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Synthesis of "simple graft" poly(isoprene-g-styrene) by anionic polymerization

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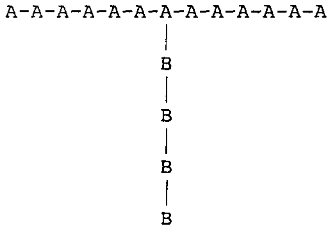
Summary

The synthesis of a well-defined near-monodisperse polyisoprene-graft-polystyrene copolymer having a single, centrally located graft site is described. The method utilized to prepare this structure involved capping "living" polystyryllithium anions by reaction with methyltrichlorosilane, followed by addition of a slight stoichiometric excess of polyisoprenyllithium. After linking, the residual polyisoprene arms were removed by fractionation to yield the pure graft copolymer.

Introduction

The fact that under appropriate conditions many anionic polymerizations are non-terminating ("living") makes this method especially suitable for the synthesis of linear and branched polymers and copolymers with well-defined structures (1,2). One structure which had not heretofore been synthesized is the "simple graft" copolymer. This structure has a single monodisperse branch centrally located along a monodisperse backbone which is different in chemical composition:



Due to the strong current interest in block and graft copolymers as tougheners, compatibilizers, and multiphase materials with unique properties, there is strong theoretical and practical interest in understanding the effects of molecular architecture on polymer miscibility. Experimental studies on true model graft systems are necessary to test recent theoretical (3) predictions. We therefore undertook the synthesis of near-monodisperse simple polyisoprene-graft-polystyrene.

Experimental

Styrene (Fisher) and isoprene (Kodak) were purified using established vacuum line methods (4). The linking agent, methyltrichlorosilane (Petrarch), was purified by fractional distillation on the vacuum line. sec-Butyllithium (Lithium Corporation) was diluted with purified benzene in evacuated ampoules.

High vacuum conditions (ca. 10^{-6} mm Hg) and all-glass reactors with breakseals were used in conducting the polymerizations and the linking reaction. Benzene was used as solvent for polymerization of both styrene (Fisher) and isoprene (Kodak). Sec-Butyllithium (Lithium Corporation) was used as initiator, and methyltrichlorosilane was used as the linking agent. Established purification and handling methods were employed (4-6).

Polymer fractionation involved addition of methanol to dilute (< 1%) solutions in toluene. Size exclusion chromatography (SEC) experiments were performed in tetrahydrofuran (THF) using a Waters model 510 pump and Waters model 410 differential refractometer. Two Waters "linear ultrastyragel" columns were used in series. These columns exhibit continuous porosities over the range of 10^2-10^6 Å. Membrane osmometry experiments were conducted using a Mechrolab model 502 unit in toluene at 25°C. Wescan regenerated cellulose (RC-51) membranes were employed. ^{1}H-NMR data were obtained using a 300 MHz Nicolet unit.

Results and Discussion

Linear polyisoprene and polystyrene with predicted number-average molecular weights, $\bar{M}_n$, of 20,000 and 60,000, respectively, were prepared under high vacuum conditions. A small aliquot of each of the polymers was removed under vacuum, terminated with methanol, and analyzed by membrane osmometry and SEC. Results are given in Table I and SEC chromatograms are presented in Figure 1. Stoichiometric and measured values of $\bar{M}_n$ are in close agreement.

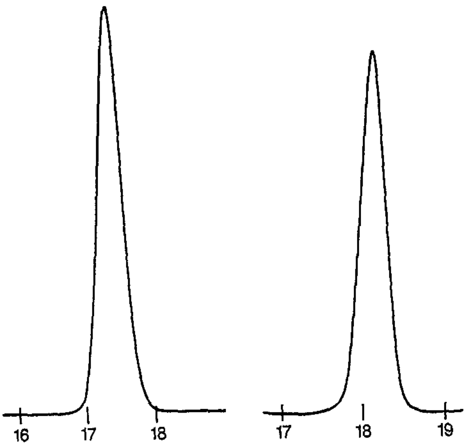


Figure 1: SEC chromatograms for the polystyrene (left) and polyisoprene (right) arm materials.

Table 1: SEC and MO Results on Polystyrene and Polyisoprene Arms

	Osmometry	SEC	
Polymer	$\bar{M}_n$ (g/mol)	$\bar{M}_w/\bar{M}_n$	$\bar{M}_z/\bar{M}_w$
polystyrene	61,700	1.03	1.03
polyisoprene	18,100	1.03	1.04

Synthesis of simple polyisoprene-graft-polystrene employed the same approach used by Pennisi and Fetters (6) for the synthesis of asymmetric 3-arm star polystyrenes, i.e. materials where 2 arms were the same length and the other arm was either lower or higher in molecular weight. The "odd" arm (living polystyrene in the present case) was added with stirring to a dilute (< 5%) solution of excess (ca. 12:1) methyltrichlorosilane. The orange color of the polystyryllithium anions instantly vanished. Pennisi and Fetters (6) have demonstrated that no detectable coupling takes place so long as the Cl:Li ratio is $\geq$ 30. Excess chlorosilane was removed by reattaching the reactor to the vacuum line, followed by freeze-drying and pumping for 4 days at 40°C to insure complete chlorosilane removal. Purified solvent (benzene) was then reintroduced into the reactor, the chlorosilane endcapped polystyrene was dissolved, and a slight stoichiometric excess of polyisoprenyllithium was added to the reactor. Linking was conducted at 40°C for 72 hours and degassed methanol was then added to terminate residual active anions.

An SEC chromatogram of the raw product is shown in Figure 2 along with a chromatogram of the fractionated simple graft, where the excess polyisoprene arm had been removed. The final product had $\bar{M}_n$ = 96,500 by membrane osmometry (97,900 predicted based on the total of arm $\bar{M}_n$'s) and $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_w$ values of 1.04 via SEC. Analysis of the styrene content by ^{1}H-NMR indicated 56 mol %. This value compares well with the expected value fof 53% based on arm molecular weights. Thus, model graft copolymers having a single, centrally-located graft site are readily prepared using anionic polymerization.

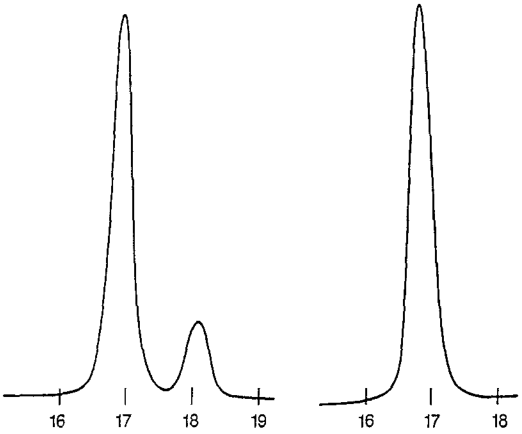


Figure 2: SEC chromatograms for the simple graft copolymer prior to fractionation (left; note residual polyisoprene arm) and after two fractionations (right) to eliminate contamination with polyisoprene.

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