Coupling of living polystyryllithium anions and living polyethyl vinyl ether cations

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Summary
Living polystyryllithium anions and living polyethyl vinyl ether cations have been successfully coupled. Indeed, no residue of any of the two original homopolymers is observed in the final product, when they are used in a stoichiometric amount. This method has been exploited in order to synthesize AB and ABA polyethyl vinyl ether (PEVE) (A) / polystyrene (PS) (B) block copolymers with a high efficiency.

Introduction
Discovery of the living anionic polymerization by Szwarc in 1956 (1) has resulted in a tremendous research effort aiming at the molecular tailoring of polymeric materials. In contrast, the molecular design of polymers by a living cationic mechanism has been next to impossible for a long time. However, the pioneering works of Higashimura et al. (2) and Kennedy et al. (3) have recently opened remarkable routes to the carbocationic macromolecular engineering. For instance, vinyl ethers can be polymerized by a combination of a protonic acid (HB) and a Lewis acid (MXN). The actual initiator is the adduct of the vinyl ether and the protonic acid (equation 1), the C-B linkage of which is activated by the Lewis acid.

\[ \text{HB} \quad \text{MX'} \quad \text{OR} \quad \text{OR} \]

Higashimura et al. (2) have convincingly demonstrated the possible tailoring of polyalkyl vinyl ethers by cationic polymerization initiated with the HI/ZnI₂ pair. One of the advantages of this living polymerization is the straightforward synthesis of end-functional polyvinyl ethers by reaction of the cationic active centers with a nucleophilic agent, such as an alcohol and the anion of diethylmalonate (4). A polymeric nucleophile might also be used as illustrated by the coupling reaction of cationically polymerized living poly(THF) and living anionic polystyrene (5). To the best knowledge of these authors,

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only two research groups have reported so far on the successful coupling reaction of a living polyvinyl ether with a macromolecular species. Riffle et al. have quenched living polybutylvinyl ether with living poly(methylmethacrylate) as prepared by GTP (6). Kleuskens et al. have used a low molecular weight poly(ethylene glycol) as a quencher for living polyvinyl ether chains (7). However, this coupling reaction leads to the formation of an acetal bond between the two blocks, which is known to be unstable under acidic conditions.

This paper will emphasize how efficient the coupling of living polyethyl vinyl ether cations and living polystyrene anions can be (equation 2). Indeed, AB and ABA polyethyl vinyl ether (A) / polystyrene (B) block copolymers have been prepared with a high efficiency, as supported by molecular weight and composition close to the expected values and a very narrow molecular weight distribution.

\[
\begin{align*}
\text{CH}_2-\text{CH}-\text{I} & + \text{CH}_3-\text{CH}-\text{Li}^+ \\
\text{CH}_3 & \rightarrow \text{CH}_2-\text{CH}_2-\text{C} & \text{Li}^+ \\
\text{CH}_3 & \text{CH}_3
\end{align*}
\]

\[2\]

**Experimental**

A 57% HI aqueous solution (Aldrich) was dried over P_2O_5 (Merck). Hydrogen iodide was then dissolved in dry n-hexane and the solution was stored in the dark at -18°C under dry nitrogen. The HI concentration was determined by extracting the acid with deionized water and titrating the aqueous layer with a standard NaOH solution (8).

A known amount of zinc iodide (Aldrich) was dried overnight under vacuum in the dark and dissolved in a known volume of dry diethyl ether. The solution was kept in the dark at -18°C under dry nitrogen until use (9).

N-hexane, toluene and ethyl vinyl ether (Merck) were dried over calcium hydride and distilled before use. Diethyl ether was dried over sodium prior to distillation. THF was purified by refluxing over a freshly prepared sodium-benzophenone complex. All chemicals were analytical reagent grade or equivalent.

Styrene and α-Methylstyrene were first vacuum distilled from calcium hydride and then stored under a nitrogen atmosphere at -20°C. The required amount of styrene was first added with the same volume of dry toluene and a few drops of α-Methylstyrene. This solution was dropwise added with fluorenyl-lithium until a persistent orange color was observed and it was finally distilled under reduced pressure just prior to polymerization.

Polymerization was carried out under dry nitrogen in balloons equipped with three-way stopcocks. All glassware was flamed under vacuum before use. Solutions were transferred with