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Synthesis and characterization of star-comb polybutadiene and poly(ethylene-co-butene)

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Abstract

A novel star-comb polybutadiene (SC–PB) was synthesized with *n*-butyllithium (*n*-BuLi) as initiator, epoxidized star liquid polybutadiene (ESPB) as coupling agent, cyclohexane as solvent by living anionic polymerization and grafting-onto technology. The SC–PB was subsequently hydrogenated by homogeneous catalysis (catalytic hydrogenation using nickel naphthenate/ triisobutyl aluminum), to transform the SC–PB into the corresponding star-comb poly(ethylene-*co*-butene) (SC–PEB). The SC–PB was characterized by SEC-TALLS, ^{1}H NMR, DSC and WAXD techniques. The hydrogenation degree and crystallinity degree of SC–PEB were also determined.

Keywords: Anionic polymerization; Grafting reaction; Epoxy group; Star-comb polymer; Hydrogenation

Highly branched polymers are of academic and industrial interest because of their peculiar mechanical and melt properties [1]. Among them, the star and comb polymers have been extensively studied for a long time, due to their markedly lower solubility and bulk viscosities [2]. However, only a few star-comb polymers have been reported. Schappacher and Deffieux [3] have synthesized highly branched starlike comb polystyrenes based on the highly selective coupling reaction of living polystyryllithium onto poly(chloroethyl vinyl ether) chains with a starlike chain architecture. Koutalas et al. [4] have reported the synthesis of well-defined SC–PB by using the macromonomer technique in combination with high-vacuum techniques. However, high-vacuum techniques are very demanding in glass blowing practice, more time consuming and usually lead to the synthesis of only a few grams of model polymeric materials [5]. In contrast, inert atmosphere techniques are simpler and lead more easily to the preparation of large quantities of materials.

Meanwhile, hydrogenation of polybutadienes to prepare well-defined polyolefins and their copolymers is of both academic and commercial interest [6]. While the linear, comb, symmetric star, and asymmetric star polyethylenes have been synthesized and researched previously [7], the star-comb polyethylene is new.

In this study, a novel SC–PB with 3-arm star PB substrate was synthesized by anionic polymerization and grafting-onto technology. Scheme 1 illustrates synthetic strategy for the preparation of the SC–PB. The synthetic procedure of

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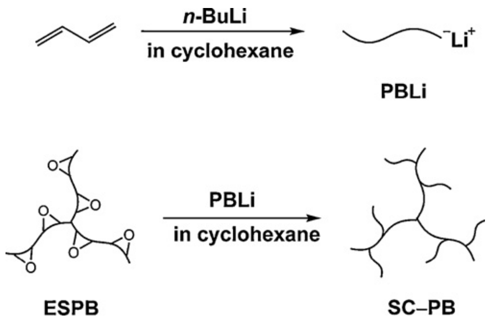

Scheme 1. Synthetic route of the SC–PB.

SC–PB was described as follows. Polybutadienyllithium (PBLi) was prepared by anionic polymerization of butadiene initiated by *n*-BuLi in cyclohexane at 50 °C for 3 h. Then PBLi was grafted with a stoichiometric amount of ESPB in situ for 3 h. The ESPB ($M_w = 1.8 \times 10^4$ g/mol, $M_w/M_n = 1.03$) was self-made with 35% of epoxidation degree determined by ^{1}H NMR. The grafting reaction was quenched with degassed 2-propanol. The crude polymer was purified by fractionation to remove nongrafted chains, using THF as a good solvent and ethanol as a nonsolvent. The fractionated SC–PB was subsequently hydrogenated in a 200 mL high-pressure reactor using nickel naphthenate/triisobutyl aluminium as catalyst to give the corresponding SC–PEB.

The linear, the crude and fractionated SC–PBs were characterized by size exclusion chromatography coupled with two-angle laser light scattering detector (SEC-TALLS). The SEC curves of the SC–PB are depicted in Fig. 1. The reaction of ESPB with the linear PBLi (Fig. 1a) yielded a crude sample (Fig. 1b). The first peak at higher molecular

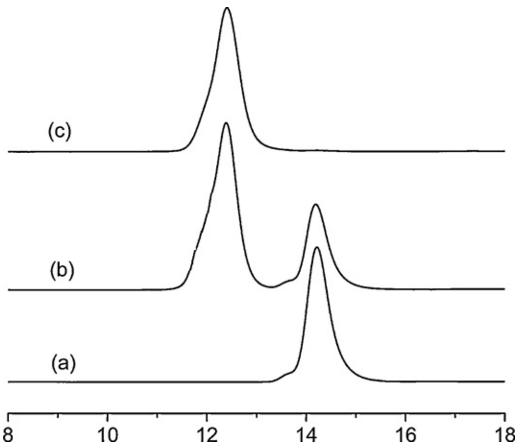

Fig. 1. SEC curves of the linear PB (a), and SC–PB before (b) and after (c) fractionation.

Table 1
Molecular characterization of branched polymer by anionic polymerization and grafting reaction.

Entry	Linear PBs			SC–PBs			
	$M_{w,desgin} \times 10^3$	$M_w \times 10^3$ [a]	M_w/M_n [a]	$M_w \times 10^3$ [a]	M_w/M_n [a]	f_w [b]	G_y [c]/%
1	3.0	3.1	1.08	135	1.09	43.5	82
2	6.0	6.0	1.06	250	1.10	41.7	79
3	9.0	9.2	1.06	379	1.08	41.2	75
4	30.0	30.5	1.05	1235	1.08	40.5	73

[a] Determined by SEC-TALLS.
[b] Branching functionality.
[c] Grafting yield.