Synthesis and Characterization of Star-Branched Polyisobutylene with SIpS Triblock Copolymer Core

Yibo Wu,[1,2] Wenli Guo,[1] Shuxin Li,[1] Huiqing Gong[2]

[1]*Department of Material Science and Engineering, Beijing Institute of Petrochemical Technology, Beijing 102617, China*
[2]*College of Material Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China*

ABSTRACT: Well-defined polystyrene-*b*-polyisoprene-*b*-polystyrene (SIpS) triblock copolymers with different microstructures were synthesized by living anionic polymerization. The synthesis of star-branched polyisobutylene (PIB) was accomplished by the cationic polymerization in 2-chloro-2,4,4-trimethylpentane/titanium tetrachloride/SIpS triblock copolymer/2,6-di-*tert*-butylpyridine initiating system. The double bonds in SIpS triblock copolymer were activated as starting points for isobutylene polymerization. The formation of star-branched architecture was demonstrated by size-exclusion chromatography with quadruple detection: refractive index, multiangle laser light scattering, viscometric, and ultraviolet detectors. SIpS triblock copolymer with high 3,4-PIp content is more reactive than that with high 1,4-PIp content in cationic initiating stage. The yields of star-branched PIB were remarkably dependent on the reaction time of TMP[+] with SIpS. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3294–3299, 2009

Key words: cationic polymerization; polystyrene-*b*-polyisoprene-*b*-polystyrene; star-branched polymer; polyisobutylene

INTRODUCTION

Star-shaped polymers have specific three-dimensional structures with a large number of arm chains radiating from a central core. These polymers have some special properties, such as their low viscosity and the large number of chain ends in a macromolecule where functional groups can be placed. The possible applications of star-shaped structures have been widely investigated in biomaterials,[1–3] catalysts,[4] and electrooptical materials.[5]

Because of the fact that polyisobutylene (PIB) is a fully saturated, chemical stable polymer with a variety and useful properties, several attempts have been reported on the synthesis of star-shaped and arborescent PIBs so far.[6–20] Star PIBs can be prepared by "arm first" strategy, where the monofunctional living PIB chains react with bifunctional monomers such as divinyl- or diisopropylbenzene to form the cross-linked core.[11–14] However, this method will lead to "ill-defined" cores and undesirable gel, and the reaction time will be very long, usually more than 10 h.

Although the "core first" strategy by using multifunctional initiators for the polymerization of isobutylene (IB) leads to star PIBs with well-known number of arms,[6–10,16,18–20] the lack of commercial initiators for IB polymerization requires laborious and time-consuming initiator syntheses. Some commercial polydiene, such as polyisoprene (PIp) can also be used to prepare the star-branched PIB by "core first" strategy. The unsaturated groups in PIp can be activated as initiating sites; IB can be grafted from backbone polymers to form the star-branched structure. From the industrial point of view, this process for the preparation of star-branched PIB is economical and practical. Furthermore, the polystyrene blocks in polystyrene-*b*-polyisoprene copolymers can improve the solubility of PIp blocks in carbocationic polymerization system. So far as we know, seldom papers have reported the cationic grafting of IB from polystyrene-*b*-polyisoprene copolymer.[21]

This article concerns our studies focusing on the effect of the reaction conditions and microstructures for SIpS triblock copolymers on intrinsic viscosity, molecular weight, molecular weight distribution, and branching indices of star-branched PIB.

EXPERIMENTAL

Materials

2-Chloro-2,4,4-trimethylpentane (TMPCl) was synthesized by reacting 2,4,4-trimethyl-1-pentene with

gaseous HCl using the method of Storey and Lee.[22] IB and methyl chloride (MeCl) were dried in the gaseous state by passing them through in-line gas-purifier columns packed with $CaSO_4$/Drierite, and they were condensed in the cold bath of a glovebox before polymerization. Styrene (St) (Beijing Chemical Co., 99.9%) and isoprene (Ip) (Beijing Yansan Petroleum Chemical Corp., 99.9%) were distilled to remove impurities. Cyclohexane and tetrahydrofuran (THF) were purified as described in the literature.[23] Titanium tetrachloride ($TiCl_4$) (Beijing Chemical Co., 99.9%), 2,6-di-*tert*-butylpyridine (DtBP) (Alfa, 97%), s-butyllithium (s-BuLi) (Alfa, 2.9 mol/L solution in heptane), and anhydrous methanol (Beijing Chemical Co., 99.8%) were used as received.

Polymerizations

Anionic polymerizations were carried out under high-vacuum condition in sealed glass reactors with break seals. Reactors were always prewashed with the initiator solutions after being sealed off from a vacuum line. Triblock copolymers were prepared by sequential addition of St (4.2 mL), Ip (1.4 mL), and St (4.2 mL) using s-BuLi (0.1 mL, 2.9 mol/L in heptane) as initiator at 30°C in 40 mL cyclohexane. THF was used as polar addition to control the microstructure of PIp. The polymerizations were terminated by adding a small amount of methanol. The polymers were coagulated in methanol before drying 24 h at 45°C in vacuum.

All carbocationic polymerizations were carried out in a stainless glove box under a dry nitrogen atmosphere at −80°C. The moisture (<5 ppm) and oxygen content (<10 ppm) were monitored. A representative experiment was carried out as follows: SIpS triblock copolymers (0.05 g), DtBP (1 mL, 0.04 mol/L in cyclohexane), and TMPCl (1 mL, 0.04 mol/L in cyclohexane) were mixed in 20 mL mixture solvent (cyclohexane/CH_3Cl, 50/50 v/v) at −80°C, followed by the addition of $TiCl_4$ (1 mL, 0.72 mol/L in cyclohexane) to generate the carbocationic centers. IB (1.6 mL) was added under vigorous stirring, and the reaction was terminated by prechilled methanol. The polymers were extracted with butanone and then dried at 45°C in vacuum for 24 h.

Characterization

Weight-average molecular weight (M_w), intrinsic viscosity($[\eta]$), Mark-Houwink (M-H) constants (a and K) and radius of gyration (R_g) were measured at room temperature with a Waters HPLC system equipped with a model 510 HPLC pump, a model 410 differential refractometer (Wyatt Technology, Optilab REX), a model 2478 tunable ultraviolet (UV) detector (Waters), an on-line multiangle laser light
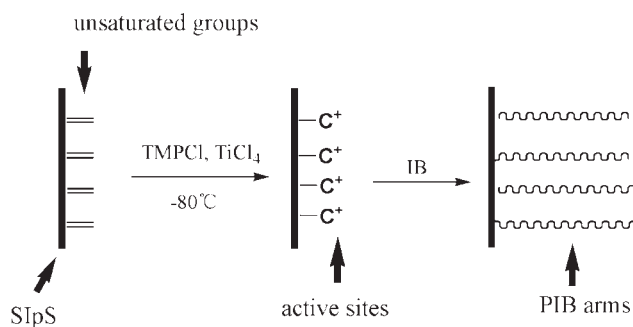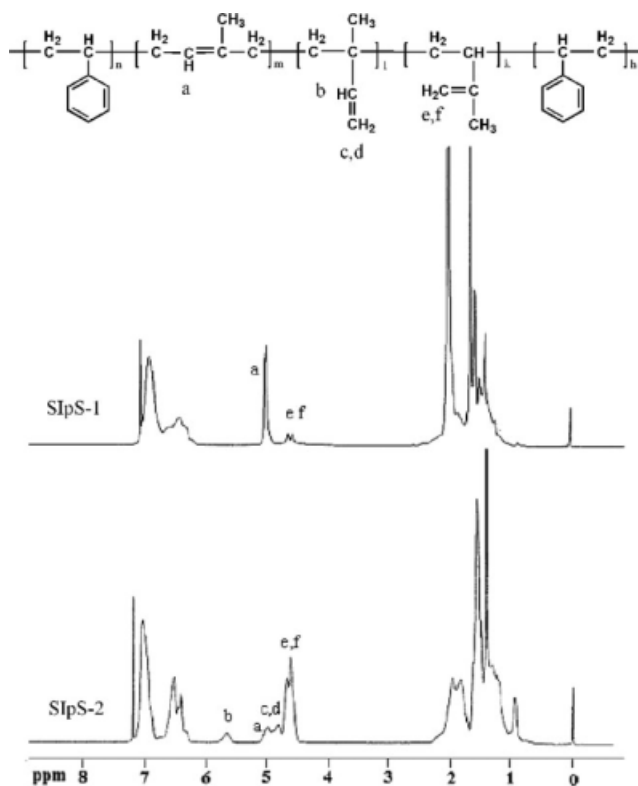
scattering (MALLS) detector (laser wavelength = 690 nm), (MiniDawn,Wyatt Technology), a viscometer detector (Wyatt Technology, ViscoStar), and four Ultrastyragel gel permeation chromatography(GPC) columns connected in the following series: 10^3, 10^4, 10^5, and 100 Å. THF was used as a carrier solvent with a flow rate of 1 mL/min. ^{1}H-NMR spectroscopy for structural analysis was carried out on a Bruker 400 MHz spectrometer using $CDCl_3$ as a solvent.

RESULTS AND DISCUSSION

Scheme 1 outlines the overall synthetic strategy for the preparation of star-branched PIB. The TMP$^+$ cations (obtained from ionization of TMPCl with $TiCl_4$) attack unsaturated groups in SIpS triblock copolymers to form macromolecular cations. Then, the resulting macromolecular cations initiate the polymerization of IB. The method of this preparation is similar to the "grafting from" techniques.
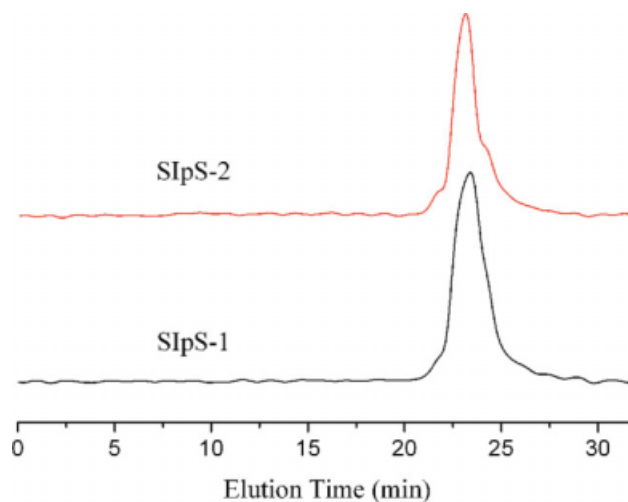
For SIpS triblock copolymers, one needs to carefully consider the type of the unsaturated groups that may influence grafting reactions. The possible segment microstructures for PIp are 1,4-, 1,2-, and 3,4-microstructures. The SIpS-1 triblock copolymer with high 1,4-PIp content was synthesized in a nonpolar synthesis procedure. While SIpS-2 triblock copolymer with high 3,4-PIp content was obtained in a cyclohexane/THF mixture solvent. ^{1}H-NMR spectrum of SIpS-1 and SIpS-2 triblock copolymers together with peaks assignment are shown in Figure 1. The microstructures and PIp content were analyzed by ^{1}H-NMR spectroscopy. SEC(RI) traces of these two triblock copolymers have the same elution time (in Fig. 2). As illustrated in Table I, two of these triblock copolymers have almost the same molar masses and PIp content but different microstructures.

A series of experiments have been carried out to get an insight into the effect of microstructures of SIpS triblock copolymers on grafting reactions while other conditions were kept the same. The linear PIB was also prepared with M_w =30,800 g/mol and

Figure 1 ^{1}H-NMR spectra of SIpS-1 and SIpS-2 triblock copolymers.

Figure 2 The SEC(RI) traces of SIpS-1 and SIpS-2 triblock copolymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

narrow MWD ($M_w/M_n = 1.08$) except for the addition of SIpS triblock copolymer [Fig. 3(a)]. As Figure 3(c) shows the addition of SIpS-2 triblock copolymer leads to an additional peak 2 in high molecular weight region, which indicates the formation of star-branched PIB (M_w: 2.06×10^5 g/mol), along with the linear polymer (peak 1, M_w: 2.97×10^4 g/mol). Moreover, the refractive index (RI), MALLS, and viscometric (Vis) traces of this resulting polymer all show bimodal molecular weight distribution (in Fig. 4). It is considered that before IB consumption, a part of TMP[+] cations do not react with SIpS triblock copolymer, which leads to the formation of linear PIB. However, there is no obvious evidence for the formation of star-branched PIB in Figure 3(b) by the addition of SIpS-1 triblock copolymers. These data demonstrated that SIpS-2 with high 3,4-PIp content

is more reactive than SIpS-1 with high 1,4-PIp content in cationic initiating stage. The result can be accounted for by the fact that the structure of 3,4-PIp is similar to IB structure and electron donating effect of methyl on double bond as well as a larger number of pendant vinyl groups may facilitate TMP[+] cations attaching to SIpS triblock copolymer. SEC(UV) trace of the resulting polymer obtained by addition SIpS-2 is also shown in Figure 4. Only the high molecular weight fraction has a strong UV signal, whereas the low molecular weight fraction shows no UV signal, because PIB component is transparent to UV. These data directly confirm that SIpS-2 triblock copolymer incorporation into the star-branched PIB.

In addition to the microstructures of SIpS triblock copolymer, the reaction time of TMP[+] with SIpS ($t_{actived}$) will influence the structure of star-branched polymers. As a result of above investigations, we decided to employ the SIpS-2 triblock copolymer in a series of copolymer syntheses. The SEC(RI) traces of the resultant polymers obtained at different $t_{actived}$ are summarized in Figure 5. It is obvious that the proportions of signals corresponding to linear and star-branched PIB change with a progress of the IB polymerization. The plot of weight-average
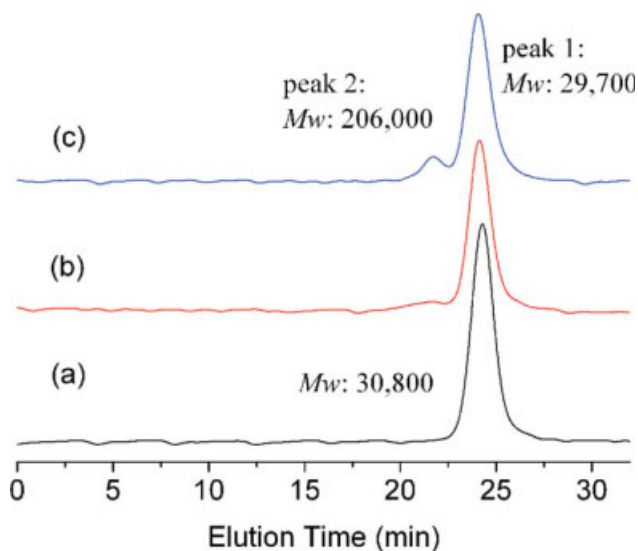
TABLE I
The Data for SIpS Triblock Copolymers with Different Microstructures

SIpS	M_n (10^{-4})	M_w/M_n	IP (wt %)[a]	1,4 (wt %)[a]	3,4 (wt %)[a]	1,2 (wt %)[a]
SIpS-1[b]	5.57	1.10	12.8	87.0	13.0	0
SIpS-2[c]	5.45	1.15	12.3	14.0	72.2	13.8

[a] Calculated from ^{1}H-NMR.
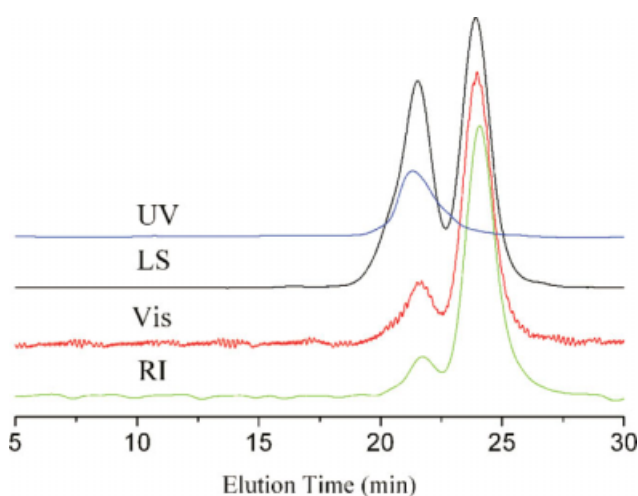[b] Reactions were carried out in cyclohexane at 30°C.
[c] Reactions were carried out in THF/cyclohexane mixtures at 30°C, [THF]/[s-BuLi] = 45.
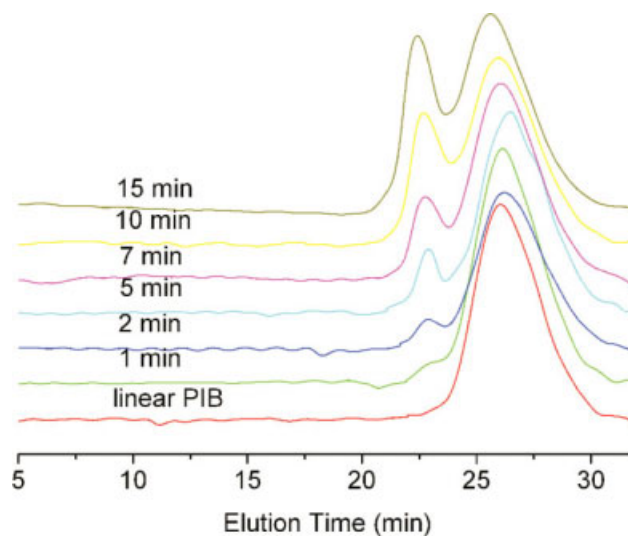
Figure 3 The SEC(RI) traces of linear PIB (a), resulting polymers (b, c) obtained by using SIpS-1 and SIpS-2 triblock copolymer as multifunctional liking agents, respectively. Conditions: [TMPCl] = 0.002M, [TiCl$_4$] = 0.036M, [DtBP] = 0.002M, [IB] = 1.0M, cyclohexane/MeCl = 50/50 (v/v), T = −80°C, W_{SIpS} = 0.05 g, $t_{actived}$ = 2 min, IB polymerization time = 60 min. Linear PIB polymerization condition is same as above except for addition of SIpS triblock copolymer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

molecular weight (M_w) of the resultant polymers versus $t_{actived}$ is displayed in Figure 6. As the figure shown, the molecular weight rapidly increases in the first 15 min, and then becomes nearly constant in about 30 min. The maximum value of molecular weight is due to the practical number of cationically reactive unsaturated groups in SIpS-2 triblock

Figure 5 The SEC(RI) traces of the linear PIB and the resultant polymers obtained at different $t_{actived}$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

copolymers reach to maximum. The average molecular weight (M_w) of the final product with bimodal molecular weight distribution is 56,800 and M_w/M_n = 3.38 after 30 min. Comparing the high and low molecular weight fraction, M_w value of star-branched PIB is about 10 times larger than that of linear PIB. This indicates the formation of PIB stars with about 10 arms in average. The relative area (%) of high molecular weight fraction in the RI trace is regarded as the yield of star-branched PIB. Although the yield of star-branched polymers was not very high (maximum for 45%), only 15% star-branched
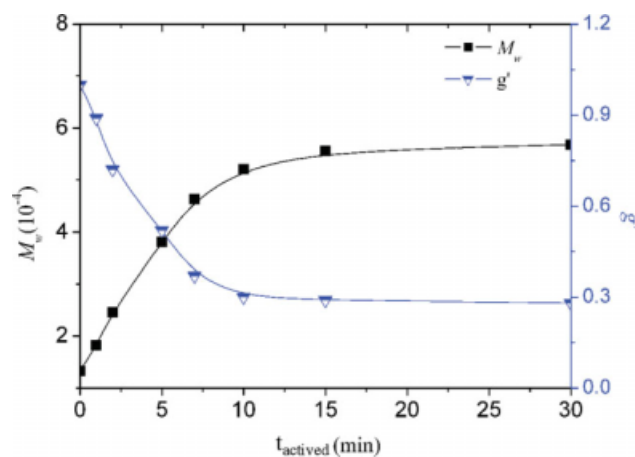

Figure 4 The SEC traces (results of LS, RI, Vis, and UV detector responses) of resulting polymer obtained by the addition of SIpS-2 triblock copolymer. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

Figure 6 The effect of the $t_{actived}$ on M_w and branching index (g'). Reaction conditions: [TMPCl] = 0.006M, [TiCl$_4$] = 0.108M, [DtBP] = 0.006M, [IB] = 1.0M, cyclohexane/MeCl = 50/50 (v/v), T = −80°C, W_{SIpS-2} = 0.05 g, IB polymerization time = 60 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

polymers in resulting polymers can considerably improve processing characteristics, such as relaxation rate.[24]

Branching index g', which is useful to predict extent of branching for unknown polymers, can be determined by comparing the intrinsic viscosity ([η]) for branched and linear polymers of with identical molar masses [eq. (1)].[25,26] It is well-known that the star-branched polymers have a lower [η] compared with a linear analog of identical molar masses. The lower the g', the more branched the polymers. The [η]s for the resultant polymers obtained at different $t_{actived}$ were evaluated by online Vis detector of SEC. According to the M-H equation ([η] = kM^a), the [η] is a function of molecular weight. The M-H constants (α = 0.628 and K = 3.16 × 10^{-2} mL/g) of linear PIB (M_w = 1,15,000g/mol, M_w/M_n = 1.12) analyzed by the SEC and calculated by ASTRA software are shown in Figure 7. Thus, the [η] of the linear PIB analogs can be calculated on the basis of this M-H equation. Branching indices g' for the resultant polymers obtained at different $t_{actived}$ are also shown in Figure 6. It can be seen that the value of g' decreases as increase the $t_{actived}$. It is evident that increasing the $t_{actived}$ facilitates the grafting reactions.

$$\langle g' \rangle = [\eta]_{br}/[\eta]_{lin} \quad (M = \text{const}) \tag{1}$$

The formation of star-branched structures by grafting from SIpS-2 backbone is also supported by R_g obtained by the MALLS detector of SEC as a function of molecular weight[27,28] (Fig. 8). As displayed in the figure, the R_g of the polymer formed by addition of SIpS-2 triblock copolymer is significantly lower at higher molecular weights than that of linear PIB. It is well known that the size of branched polymers is also smaller than that of linear chains with the same molecular weights. In other words, the lower R_g found for the PIB clearly indicates the formation of
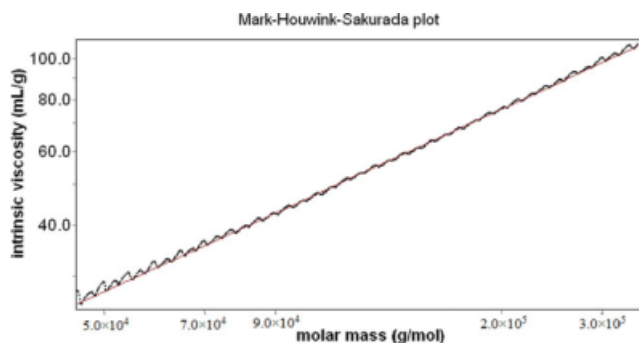
Figure 7 Mark-Houwink plot of linear PIB based on SEC software (ASTRA) analysis. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
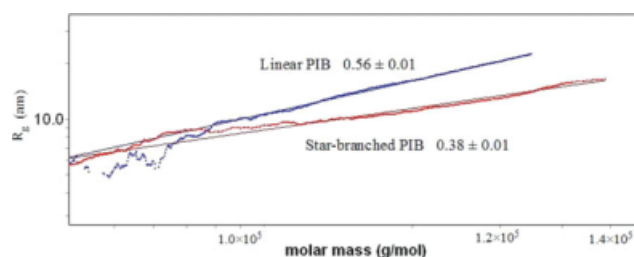
Figure 8 Plots of radius of gyration versus molar mass for star-branched PIB and linear PIB based on SEC analysis. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

branched structures. Another indication of star-branched polymer formation is the lower slope of the logarithmic R_g versus molecular weight curve. The typical values of the slope for linear random coils lie between 0.5 and 0.6, whereas lower values indicate the presence of branched molecules.[27,29] The slope for the polymer formed by addition of SIpS-2 triblock copolymer is 0.38 in Figure 8, as expected for compact star polymers, in comparison with around 0.58 expected for linear PIB.

CONCLUSIONS

The synthesis of star-branched PIB was accomplished by the cationic polymerization in TMPCl/TiCl₄/SIpS triblock copolymer/DtBP initiating system. SIpS triblock copolymer with high 3,4-PIp content is more reactive than that with high 1,4-PIp content in cationic initiating stage. The UV detector of SEC directly confirms SIpS triblock copolymers incorporation into the star-branched polymers. Based on M-H equation, branching indices g' can be obtained. The value of g' decreases as increase $t_{actived}$, whereas M_w increase with $t_{actived}$. These indicate increasing $t_{actived}$ facilitates the grafting reactions. The lower slope of the polymer obtained by addition of SIpS-2 triblock copolymer in the logarithmic R_g versus molecular weight plot than that of linear PIB indicates the formation of compact star-branched architecture.

References

1. Tooru, O.; Jaehwi, L.; Kinam, P. J Controlled Release 2003, 93, 121.
2. Georgiou, T. K.; Vamvakaki, M.; Patrickios, C. S. Biomacromolecules 2004, 5, 2221.
3. Georgiou, T. K.; Vamvakaki, M.; Phylactou, A.; Patrickios, C. S. Biomacromolecules 2005, 6, 2990.
4. Twyman, L. J.; King, S. H.; Martin, I. K. Chem Soc Rev 2002, 31, 69.
5. Thelakkat, M. Macromol Mater Eng 2002, 287, 442.
6. Jacob, I.; Majoros, I.; Kennedy, J. P. Macromolecules 1996, 29, 8631.

7. Huang, K. J.; Zsuga, M.; Kennedy, J. P. Polym Bull 1988, 19, 43.
8. Mustafa, K. J.; Yankovski, S. A.; Kennedy, J. P. Polym Bull 2001, 47, 9.
9. Peetz, R. M.; Mustafa, A. F.; Kennedy, J. P. J Polym Sci Part A: Polym Chem 2003, 41, 740.
10. Taylor, S. J.; Storey, R. F. J Polym Sci Part A: Polym Chem 2004, 42, 5942.
11. Storey, R. F.; Shoemake, K. A.; Chisholm, B. J. J Polym Sci Part A: Polym Chem 1996, 34, 2003.
12. Storey, R. F.; Shoemake, K. A.; Mays, J. W.; Chisholm, B. J. J Polym Sci Part A: Polym Chem 1997, 35, 3767.
13. Storey, R. F.; Shoemake, K. A. J Polym Sci Part A: Polym Chem 1998, 36, 471.
14. Bae, Y. C.; Faust, R. Macromolecules 1998, 31, 2480.
15. Shim, J. S.; Kennedy, J. P. J Polym Sci Part A: Polym Chem 2000, 38, 279.
16. Iván, B.; Kennedy, J. P. J Polym Sci Part A: Polym Chem 1990, 28, 89.
17. Storey, R. F.; Shoemake, K. A. J Polym Sci Part A: Polym Chem 1999, 37, 1629.
18. Kwon, Y.; Puskas, J. E. Eur Polym J 2004, 40, 119.
19. Storey, R. F.; Chisholm, B. J.; Lee, Y. Polymer 1993, 34, 4330.
20. Kwee, T.; Taylor, S. J.; Mauritz, K. A.; Storey, R. F. Polymer 2005, 46, 4480.
21. William, P. K.; Wang, H.C.; Clark, H. D. U.S. Pat.5,182,333 (1993).
22. Storey, R. F.; Lee, Y. J Polym Sci Part A: Polym Chem 1991, 29, 317.
23. Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M. J Polym Sci Part A: Polym Chem 2000, 38, 3211.
24. William, P. K.; Clark, H. D.; Wang, H. C. Eur Pat. 0678529A2 (1995).
25. Daniel, M. K.; Tianzi, H. Macromolecules 2002, 35, 2055.
26. Grzegorz, L.; Stanislaw, P. Biomacromolecules 2005, 6, 752.
27. Podzimek, S.; Vlcek, T.; Johann, C. J Appl Polym Sci 2001, 81, 1588.
28. Podzimek, S. J Appl Polym Sci 1994, 54, 91.
29. Puskas, J. E. Macromol Mater Eng 2001, 286, 565.