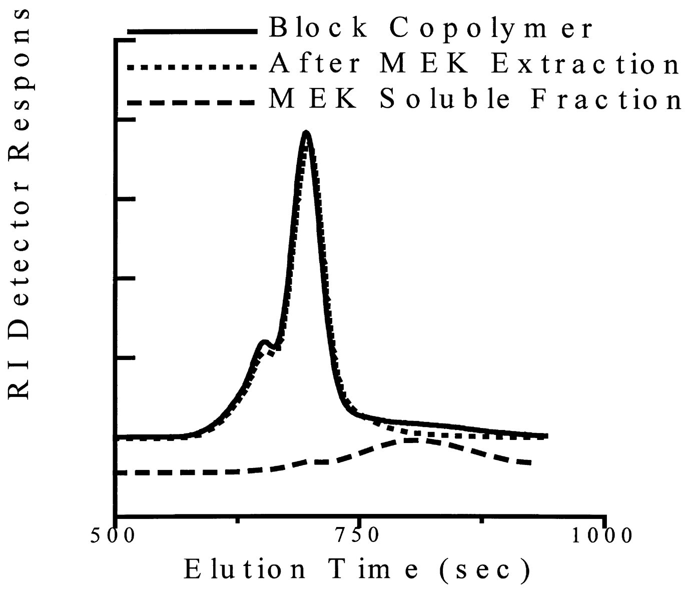

Fig. 5. G.p.c. chromatograms of block copolymer BCP02 before and after MEK extraction and of MEK-soluble fraction.

initiator. Further, the initiator used in this work, ^{t}Bu-*m*-DCC (*tert*-butyl blocked dicumyl chloride), is protected against the most common failure mode associated with aromatic cationic initiators, namely, intramolecular alkylation of the ring after addition of one unit of isobutylene, i.e. so-called indanyl ring formation.

All but one of the PS-PIB-PS triblock copolymers showed the presence of a very small amount (~2 wt% or less) of low molecular weight PS with broad molecular weight distribution. This contaminant could form either by chain transfer to monomer during the styrene polymerization or by initiation from protons liberated by the electrophilic aromatic substitution reactions discussed earlier. The presence of DTBP (proton trap) in the polymerization mixture would argue against the latter explanation, but without further evidence a firm conclusion cannot be made.

In summary, PS-PIB-PS triblock copolymers produced by living cationic polymerization appear to be compositionally less well defined and of broader molecular weight distribution than the best triblock copolymers made by living anionic polymerization under rigorous conditions. However, the major impurity, PS-PIB-PS-PIB-PS pentablock copolymers caused by coupling, would be expected to enhance physical properties, e.g. tensile strength, and steps can be taken to minimize the other impurities that have been identified in this work. Finally, PS-PIB-PS triblocks are conveniently made from a difunctional initiator, and thus compare very favorably to triblock copolymers made commercially by anionic polymerization, which require a coupling step and are contaminated by appreciable quantities of diblock copolymers.

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