Aspects of the Synthesis of Poly(styrene-*b*-isobutylene-*b*-styrene) Block Copolymers Using Living Carbocationic Polymerization

Robson F. Storey* and Bret J. Chisholm

Department of Polymer Science, The University of Southern Mississippi, Hattiesburg, Mississippi 39406

Received July 6, 1993; Revised Manuscript Received September 27, 1993®

ABSTRACT: The effect of the time of styrene addition on the composition of poly(styrene-isobutylene-styrene) (PS-PIB-PS) block copolymers synthesized using a dicumyl chloride/$TiCl_4$/pyridine initiating system and the sequential addition of monomers was investigated at -80 °C. It was found that the addition of styrene at an isobutylene (IB) reaction time significantly exceeding the time necessary for complete IB consumption results in contamination of the material with a substantial amount of homo-PS. Conversely, the addition of styrene to PIB chains formed under conditions of intermediate IB conversion resulted in a very slow buildup in molecular weight after the addition of styrene. This retardation of the rate after the addition of styrene was proven to be the result of a random copolymerization between styrene and unreacted IB. It was also found that the addition of the proton trap 2,6-di-*tert*-butylpyridine resulted in a narrowing of product polymer molecular weight distribution.

Introduction

In 1965, Shell announced the commercial production of thermoplastic elastomers (TPEs) from block copolymers of styrene and butadiene and of styrene and isoprene.[1] The synthetic procedure followed from the work of Szwarc,[2,3] who in 1956 reported that certain anionic polymerizations gave "living" characteristics and that a second monomer could be added without termination. Since these developments, living anionic polymerization has been thoroughly characterized and utilized to synthesize a wide variety of polymers with well-defined architectures such as star-branched polymers,[4] star-branched block copolymers,[5] block copolymer ionomers,[6-8] and telechelic polymers.[9]

Unfortunately, the number of monomers which can be polymerized anionically is quite limited. As a result, there has been a great effort to produce living polymerizations of cationically polymerizable monomers, enabling the synthesis of many new materials. However, due to the high reactivity of carbocations, the realization of living carbocationic polymerizations has been very difficult and slow in development. In fact, the first truly living carbocationic polymerization was not reported until 1984, by Higashimura et al.,[10] for the polymerization of isobutyl vinyl ether by an HI/I_2 initiating system. Living polymerization for this system was achieved, as described by Sawamoto,[11] through the insertion of monomer into an I_2-activated carbon-iodine bond. The intimate interaction between growing chain ends and their binary $I^- \cdots I_2$ counterionic moieties renders the chain ends reactive toward propagation but unreactive toward higher energy chain transfer and termination reactions. This method of living carbocationic polymerization has been termed "stabilization by a suitably nucleophilic counterion" and has been successfully used to produce living carbocationic polymerizations of monomers such as vinyl ethers,[10] *p*-methoxystyrene,[12] and *N*-vinylcarbozole,[13] which form highly stabilized carbocations.

A more recent development involving the addition of Lewis bases such as ethyl acetate, dimethyl sulfoxide, and dimethylacetamide to the reaction medium of a carbocationic polymerization, has been found to provide living characteristics to the cationic polymerization of monomers which form relatively unstable carbocations, such as isobutylene (IB)[14] and styrene,[15] in addition to those monomers which form relatively stable carbocations. This method of living carbocationic polymerization has been termed "electron donor mediated cationic polymerization", since the Lewis base or a Lewis base:Lewis acid (coinitiator) complex is believed to provide stabilization to growing polymer chains. The most obvious manifestation of this stabilization is a dramatic decrease in the overall rate of polymerization, which is most often attributed to the formation of an equilibrium between a large number of dormant (reversibly terminated) chain ends and a small number of active chains.[16-19]

As a result of the development of living carbocationic polymerization, many new polymers of sophisticated architecture have been produced, such as triblock copolymers,[20-25] star-branched polymers,[26-28] star-branched block copolymers,[29-32] and telechelic polymers.[33-37]

Recently, Kaszas et al. synthesized new TPEs from block copolymers of IB and styrene[20,21] as well as IB and other comonomers such as *p*-chlorostyrene,[22] *p*-methylstyrene,[23] *p*-*tert*-butylstyrene,[24] and indene.[25] The method of synthesis used to produce these block copolymers involved the addition of styrene to living polyisobutylene (PIB) chains produced from a difunctional initiator. The most important aspects of these polymerizations would seem to be the adherence to living polymerization characteristics throughout the block copolymerization and the efficiency of crossover from the PIB block to the end blocks. Kaszas et al.[20] reported the effect of the electron donor *N*,*N*-dimethylacetamide and a proton trap, 2,6-di-*tert*-butylpyridine, on the molecular weight distribution (MWD) and tensile strength of poly(styrene-*b*-isobutylene-*b*-styrene) (PS-PIB-PS) block copolymer samples synthesized using a 1,4-bis(2-methoxy-2-propyl)benzene/$TiCl_4$ initiating system in a 60/40 methylcyclohexane/methyl chloride solvent mixture at -80 °C. This paper reports upon the effect of the time of addition of styrene to PIB chains on block copolymer composition and illustrates the importance of proper timing of the styrene addition for the synthesis of polymers with well-defined structures. The impetus for this study follows from previous observation by ouselves[16,38] and others[39-41] that, for the living polymerization of IB, a deviation from living charactertistics occurs at high monomer conversion.

® Abstract published in *Advance ACS Abstracts*, November 1, 1993.

0024-9297/93/2226-6727$04.00/0

Experimental Section

Materials. Hexane and styrene were dried by distillation from calcium hydride. IB and methyl chloride were dried by passing the gaseous material through a column packed with BaO and $CaCl_2$. Titanium tetrachloride, pyridine, 2,6-di-*tert*-butylpyridine, and anhydrous methanol were used as received.

1,4-Bis(2-chloro-2-propyl)benzene (dicumyl chloride) (DCC) was produced by passing gaseous HCl through a methylene chloride solution of 1,4-bis(2-hydroxy-2-propyl)benzene (dicumyl alcohol) at 0 °C.[16]

Synthesis of Poly(styrene-*b*-isobutylene-*b*-styrene) Block Copolymers. Block copolymerizations were carried out at −80 °C in a drybox using dry 1000-mL three-necked, round-bottomed flasks equipped with a mechanical stirrer. First, living PIB dications were produced by adding 1.50×10^{-2} mol of $TiCl_4$ to a solution of 0.50 mol of IB, 1.53×10^{-3} mol of pyridine, and 7.62×10^{-4} mol of DCC in hexane/methyl chloride (60/40 (v/v)) (total solution volume = 400 mL). After a predetermined reaction time for the IB polymerization, the polystyrene blocks were formed by addition to the living PIB chains of 100 mL of a prechilled 2 M solution of styrene in 60/40 (v/v) hexane/methyl chloride. Polymerization was stopped after 40 min by the addition of 30 mL of prechilled methanol.

Study of the Effect of 2,6-Di-*tert*-butylpyridine on PS–PIB–PS Block Copolymers. Block copolymerizations were carried out at −80 °C in a drybox using dry three-necked, round-bottomed flasks equipped with a mechanical stirrer. Into a 200-mL flask were charged 1.09 mol of IB, 1.66×10^{-3} mol of DCC, 3.34×10^{-3} mol of pyridine, and 1000 mL of a 60/40 (v/v) mixture of hexane/methyl chloride. With stirring, 4.09×10^{-2} mol of $TiCl_4$ was added to the reaction mixture to begin IB polymerization. Two 400-mL portions of the polymerizing reaction mixture were poured individually into two 1000-mL round-bottomed flasks equipped with a mechanical stirrer. To one of the 400-mL portions was added 4.00×10^{-4} mol of 2,6-di-*tert*-butylpyridine at a reaction time of 17 min. After a reaction time of 100 min, 100 mL of a prechilled 2 M solution of styrene in 60/40 (v/v) hexane/methyl chloride was added to each reaction vessel. Each polymerization was stopped after a reaction time of 160 min by the addition of 30 mL of prechilled methanol.

Random Copolymerizations. Random copolymerizations between IB and styrene were carried out at −80 °C in a drybox by adding 3.0×10^{-3} mol of DCC and 6.0×10^{-3} mol of pyridine to a 3000-mL solution of 60/40 (v/v) hexane/methyl chloride and then dividing the solution into seven fractions by transferring the solution to chilled round-bottomed flasks via chilled graduated cylinders. To each individual solution, of a given volume, the appropriate amounts of IB and styrene were charged to give a solution containing a total monomer concentration (IB plus styrene) of 1 M. The polymerizations were started by the addition of neat $TiCl_4$ to the reaction mixture in an amount resulting in a Lewis acid concentration of 2.0×10^{-2} M. After 10 min, the polymerizations were stopped by the addition of 30 mL of prechilled methanol.

Homopolymer Extraction. The extraction of polystyrene from PS–PIB–PS block copolymers was carried out using a method described previously by Kaszas et al.[16] Approximately 10 g of block copolymer sample was placed in a cellulose thimble and extracted with refluxing MEK for 3 days. Extracts were isolated by solvent evaporation, dried under vacuum, weighed, and analyzed by gel permeation chromatography (GPC) and ^1H NMR spectroscopy.

Instrumentation. Molecular weights were determined by GPC using an instrument composed of a Waters high-pressure 510 HPLC pump, three Waters Ultrastyragel columns of pore sizes 500, 10^3, and 10^4 Å, and a Waters differential refractometer, Model 410. A PIB calibration curve was constructed using standards obtained from American Polymer Standards Corp.

^1H NMR spectra were obtained using a 200-MHz Bruker ACE-200 NMR spectrometer.

Domain morphology was analyzed by scanning transmission electron microscopy (STEM) using a JEOL 100CX instrument on microtomed samples of 800–1000-Å thickness stained with RuO_4.

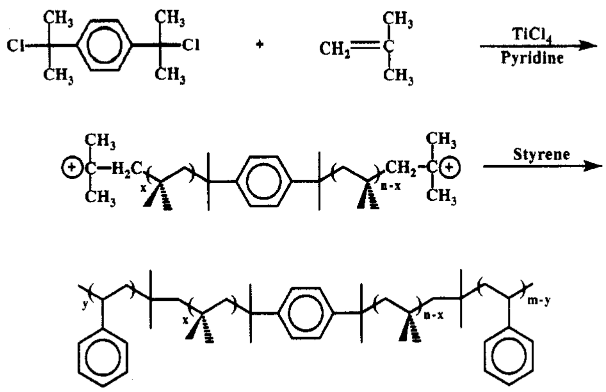

Figure 1. Synthesis of PS–PIB–PS block copolymers.

Results and Discussion

In our laboratory, we have developed and extensively characterized a living IB polymerization process which utilizes a di- or trifunctional cumyl chloride/$TiCl_4$/pyridine initating system.[16] This system has been successfully applied to the synthesis of telechelic ionomers[42] with near-monodisperse MWDs and, more recently, to the synthesis of PS–PIB–PS block copolymers[38] and block copolymer ionomers.[43] As shown in Figure 1, our synthesis of PS–PIB–PS block copolymers consists of the addition of styrene monomer to living PIB chains produced from the DCC/$TiCl_4$ initiating system with pyridine as electron donor. The most important aspects of the polymerization have been found to be the maintenance of living polymerization characteristics throughout the block copolymerization and an efficient crossover from the polyisobutylene block to the styrene blocks.

Characteristic of the living cationic polymerization of IB is a deviation from living characteristics at high monomer conversions.[16,39,40,44] This deviation has been suggested by Faust,[41] for the living polymerization system consisting of a 1,4-bis(2-methoxy-2-propyl)benzene/$TiCl_4$ initiating system in 60/40 (v/v) *n*-hexane/methyl chloride solvent mixture at −80 °C, to be due to proton elimination from growing chain ends. For our living isobutylene polymerization, we also observed a deviation from living characteristics at monomer conversions above ca. 90%.[38,45]

Since active PIB chains tend to undergo proton elimination reactions when monomer becomes depleted, the time of styrene addition is critical to blocking efficiency. A late addition of styrene may result in the formation of block copolymer samples contaminated with AB block architectures and homopolymers. Conversely, an early addition of styrene, i.e., one occurring at a time when a significant fraction of the IB remains, may result in the formation of block copolymers lacking a distinct crossover from the PIB block to PS blocks as a result of random copolymerization between styrene and residual IB.

To illustrate the effect of the time of styrene addition on block copolymer sample composition, an IB polymerization reaction mixture with a difunctional initiator was divided into three equivalent fractions, each of which was injected with a standard charge of $TiCl_4$ and allowed to polymerize to three different degrees of IB conversion, i.e., to three different IB polymerization times, before receiving a charge of styrene monomer. These polymerizations were monitored by removing aliquots from the reaction mixture, quenching the aliquots with methanol, and determining the molecular weight and MWD of polymers formed by GPC.

Late Addition of Styrene. As shown in Figure 2, the addition of styrene at an IB reaction time far exceeding the time necessary for complete monomer consumption,

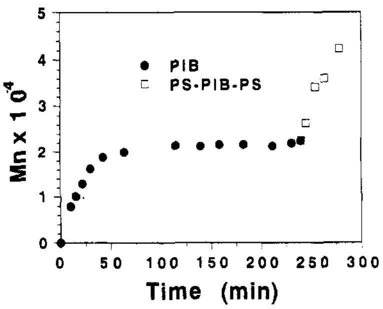

Figure 2. M_n buildup for the block copolymerization of IB and styrene at −80 °C using an excessively long IB reaction time ([IB] = 1.2 M, [DCC] = 1.9×10^{-3} M, [pyridine] = 3.8×10^{-3} M, [$TiCl_4$] = 3.8×10^{-2} M, [styrene] = 0.4 M).

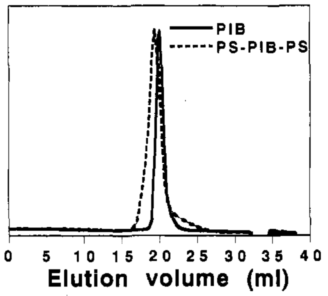

Figure 3. GPC traces of the PIB midblock and PS–PIB–PS block copolymer synthesized at −80 °C using an excessively long IB reaction time ([IB] = 1.2 M, [DCC] = 1.9×10^{-3} M, [pyridine] = 3.8×10^{-3} M, [$TiCl_4$] = 3.8×10^{-2} M, [styrene] = 0.4 M).

indicated by the plateau in the PIB polymerization portion of the curve, effects a further, rapid increase in molecular weight. This result, in conjunction with a shift to smaller elution volumes in the GPC trace of the block copolymer relative to the GPC trace of PIB polymers removed from the reaction just prior to the addition of styrene, as shown in Figure 3, indicates that styrene was added to PIB chains.

The MWDs of the PIB block and the block copolymer were determined from GPC to be 1.13 and 1.29, respectively. As may be seen from Figure 3, the GPC trace of the block copolymer possesses a low molecular weight tail that is not present in the GPC trace of the PIB midblock; this suggests that the block copolymer is contaminated with PS homopolymer produced from chain transfer during the crossover to styrene polymerization, involving protons expelled from PIB chains. To examine this contention, the block copolymer was subjected to solvent extraction with methyl ethyl ketone (MEK), which has been previously shown to be a fairly effective method for removing homo-PS from PS–PIB–PS block copolymer samples.[20,38] Extraction of this sample with MEK resulted in 13 wt % solubilization. The GPC trace of the MEK-soluble fraction, shown in Figure 4, indicates a bimodal MWD, with a high molecular weight peak corresponding to the GPC trace of the MEK-insoluble fraction, indicating that the block copolymer was slightly soluble in refluxing MEK, and a low molecular weight peak, believed to be homo-PS since the ^1H NMR spectrum of the MEK extract showed a much higher relative intensity of aromatic resonance peaks to aliphatic resonance peaks as compared to that for the unextracted material. By comparing the integrated area under the homo-PS peak in Figure 4 to the area under the peak corresponding to PS–PIB–PS block copolymers, the amount of homo-PS was estimated to be 9.2 wt % of the total crude block copolymer sample. Unfortunately, the fraction of homo-PIB or PIB–PS diblock copolymer in the sample could not be determined by selective solvent extraction since, as shown previously,[20,38] extraction with hydrocarbon solvents results in significant solubilization of PS–PIB–PS block copolymers or the formation of an emulsion.

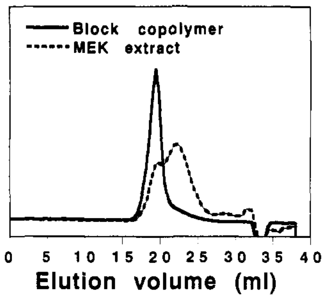

Figure 4. GPC trace of the MEK-soluble fraction of the PS–PIB–PS block copolymer sample synthesized at −80 °C using an excessively long IB reaction time ([IB] = 1.2 M, [DCC] = 1.9×10^{-3} M, [pyridine] = 3.8×10^{-3} M, [$TiCl_4$] = 3.8×10^{-2} M, [styrene] = 0.4 M).

Kaszas et al.[20] have shown that use of a proton trap, namely 2,6-di-*tert*-butylpyridine (DtBuP), in the block copolymerization of IB and styrene is beneficial toward synthesizing block copolymers with little or no homo-PS contamination. The absence of homo-PS in block copolymer samples synthesized in the presence of DtBuP was attributed by Kaszas et al.[20] to the proton-trapping capabilities of DtBuP, which prevents protons, present as an impurity or as the result of alkylative side reactions shown to occur during styrene block formation,[15] from initiating new polymer chains. In addition, Faust et al.[46] have shown that DtBuP favorably influences the cationic homopolymerization of styrene using a 2,4,4-trimethyl-2-pentyl chloride/$TiCl_4$ initiating system. In our view, DtBuP operates to prevent homo-PS formation primarily by scavenging protons which are spontaneously expelled from growing chains during the late stages of formation of the PIB block. To a lesser extent, it may also operate by trapping protons which result from alkylative side reactions during PS block formation and which derive from impurities. With regard to the relative importance of these sources of protons, it should be noted that differences in PS–PIB–PS block copolymer composition resulting from use of different times of styrene addition can only be attributed to β-proton elimination from growing PIB chains. All polymerizations, regardless of the time of styrene addition, were derived from the same isobutylene reaction mixture and were subjected to identical styrene charges; thus, the level of impurities should be the same in all experiments. Furthermore, the influence on PS–PIB–PS composition of alkylative side reactions during PS block growth is considered to be fairly independent of the time of styrene addition using this procedure.

To investigate the effect of DtBuP on our block copolymerization system, a difunctional IB reaction mixture was initiated with $TiCl_4$, and then the living, polymerizing mixture was divided into two portions, one of which received a charge of DtBuP equilvalent to 1×10^{-3} M, while the other did not. After 100 min of reaction time, which corresponds to nearly complete monomer conversion, a charge of styrene was added to each IB reaction mixture, and after a reaction time of 160 min, each reaction was quenched with methanol. Each polymerization was monitored by removing aliquots from the reaction mixture, quenching the aliquots with methanol, and determining the molecular weight and MWD of polymers formed by GPC. Since each block copolymer was derived from the same parent polymerization mixture and the reaction times of PIB block formation and PS

Table I. MWDs of PIB Midblocks and PS–PIB–PS Copolymers Synthesized at -80 °C in the Presence and Absence of 2,6-Di-*tert*-butylpyridine (DtBuP)[a]

	absence of DtBuP	presence of DtBuP (1.0 × 10^{-3} M)
MWD of PIB midblock	1.26	1.16
MWD of PS–PIB–PS	1.36	1.17

[a] [IB] = 1.0 M, [DCC] = 1.5 × 10^{-3} M, [pyridine] = 3.1 × 10^{-3} M, [$TiCl_4$] = 3.7 × 10^{-2} M, [styrene] = 0.4 M.

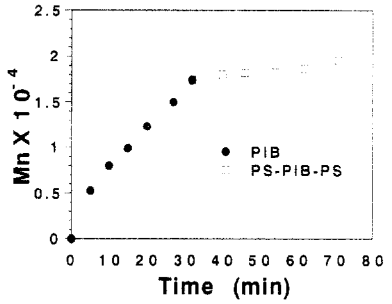

Figure 5. M_n buildup for the block copolymerization of IB and styrene at -80 °C using an exceptionally short IB reaction time ([IB] = 1.2 M, [DCC] = 1.9 × 10^{-3} M, [pyridine] = 3.8 × 10^{-3} M, [$TiCl_4$] = 3.8 × 10^{-2} M, [styrene] = 0.4 M).

block formation were identical, any differences in polymer composition were attributed to the presence of DtBuP. Comparing the MWD of PIB midblocks and PS–PIB–PS block copolymers formed in the absence and presence of DtBuP, it was found that both possessed a narrower MWD when synthesized in the presence of DtBuP, as shown in Table I. From this experiment, it is reasonable to conclude that DtBuP reduces the amount of contamination by homopolymers and diblock polymers and maintains a narrower MWD, principally by preventing initiation by protons which are expelled from the β-position of growing PIB chains and, secondarily, by protons which result from alkylative side reactions during PS block growth or from impurities. However, samples produced using DtBuP will still be contaminated with PIB homopolymers and diblocks and possibly branched polymers since, for every proton that is expelled from a PIB chain, one of the following pair of isomeric unsaturated end groups is formed, $\sim\sim\sim PIB\sim\sim\sim CH_2C(CH_3){=}CH_2$ or $\sim\sim\sim PIB\sim\sim\sim C(CH_3)_2CH{=}C(CH_3)_2$, and branched polymers could conceivably be formed from the addition of one of these unsaturated end groups to another propagating chain or by Freidel–Crafts alkylation during PS polymerization.

Early Addition of Styrene. As indicated in Figure 5, addition of styrene to living PIB chains under conditions of intermediate IB conversion results in a very slow further buildup in molecular weight. Since a considerable amount of IB was still present at the time of the styrene addition, it was unclear whether the increase in molecular weight after the addition of styrene was the result of the incorporation of styrene into the polymer or just the further conversion of isobutylene or a random copolymerization of the two monomers. Evidence for the incorporation of styrene into the polymer was provided by first extracting the crude product with MEK, to remove any homo-PS that may have been present in the sample, and then analyzing by ^1H NMR the vacuum-dried MEK-insoluble fraction. The amount of styrene incorporated into the polymer was determined to be 10 mol % by comparing the area under the aromatic resonance peaks in the ^1H NMR spectrum to the area under the aliphatic resonance peaks. In addition, the presence of styrene in the polymer was indicated by inspection of the produced polymer, i.e., the polymer exhibited elastic behavior.

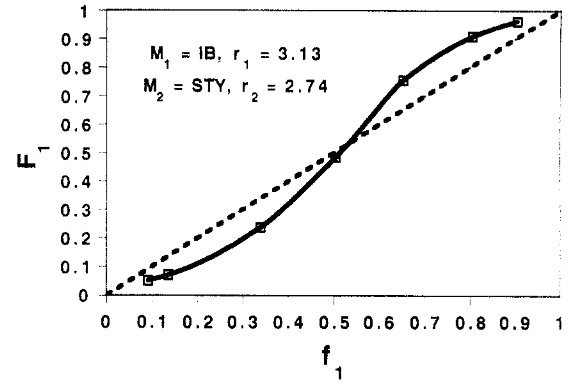

Figure 6. Dependence of IB–styrene copolymer composition on monomer feed composition.

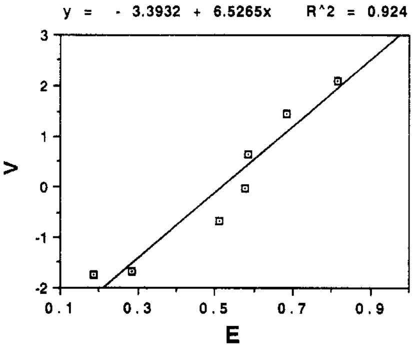

Figure 7. Kelen–Tudos[47] plot for the determination of reactivity ratios for IB and styrene.

The slow buildup in molecular weight after the addition of styrene is believed to be due to the occurrence of a simultaneous copolymerization between styrene and unreacted isobutylene. To test this hypothesis, several simultaneous copolymerizations of styrene and isobutylene were conducted under conditions designed to simulate those which prevailed during block copolymer synthesis with an early addition of styrene. It was observed that the rate of copolymerization was considerably slower than the rate of IB homopolymerization and, importantly, slower also than the rate of styrene block formation when either a proper or late time of styrene addition was employed. The product copolymers, obtained at monomer conversions below 10%, were analyzed using GPC and ^1H NMR. For all copolymerizations conducted, monomodal MWDs were obtained for the product polymer samples, indicating conventional copolymerization occurred, without the interference of simultaneous homopolymerization of either monomer. This conclusion was further substantiated by the fact that the polymers produced were transparent and that their physical properties changed continuously along the spectrum of possible feed compositions, from tacky and rubbery at low styrene feed compositions, to hard and tough at a 1:1 feed ratio, to brittle at high styrene feed compositions. Copolymer compositions were determined using ^1H NMR in the same manner that block copolymer compositions were determined. Figure 6 displays the dependence of copolymer composition on monomer feed composition. Using the method of Kelen and Tudos,[47] reactivity ratios for the two monomers under the polymerization conditions employed were calculated. Figure 7 displays the Kelen–Tudos plot, from which the following reactivity ratios were extracted: $r_{IB} = 3.1$, $r_{STY} = 2.7$. These results are very similar to the results of Imanishi et al.,[48] who in the course of a study of the dependence on solvent polarity of the reactivity ratios of IB and styrene using $TiCl_4$ at -78 °C calculated reactivity ratios of $r_{IB} = 3.25$ and $r_{STY} = 2.75$ in a solvent

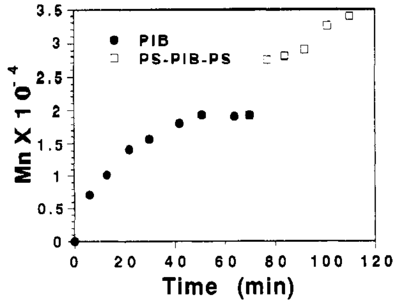

Figure 8. M_n buildup for the block copolymerization of IB and styrene at −80 °C using an IB reaction time corresponding to nearly complete IB conversion ([IB] = 1.2 M, [DCC] = 1.9×10^{-3} M, [pyridine] = 3.8×10^{-3} M, [$TiCl_4$] = 3.8×10^{-2} M, [styrene] = 0.4 M).

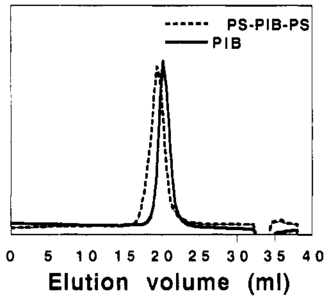

Figure 9. GPC traces of the PIB midblock and PS–PIB–PS block copolymer synthesized at −80 °C using an IB reaction time corresponding to nearly complete IB conversion ([IB] = 1.2 M, [DCC] = 1.9×10^{-3} M, [pyridine] = 3.8×10^{-3} M, [$TiCl_4$] = 3.8×10^{-2} M, [styrene] = 0.4 M).

system consisting of 50/50 (v/v) hexane/methylene chloride. This result of Imanishi et al.,[48] which agrees so closely with the reactivity ratios we have calculated, indicates that the presence of pyridine has essentially no effect on the crossover from an isobutylene cation to a styrene cation and vice versa. The curvature displayed in Figure 7 was also observed by Kelen and Tudos[49] upon examination of the copolymerization data of Imanishi et al.[48] According to Kelen and Tudos,[49] this curvature indicates that the conventional copolymerization equation, on which the Kelen and Tudos reactivity ratio determination method is based, may not be adequate for describing this copolymerization system, and as a result the reactivity ratios calculated may be somewhat misleading.

Demonstration of the simultaneous copolymerization of styrene and isobutylene using the conditions utilized for block copolymerization suggests that an early addition of styrene leads to a "tapered" triblock copolymer possessing chain sections characterized by a gradual crossover from one to the other homopolymer. In addition, the fact that both reactivity ratios were determined to be greater than one indicates that each monomer has a predisposition to react with itself, forming long blocks of each monomer within the crossover section.

Proper Time for Styrene Addition. When styrene was added to the IB reaction mixture at a time corresponding to the onset of the PIB molecular weight plateau, as shown in Figure 8, an abrupt increase in molecular weight occurred similar to the case when styrene was added very late in the IB polymerization (Figure 2). The addition of styrene to PIB chains was illustrated by the shift of the GPC trace of PIB to lower elution volumes upon the addition of styrene, as shown in Figure 9. The MWDs of the PIB block and the block copolymer were determined to be 1.19 and 1.25, respectively. The presence of homo-PS in the sample was investigated by extraction with MEK. A large fraction, 31 wt %, of the sample was found to be MEK soluble. However, comparison of the GPC trace of the MEK-soluble fraction to the MEK-insoluble fraction, as shown in Figure 10, indicated that the two fractions were the same except for a slight low molecular weight tail in the GPC of the MEK-soluble fraction. The high solubility in MEK of this particular block copolymer did not allow for an accurate determination of the amount of contamination by homo-PS; however, comparing the magnitude of the low molecular weight tail in the GPC trace for the block copolymer in Figure 9 to that of the block copolymer synthesized using a long PIB reaction time (Figure 3) indicates that the amount of contamination of homo-PS is considerably less for the block copolymer illustrated in Figure 9.

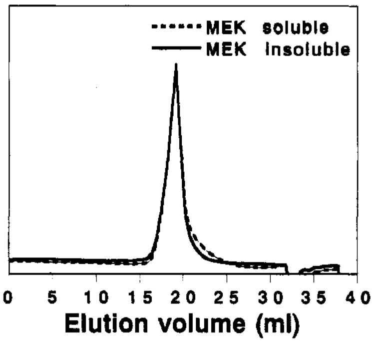

Figure 10. GPC traces of the MEK-soluble and -insoluble fractions of the PS–PIB–PS block copolymer synthesized at −80 °C using an IB reaction time corresponding to nearly complete IB conversion ([IB] = 1.2 M, [DCC] = 1.9×10^{-3} M, [pyridine] = 3.8×10^{-3} M, [$TiCl_4$] = 3.8×10^{-2} M, [styrene] = 0.4 M).

From these results, it is clear that the time of styrene addition is critical to block copolymer sample composition. Excessive aging of PIB carbocations, after depletion of IB, leads to the production of a very significant concentration of homo-PS due to the presence of protons which are generated primarily from β-proton expulsion reactions which become prevalent at high IB conversions. Conversely, premature addition of styrene, at low to medium conversion of IB, leads to troublesome retardation of polymerization due to random copolymerization of unreacted IB and styrene and the formation of tapered end blocks. In regard to these findings, it is apparent that the time of addition of styrene to the IB polymerization mixture must be precisely controlled to ensure the synthesis of block copolymers having well-defined ABA block architectures. Styrene must be added to the IB reaction mixture just prior to the time of the onset of deviation from living characteristics, preventing the formation of homopolymers and diblock copolymers and allowing for a distinct crossover from the PIB midblock to the PS end blocks.

To illustrate the synthetic utility of the DCC/$TiCl_4$/pyridine polymerization system and the information obtained with regard to the effects of the time of styrene addition and the presence of the proton trap, DtBuP, on PS–PIB–PS block copolymer composition, some previously reported results may be examined.[38] The morphology of an ABA block copolymer is an excellent indicator of the uniformity of the molecular architecture since the production of a highly ordered dual-phase morphology will only be possible with materials containing polymers with uniform ABA block architecture. Figure 11 is a transmission electron micrograph of a PS–PIB–PS block copolymer synthesized using the polymerization system described in this paper, in conjunction with the proton trap DtBuP, and an IB reaction time corresponding to

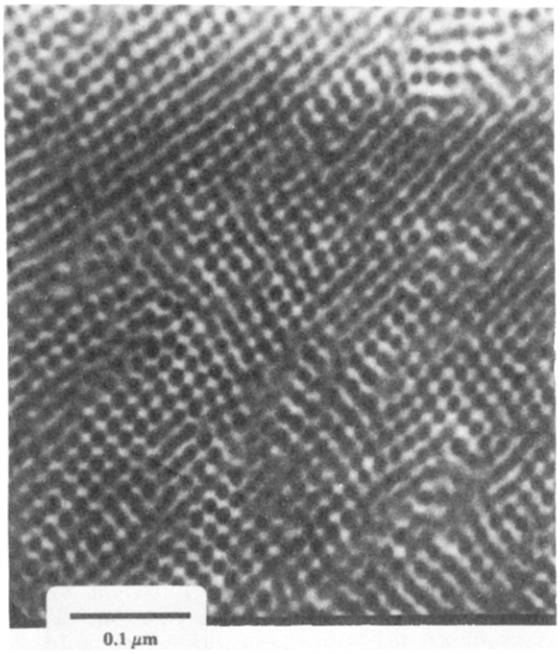

Figure 11. Transmission electron micrograph of a PS–PIB–PS block copolymer synthesized at −80 °C using an IB reaction time corresponding to close to complete IB conversion.

91% conversion, based on the molecular weight of the PIB midblock and the assumption of 100% initiation efficiency. It can be clearly seen that this block copolymer sample possesses a heterogeneous morphology consisting of cylindrical polystyrene domains (dark) dispersed within a matrix of PIB (light). The cylindrical PS domains are aligned with their long axes parallel to one another and, when viewed in the direction of their long dimension, can be seen to form a hexagonal array, as shown in Figure 11. The high degree of order exhibited in the morphology of this material attests to the utility of this polymerization system when used in conjunction with a carefully timed styrene addition for the synthesis of very well-defined block copolymers.

Conclusions

It was found that a very important aspect of the synthesis of PS–PIB–PS block copolymers using a DCC/$TiCl_4$/pyridine initiating system is the time of addition of styrene to PIB cations. The addition of styrene at an IB reaction time significantly exceeding the time necessary for complete IB consumption results in contamination of the material with a substantial amount of homo-PS. The presence of homo-PS resulting from use of an unnecessarily long IB reaction time is believed to be due to a buildup of protonic acids in the reaction mixture resulting from the elimination, from PIB chains at high IB conversions, of β-protons which initiate styrene homopolymerization upon the addition of styrene to the reaction mixture. The buildup of protons at high isobutylene conversion, which corresponds to the loss of living character late in the polymerization,[37–41] is consistent with the known kinetics of isobutylene polymerization. β-Proton expulsion is a unimolecular reaction. Its rate, although certainly depressed by the presence of pyridine, is nonetheless finite and constant with monomer conversion, since the chain end concentration remains more or less constant. On the other hand, the rate of propagation, which is bimolecular and first order in monomer, decays exponentially with time, and thus β-proton expulsion only begins to compete significantly with propagation very late in the polymerization. This hypothesis is further supported by the fact that addition of the proton trap DtBuP resulted in a narrowing of product polymer MWD. Conversely, the addition of styrene to PIB chains formed under conditions of intermediate IB conversion results in a significantly retarded rate of further polymerization and leads to the formation of outer blocks which taper only slowly toward homopolystyrene due to copolymerization between styrene and unreacted IB. Simultaneous copolymerizations conducted under conditions similar to those utilized for block copolymer sythesis yielded reactivity ratios of $r_{IB} = 3.1$ and $r_{STY} = 2.7$, indicating that the tapered sections of the copolymer contain long blocks of each monomer.

Therefore, the optimum conditions for producing block copolymers which possess a sharp crossover from IB to styrene and which contain a minimum amount of homopolymer contamination are realized when the addition of styrene is timed to occur at the highest IB conversion which is still consistent with the preservation of the living character of the polyisobutylene dications. In practice, this occurs at ca. 85–90% IB conversion for the DCC/$TiCl_4$/pyridine system in 60/40 (v/v) hexane/methyl chloride, and even slightly higher conversions may be tolerated in the presence of a proton trap such as 2,6-di-*tert*-butylpyridine.

Acknowledgement is made to Shell Development Co. for support of this research. The authors would also like to acknowledge GE Plastics for the graduate fellowship awarded to B.J.C.

References and Notes

(1) Legge, N. R.; Davison, S.; De La Mare, H. E.; Holden, G.; Martin, M. K. *Applied Polymer Science*; Tess, R. W., Poehlin, G. W., Eds.; American Chemical Society: Washington, DC, 1985.

(2) Milkovich, R.; Levy, M.; Szwarc, M. *J. Am. Chem. Soc.* **1956**, *78*, 778.

(3) Szwarc, M. *Nature* **1956**, *178*, 1168.

(4) Eschwey, H.; Burchard, W. *Polymer* **1975**, *16*, 180.

(5) Bi, L.; Fetters, L.; Morton, M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1974**, *15*, 157.

(6) Weiss, R. A.; Sen, A.; Pottick, L. A.; Willis, C. L. *Polymer* **1991**, *32*, 2785.

(7) Gauthier, S.; Eisenberg, A. *Macromolecules* **1987**, *20*, 760.

(8) Storey, R. F.; George, S. E.; Nelson, M. E. *Macromolecules* **1991**, *24*, 2920.

(9) Broze, G.; Jerome, R.; Teyssie, Ph. *Macromolecules* **1982**, *15*, 920.

(10) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 265.

(11) Sawamoto, M. *Prog. Polym. Sci.* **1991**, *16*, 111.

(12) Kojima, K.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1990**, *23*, 948.

(13) Sawamoto, M.; Fujimori, J.; Higashimura, T. *Macromolecules* **1987**, *20*, 916.

(14) Kaszas, G.; Puskas, J. E.; Chen, C. C.; Kennedy, J. P. *Polym. Bull.* **1988**, *20*, 413.

(15) Kaszas, G.; Puskas, J. E.; Kennedy, J. P.; Hager, W. G. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 421.

(16) Storey, R. F.; Lee, Y. *Pure Appl. Chem.* **1992**, *A29* (11), 1017.

(17) Kaszas, G.; Puskas, J. E.; Chen, C. C.; Kennedy, J. P. *Macromolecules* **1990**, *23*, 3909.

(18) Ivan, B.; Kennedy, J. P. *Macromolecules* **1990**, *23*, 2880.

(19) Aoshima, S.; Higashimura, T. *Macromolecules* **1989**, *22*, 1009.

(20) Kaszas, G.; Puskas, J. E.; Kennedy, J. P.; Hager, W. G. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 427.

(21) Puskas, J. E.; Kaszas, G.; Kennedy, J. P.; Hager, W. G. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 41.

(22) Kennedy, J. P.; Kurian, J. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 3725.

(23) Tsunogae, Y.; Kennedy, J. P. *Polym. Bull.* **1992**, *27*, 631.

(24) Kennedy, J. P.; Meguyira, N.; Keszler, B. *Macromolecules* **1991**, *24*, 6572.

(25) Kennedy, J. P.; Midha, S.; Tsunogae, Y. *Macromolecules* **1993**, *26*, 429.

(26) Huang, K. J.; Zsuga, M.; Kennedy, J. P. *Polym. Bull.* **1988**, *19*, 43.

(27) Ivan, B.; Kennedy, J. P. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 89.

(28) Shohi, H.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1991**, *24*, 4926.

(29) Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1991**, *24*, 2309.

(30) Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1991**, *24*, 5741.

(31) Kanaoka, S.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1992**, *25*, 6414.

(32) Fukui, H.; Sawamoto, M.; Higashimura, T. *J. Polym. Sci., Polym. Chem. Ed.* **1993**, *31*, 1531.

(33) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1985**, *18*, 123.

(34) Wang, B.; Mishra, M.; Kennedy, J. P. *Polym. Bull.* **1987**, *17*, 205.

(35) Wang, B.; Mishra, M. K.; Kennedy, J. P. *Polym. Bull.* **1987**, *17*, 213.

(36) Sawamoto, M.; Enoki, T.; Higashimura, T. *Macromolecules* **1987**, *20*, 1.

(37) Lubnin, A. V.; Kennedy, J. P.; Goodall, B. L. *Polym. Bull.* **1993**, *30*, 19.

(38) Storey, R. F.; Chisholm, B. J.; Lee, Y. *Polymer*, in press.

(39) Wang, B.; Mishra, M.; Kennedy, J. P. *Polym. Bull.* **1987**, *17*, 205.

(40) Kaszas, G.; Puskas, J. E.; Kennedy, J. P. *Polym. Bull.* **1987**, *18*, 123.

(41) Gyor, M.; Wang, H. C.; Faust, R. *Pure Appl. Chem.* **1992**, *A29*, 639.

(42) Storey, R. F.; Lee, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1991**, *29*, 317.

(43) Storey, R. F.; Chisholm, B. J.; Lee, Y. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33*, 184.

(44) Kaszas, G.; Puskas, J.; Kennedy, J. P. *Makromol. Chem., Macromol. Symp.* **1988**, *13/14*, 473.

(45) Storey, R. F.; Chisholm, B. J.; Mowbray, E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34*, 568.

(46) Fodor, Z.; Gyor, M.; Wang, H.-C.; Faust, R. *Pure Appl. Chem.* **1993**, *A30* (5), 349.

(47) Kelen, T.; Tudos, F. *J. Macromol. Sci., Chem.* **1975**, *A29* (1), 1.

(48) Imanishi, Y.; Higashimura, T.; Okamura, S. *J. Polym. Sci., Polym. Chem. Ed.* **1965**, *3*, 2455.

(49) Kelen, T.; Tudos, F.; Turcsanyi, B. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 3047.