Radical polymerization of (trimethylsilylethynyl)styrene and thermal properties of polystyrene with ethynyl group

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Summary

The radical polymerizations of 2-, 3-, and 4-(trimethylsilylethynyl)styrenes (1a-c) and copolymerizations of 1a-c (M\textsubscript{1}) with styrene (M\textsubscript{2}) have been studied. Copolymerization parameters were determined as \( r_1 = 1.22 \) and \( r_2 = 0.54 \) for 1a, \( r_1 = 1.10 \) and \( r_2 = 0.90 \) for 1b, and \( r_1 = 1.42 \) and \( r_2 = 0.38 \) for 1c. The deprotection of the trimethylsilyl groups in poly[(trimethylsilylethynyl)styrene] (2a-c) and poly[(trimethylsilylethynyl)styrene-co-styrene] (4a-c) using \((\text{C}_4\text{H}_9)_4\text{NF}\) smoothly proceeded to yield poly(ethynylstyrene) (3a-c) and poly(ethynylstyrene-co-styrene) (5a-c), respectively, which underwent curing reactions at elevated temperature to form crosslinking polystyrenes.

Introduction

In order to produce matrix resins for advanced composites, a great deal of effort has gone into designing polymers with reactive functional groups which can be crosslinked by heating. The volatile, low molecular weight compounds are avoided to form during crosslinking reaction, though limited functional groups are available (1). The polymer with an ethynyl group, therefore, is one of the candidates for thermal curing materials. Although the ethynyl groups have been introduced as a terminal group in the polymer chains (2), only a few attempts have so far been made to produce polymers containing internal and pendent ethynyl groups (3,4).

Previously, we reported the synthesis of poly(ethynylstyrene) (3) with a predictable molecular weight and a narrow molecular weight distribution by the anionic living polymerization of (trimethylsilylethynyl)styrene (1), followed by deprotection of the silyl protecting group in poly[(trimethylsilylethynyl)styrene] (2) (5). Thus, 1 is a suitable monomer for producing a polymer containing a pendant ethynyl group and the crosslinking property of such a polymer is also interesting to study.

In this study, we report the radical polymerizations of 2-, 3-, and 4-(trimethylsilyl-ethynyl)styrenes (1a-c) and the radical copolymerization of 1 with styrene. Their
copolymerization parameters, i.e., the monomer reactivity ratio and the $Q$ and $e$ values, were determined. Deprotection of the silyl protecting group in poly[(trimethylsilylethynyl)-styrene] (2) and poly[(trimethylsilylethynyl)styrene-co-styrene] (4) easily proceeded to allow conversion into poly(ethynylstyrene) (3) and poly(ethynylstyrene-co-styrene) (5), respectively. The thermal crosslinking properties of 3 and 5 were then characterized.

**Experimental**

**Measurements.** FT-IR spectra were measured using a Perkin Elmer Paragon 1000. Differential scanning calorimetry (DSC) measurements were carried out in an enclosed heating chamber under flowing $N_2$ gas using a Seiko Instruments SSC/5200. A heating scan rate of 10 °C/min was used in all experiments.

**Materials.** 2-, 3-, and 4-(Trimethylsilylethynyl)styrenes (1a-c) were prepared as previously reported (5). Tetrabutylammonium fluoride ($\left(C_4H_9\right)_4NF$) solution in THF was purchased from Aldrich.

**Polymerization.** Radical polymerizations were carried out using AIBN as the initiator in toluene at 60 °C in sealed tubes under $N_2$ gas in the usual manner. The reaction mixtures were poured into a large amount of methanol. The precipitated polymers were purified by two reprecipitations from a THF/methanol system and freeze-dried from the benzene solution.

**Deprotection.** The deprotection of the trimethylsilyl groups from the copolymers was carried out as previously described (4).