Macromol. Symp. **2013**, 323, 37–41 DOI: 10.1002/masy.201100116

Star and Hyperbranched Polyisobutylenes via Terminally Reactive Polyisobutylene-Polystyrene Block Copolymers

Gergely Kali,[1] Márta Szesztay,[1] Andrea Bodor,[2] Béla Iván*[1]*

Summary: Unique, highly branched polyisobutylenes (PIB) were prepared via quasiliving carbocationic copolymerization of isobutylene and styrene (St) monomers. The junction points were formed by Friedel-Crafts self alkylation of PSt segments by the carbocationic chain ends. First, linear PIB was prepared with reactive chain ends. This was reacted with St monomer to form PIB-*b*-PSt AB, and PSt-*b*-PIB-*b*-PSt ABA type triblock copolymers with reactive carbocationic chain ends. The terminal carbonations react with the phenyl group of the polystyrene end-segments of the block copolymers leading to chain coupling, and thus PIB star polymers in the case of AB and hyperbranched PIB from ABA block copolymers. The resulting branched polymers were characterized and the branch formation was confirmed by gel permeation chromatography (GPC) and proton nuclear magnetic resonance spectroscopy (^{1}H NMR).

Keywords: block copolymers; Friedel-Crafts self-alkylation; hyperbranched polymers; star polymers; polyisobutylene; polystyrene; quasiliving carbocationic polymerization

Introduction

Dendrimers, hyperbranched and star polymers are macromolecules with highly branched structure and usually numerous reactive groups on their chain-ends.[1-10] Due to the high cost and long reaction time of the synthesis of perfectly branched dendrimers, these are not the best choices for a large variety of the application fields.[1–4] Although hyperbranched and star polymers posses much less perfection in their branching topology, their syntheses are cheaper, less complicated and the reaction time is much shorter than that of dendrimers.[4–7] The advantages of the highly branched structures are their low viscosity, compared to the corresponding linear polymers with similar molecular weight, and the possibility of placement of many functional groups at the large number of their termini. These unique properties can be controlled by the variation of the monomers, the chain lengths/molecular weights of the polymer chains between the branching points and/or the branching frequencies etc.[8–10]

Polyisobutylene (PIB) is a unique, fully saturated, extremely hydrophobic and chemically stable polymer with good biocompatibility. The low glass transition temperature (T_g) of PIB makes it useful as a component of thermoplastic elastomers in linear as well as in branched forms.[11–19] Due to these special properties, several attempts have been reported on the synthesis of highly branched polyisobutylenes so far.[12–16,20–33] Previously, it was found that intra- and intermolecular Friedel-Crafts alkylation of the benzene rings of styrene (St) units in polystyrene (PSt) segments

---

[1] Department of Polymer Chemistry, Institute of Organic Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences H-1525 Budapest, Pusztaszeri u. 59-67, P. O. Box 17, Hungary
E-mail: g.kali@chemres.hu; bi@chemres.hu

[2] Loránd Eötvös University, Institute of Chemistry, H-117 Budapest, Pázmány Péter sétány 1/A, Hungary

might occur by carbocationic chain ends.[13,16–23,34,35] This undesired side reaction was observed not only during the cationic polymerization of pure St,[35] but in the case of the preparation of thermoplastic elastomer block copolymers composed of PIB and PSt[13–19] as well. The goal of this work was to utilize this, otherwise unwanted side reaction for the synthesis of star and hyperbranched PIBs based on monofunctional polyisobutylene-*block*-polystyrene (PIB-*b*-PSt) and bifunctional polystyrene-*block*-polyisobutylene-*block*-polystyrene (PSt-*b*-PIB-*b*-PSt) copolymers, respectively.

Polymerization

The polymerization of isobutylene (IB, 0,21 mol) was carried out in 300 mL *n*-hexane/methylenedichloride (Hx/DCM, 60/40 V/V%) solvent mixture under dry N_2 atmosphere at –78 °C. The monofunctional 2-chloro-2,4,4-trimethylpentane (0.006 mol) and the bifunctional initiator, *tert*-butyldicumyl chloride (0.006 mol), were used in the presence of $TiCl_4$ coinitiator (16 fold excess to the initiator) and TMEDA Lewis-base additive (1 fold excess to the initiator) for the preparation of AB and ABA block copolymers, respectively. The monofunctional initiator was used to obtain PIB-*b*-PSt block copolymer with only one reactive chain end, which can form star shaped polymer. With the bifunctional initiator, PSt-*b*-PIB-*b*-PSt triblock copolymer was synthesized with two reactive chain ends leading to hyperbranched polymeric structure. After complete polymerization of IB, within 15 mins, low amount of prechilled comonomer, styrene (in Hx/DCM solution) was added. The amount of styrene was calculated to have three monomer units per chain ends. Samples were taken in every five minutes to follow St consumption and the appearance of coupling. The reactions were stopped after one hour by prechilled (–78 °C) methanol addition. The resulting polymers were precipitated twice in methanol and were dried overnight in a vacuum oven.

Results and Discussion

After quasiliving carbocationic polymerization[32,36] of isobutylene near to 100% conversion, a small amount of styrene was added to yield block copolymers of PIB and PSt. This process is displayed on the top of Figure 1. The resulting PIB-*b*-PSt and PSt-*b*-PIB-*b*-PSt copolymers are expected to lead to branched structures.[13–19,31,32,35] As it can be seen in Figure 1, the styryl cations can alkylate the benzene rings in the PSt chains. This self-grafting Friedel-Crafts alkylation reaction between the PSt segments result in coupling of two polymer chains and thus forming a branching point.

When monofunctional initiators are used, the coupled PSt chains form a core for a star polymer in which the PIB chains become the arms. In the case of the bifunctional initiator, the coupling of the chain segments results in hyperbranched PIB in wich the PIB chains are the linear segments between the junction points.

Some side reactions, such as backbiting and Friedel-Crafts alkylation of a monomer with unreacted vinyl groups are possible. The first side reaction decreases the active chain end concentration and thus the branching efficiency. The alkylation of the monomer is negligible, because the reaction rate of chain propagation is much higher than that of the Friedel-Crafts alkylation.[34]

Figure 2 shows the MWD curves of the polymer samples determined by GPC before the St addition and at different reaction times (5 mins in Figure 2a and 60 mins in Figure 2b) after styrene addition. It is evident from the data in these Figures that the molecular weights are shifted to higher region even after 5 min after the styrene addition. This is a nonuniform shift, and the MWD starts to be broadened shortly after St addition. The higher molecular weights and the multimodal MWD indicate that chain coupling occurs during and after the styrene polymerization. As the reaction time increases, the coupling of the copolymers is more evident.

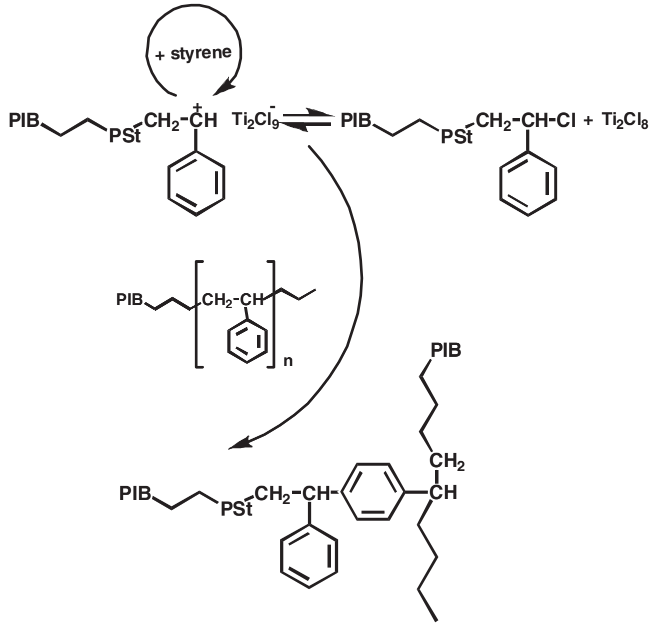

Figure 1.
Synthesis route of hyperbranched PIB formation.

The nonuniform shift of the molecular weight of the resulting polymer is more significant and the MWD becomes broader at higher reaction times. In the case of star polymer the M_w increased from the initial 2070 to 17400 and the MWD broadened indicated by the increase of the polydispersity from 1.04 of the starting PIB to 3.39 of the product at 60 mins after the styrene addition. For the hyperbranched PIB, the change, and thus the branching of the polymer is even more significant. The M_w increased from 2500 to 30100 and the narrow MWD of the starting bifunctional PIB ($M_w/M_n = 1.19$) became multimodal and quite broad ($M_w/M_n = 4.03$).

^{1}H NMR spectroscopy was also used to confirm the success of the formation of branched PIB by Friedel-Crafts self alkylation. Figure 3 shows the ^{1}H NMR spectra of polymer samples at different reaction times after styrene addition. This Figure indicates that part of the chains has non-coupled, 2-chloro-2-phenylethyl, chain ends after

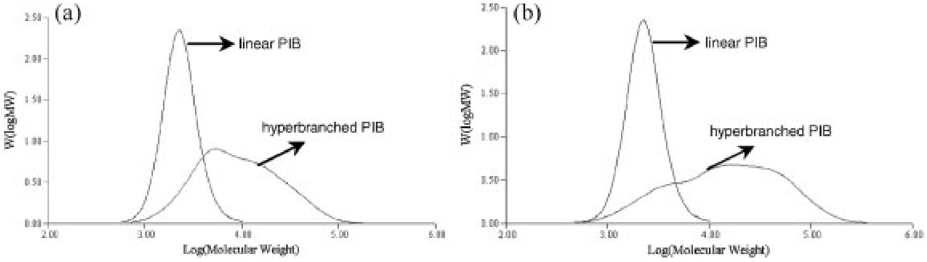

Figure 2.
Molecular weight distributions of linear and hyperbranched PIB structures after the addition of styrene at (a) 5 and (b) 60 mins.

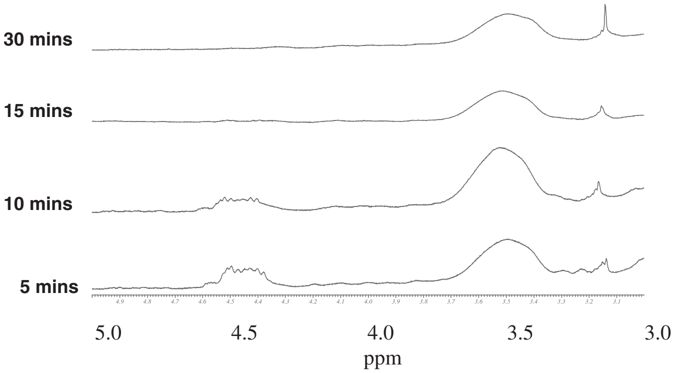

Figure 3.
^{1}H NMR signals of the branched polymers at different reaction times after styrene addtion.

5 mins reaction time confirmed by the signal at 4.3–4.6 ppm. The ^{1}H NMR signal at 3.3–3.6 ppm corresponds to the methine protons connecting two phenyl rings. As the reaction time increases, the relative intensity of the NMR peak of the methine protons increases indicating branching point formation. Thus the ^{1}H NMR spectroscopy gives complementary information to GPC and provide evidence of the occurrence of Friedel-Crafts self-grafting by the PSt segments, that is for the formation of hyperbranched PIBs with PSt junction points.

Conclusion

Star and hyperbranched PIBs were successfully prepared by quasiliving carbocationic polymerization via the utilization of an otherwise undesired side reaction, i. e. chain coupling by Friedel-Crafts alkylation of PSt segments by the terminal carbocations, in such processes. After linear PIB synthesis, addition of small amount of styrene formed PIB-*b*-PSt and PSt-*b*-PIB-*b*-PSt block copolymers with reactive chain ends. Self-grafting Friedel-Crafts alkylation of the PSt segments by polystyryl cations under quasiliving carbocationic polymerization conditions leads to star PIB in the case of monofunctional PIB-*b*-PSt and hyperbranched PIB using bifunctional PSt-*b*-PIB-*b*-PSt. Compared to previous attempts, this is a simple, rapid and suitable new method for the synthesis of star shaped and hyperbranched PIB structures.

[1] J. M. J. Fréchet, D.A. Tomalia, Dendrimers Other Dendritic Polymers, Eds., John Wiley & Sons, West Sussex UK **2001**.

[2] S. M. Grayson, J. M. J. Fréchet, *Chem. Rev.* **2001**, *101*, 3819.

[3] M. Ballauff, C. N. Likos, *Angew. Chem., Int.* Ed. **2004**, *43*, 2998.

[4] J. M. J. Frechet, C. J. Hawker, I. Gitsov, J. W. Leon, *J. Macromol. Sci., Pure Appl. Chem.*, **1996**, *A33*, 1399.

[5] M. Mishra, S. Kobayashi, "*Star and Hyperbranched Polymers*", Marcel Dekker New York **1999**.

[6] M. Sawamoto, S. Kanaoka, T. Higashimura, *Hyper-Structured Molecules I: Chemistry, Physics and Applications*, H. Sasabe, (Ed., Gordon and Breach Science Publisher, Amsterdam **1999**.

[7] . Hult, M. Johansson, E. Malmström, *Adv. Polym. Sci.* **1999**, *143*, 1.

[8] G. Robertson, C. M. Roland, C. Paulo, J. E. Puskas, *J. Rheol.*, **2001**, *45*, 759.

[9] J. E. Puskas, Y. H. Chen, K. Kulbaba, G. Kaszas, A. Soleymannezhad, *J. Polym. Sci., Part A: Polym. Chem.*, **2006**, *44*, 1770.

[10] C. P. Sui, G. B. McKenna, *J. Rheol.*, **2007**, *51*, 1143.

[11] H. Bouchekif, A. Som, L. Sipos, R. Faust, *J. Macromol. Sci., Pure Appl. Chem.*, **2007**, *44*, 359.

[12] J. S. Shim, J. P. Kennedy, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 279.

[13] a) R. F. Storey, K. A. Shoemake, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 1629; b) R. F. Storey, B. J. Chisholm, M. A. Masse, *Polymer*, **1996**, *37*, 2925.

[14] Y. Kwon, J. E. Puskas, *Eur. Polym. J.* **2004**, *40*, 119.

[15] R. F. Storey, B. J. Chisholm, Y. Lee, Y. Polymer, **1993**, *34*, 4330.

[16] T. Kwee, S. J. Taylor, K. A. Mauritz, R. F. Storey, *Polymer*, **2005**, *46*, 4480.

[17] G. Kaszás, J. E. Puskás, J. P. Kennedy, W. G. Hager, *Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 421.

[18] a) T. Fónagy, B. Iván, M. Szesztay, *Macromol. Rapid Commun.* **1998**, *19*, 479; b) T. Fónagy, B. Iván, M. Szesztay, *J. Reinf. Plast. Comp.* **2002**, *21*, 1411.

[19] Zs. Fodor, R. Faust, *J. Macromol. Sci., Pure Appl. Chem.* **1996**, *A33*, 305.

[20] S. Jacob, I. Majoros, J. P. Kennedy, *Macromolecules*, **1996**, *29*, 8631.

[21] K. J. Huang, M. Zsuga, J. P. Kennedy, *Polym. Bull.* **1988**, *19*, 43.

[22] F. Mustafa, S. A. Yankovski, J. P. Kennedy, *Polym. Bull.* **2001**, *47*, 9.

[23] R. M. Peetz, A. F. Mustafa, J. P. Kennedy, *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 740.

[24] S. J. Taylor, R. F. Storey, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5942.

[25] R. F. Storey, K. A. Shoemake, B. J. Chisholm, *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 2003.

[26] R. F. Storey, K. A. Shoemake, J. W. Mays, S. Harville, *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 3767.

[27] R. F. Storey, K. A. Shoemake, *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 471.

[28] Y. C. Bae, R. Faust, *Macromolecules*, **1998**, *31*, 2480.

[29] H. F. Liu, Y. Li, Y. R. Wang, Y. Ren, Z. X. Lu, J. B. Zhao, *Chin. Chem. Lett.* **2006**, *17*, 1117.

[30] B. Iván, J. P. Kennedy, *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 89.

[31] a) T. M. Marsalkó, I. Majoros, J. P. Kennedy, *Macromol. Symp.* **1995**, *95*, 39; b) J. P. Kennedy, T. M. Marsalkó, I. Majoros, *Macromol. Symp.* **1996**, *107*, 319; c) T. M. Marsalkó, I. Majoros, J. P. Kennedy, *J. Macromol. Sci., Pure Appl. Chem.* **1997**, *A34*, 775; d) I. Majoros, T. M. Marsalkó, J. P. Kennedy, *Polym. Bull.* **1997**, *38*, 15.

[32] J. P. Kennedy, B. Iván, *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice*, Hanser Publishers, Münich, New York **1992**.

[33] J. P. Kennedy, L. R. Ross, J. E. Lackey, O. Nuyken, *Polym. Bull.* **1981**, *4*, 67.

[34] G. Kali, M. Szesztay, A. Bodor, B. Iván, *Macromol. Chem. Phys.*, **2007**, *208*, 1388.

[35] Zs. Fodor, M. Győr, H.-C. Wang, R. Faust, *J. Macromol. Sci. Pure Appl. Chem.* **1993**, *A30*, 349.

[36] B. Iván, *Macromol. Chem. Phys.* **2000**, *201*, 2621.