

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_1) with styrene (M_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 $(C_4H_9)_4NF$ 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.

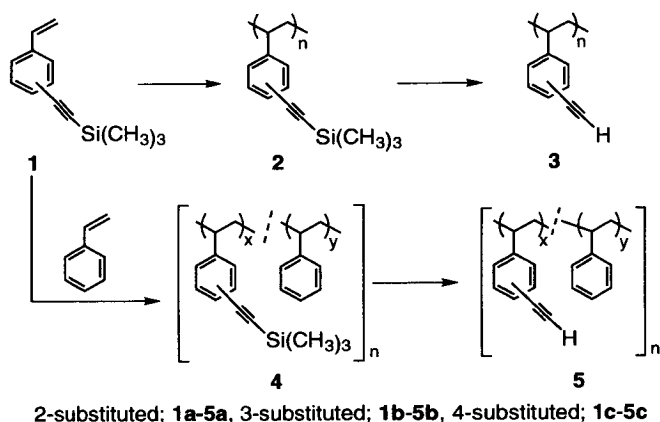
Introduction

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 pendent 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-(trimethylsilylethynyl)styrenes (**1a-c**) and the radical copolymerization of **1** with styrene. Their

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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 $10\text{ }^\circ\text{C}/\text{min}$ was used in all experiments.

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

Polymerization. Radical polymerizations were carried out using AIBN as the initiator in toluene at $60\text{ }^\circ\text{C}$ 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).

Table 1. Radical polymerizations of 2-, 3-, and 4-(trimethylsilylethynyl)styrenes (**1a-c**) (M_1) with styrene (M_2)^a

1 (M_1)	mole fraction of M_1 in monomer feed (F_1)	time h	yield %	mole fraction of M_1 unit in copolymer (f_1) ^b	M_n (M_w/M_n) ^c
1a	1.00	22	47	1.00	7800 (1.77)
1a	0.50	22	74	0.59	7300 (1.81)
1a	0.05	22	66	0.07	13100 (1.80)
1b	1.00	8.3	78	1.00	50800 (1.95)
1b	0.49	6.5	44	0.49	55400 (1.74)
1b	0.05	29	71	0.05	18500 (1.78)
1c	1.00	12	47	1.00	54200 (2.09)
1c	0.49	6.0	40	0.54	40500 (1.85)
1c	0.06	30	70	0.08	18500 (1.79)

^a Initiator, AIBN; $[1]$ or $[1 + \text{St}] = 5.0 \text{ mol}\cdot\text{L}^{-1}$; $[\text{AIBN}] = 50 \text{ mmol}\cdot\text{L}^{-1}$; temp. $60 \text{ }^\circ\text{C}$; solvent, toluene. ^b Determined by $^1\text{H NMR}$ spectra. ^c Determined by GPC using polystyrene standard.

Results and Discussion

Table 1 lists the results of the polymerizations of 2-, 3-, and 4-(trimethylsilylethynyl)styrene (**1a-c**) and the copolymerizations of **1a-c** with styrene. For all the polymerization, the organic solvent-soluble, powdery polymers, **2a-c** and **4a-c**, were obtained. This means that the ethynyl groups did not interfere the radical polymerization. Figure 1 shows the copolymerization composition curves for **1** (M_1) and St (M_2). The

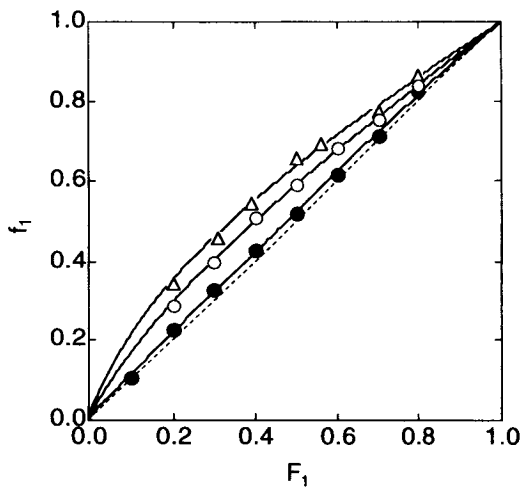


Figure 1. Composition curves for the copolymerizations of 2-(trimethylsilylethynyl)styrene (**1a**) with styrene (O), 3-(trimethylsilylethynyl)styrene (**1b**) with styrene (●), and 4-(trimethylsilylethynyl)styrene (**1c**) with styrene (Δ).

(trimethylsilylethynyl)styrene units (f_1) in the copolymers, which were determined by their $^1\text{H-NMR}$ spectra, were higher than the F_1 in monomer feeds for **1a** and **1c**, whereas the curve for **1b** was very close to the azeotropic copolymerization. The monomer reactivity ratios, which were determined by the Kelen-Tüdös method (6), were $r_1 = 1.22$ 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 Q and e_1 values were 3.1 and -1.5 for **1a** and 3.3 and -1.6 for **1c**, respectively, indicating that they are conjugated and electron-donating monomers. On the other hand, the Q and e_1 values of 1.0 and -0.7 for **1b** means that the 3-trimethylsilylethynyl group exhibits a slight resonance effect.

The deprotections of the silyl groups in **2** and **4** were carried out using $(\text{C}_4\text{H}_9)_4\text{NF}$ in THF at 0°C for 2 h. For the conversion of **4c** into **5c**, the respective absorptions at 2104 and 3293 cm^{-1} due to the $\equiv\text{C-H}$ and $-\text{C}\equiv\text{C}-$ stretch vibrations of the $\text{C}\equiv\text{C-H}$ group were observed and the absorption at 2158 cm^{-1} due to the $\text{C}\equiv\text{C-Si}(\text{CH}_3)_3$ group in **4c** disappeared in the IR-spectrum of **5c**, indicating that the trimethylsilyl groups were completely deprotected. This was also confirmed by the NMR spectra.

The thermal reactions of **3** and **5** were examined by heating at 240°C for 5 h in the absence of air. After thermal treatment, the absorptions at 3293 and 2104 cm^{-1} due to the ethynyl group remarkably diminished. All the cured polymers was insoluble in common organic solvents, such as benzene, chloroform, and THF.

The thermal properties of **3a-c** and **5a-c** were characterized by the TG and DSC measurements. Figure 2 shows the TG and DSC curves of **5c** ($f_1 = 0.54$). For the TG curve, a 10 % weight loss (T_d) was observed at 391°C . For the DSC curve, the endothermic peak corresponding to a glass transition temperature (T_g) was observed at 116°C , and the large

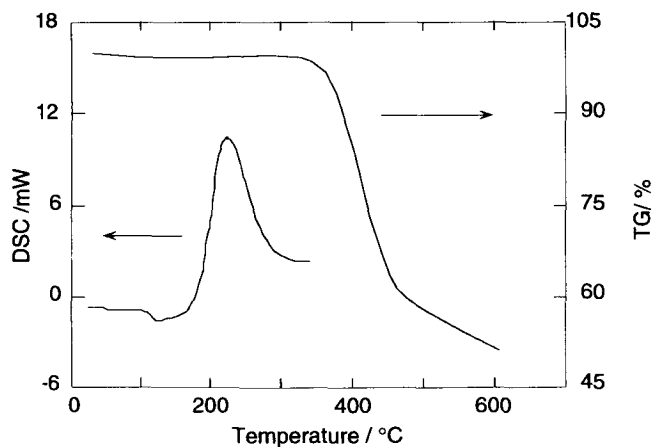


Figure 2. TG and DSC thermograms of poly(4-ethynylstyrene-*co*-styrene) ($f_1 = 0.54$) (**5c**).

Table 2. Thermal properties of poly(ethynylstyrene) (**3**) and poly(ethynylstyrene-*co*-styrene) (**5**)

polymer ^a	T _g , °C	T _r ^b , °C	T _d ^c , °C
3a	107	145 (221)	393
5a (0.59)	98	153 (221)	368
5a (0.07)	95	218 (276)	330
3b	80	152 (212)	452
5b (0.49)	82	153 (223)	410
5b (0.05)	87	228 (286)	385
3c	117	140 (218)	428
5c (0.54)	116	162 (222)	391
5c (0.08)	94	209 (266)	393

^a Values in parenthesis are molar ratio of ethynylstyrene units. ^b Beginning temperature of crosslinking reaction (peak top temperature of exothermic peak). ^c Temperature of 10 % weight loss.

exothermic peak appeared at 203 °C and its peak top was 222 °C. The latter peak was due to the crosslinking reaction, because it was not observed during the 2nd heating and the annealed **5c** was insoluble in common organic solvents.

Table 2 summarizes the T_g and T_d and the beginning temperature of the crosslinking reaction (T_r) for **3** and **5**. The T_g decreased with increasing St units for the **3a** / **5a** and **3c** / **5c** systems, whereas it increased with increasing St units for the **3b** / **5b** system. The T_r increased with increasing St units, i.e., from 145 to 218 °C for **3a** / **5a**, from 152 to 228 °C for **3b** / **5b**, and from 140 to 209 °C for **3c** / **5c**. The T_ds for **3** and **5** with similar copolymer compositions increased in the order of **3b** > **3c** > **3a** and **5b** > **5c** > **5a**, respectively. Except for **5a** (f₁ = 0.07), the T_ds of polystyrenes having pendant ethynyl groups were higher than that of poly(styrene) (M_n = 19500 and M_w/M_n = 1.54) obtained by a radical polymerization, T_d = 362 °C.

When **5a** (f₁ = 0.07), **5b** (f₁ = 0.05), and **5c** (f₁ = 0.08) were heated, they melted, flowed, and then cured. In addition, their cured sheet samples were obtain using an injection molding apparatus, indicating that the polystyrene having the pendant ethynyl group is a new thermosetting material. Further investigations on the curing mechanism and the mechanical properties of the cured polystyrene are currently under investigation.

Conclusion

The radical polymerizations of (trimethylsilylethynyl)styrene and its use with styrene produced gel-free polystyrenes with trimethylsilylethynyl groups. The deprotection of the silyl group in polystyrenes with trimethylsilylethynyl groups smoothly proceeded for

conversion into polystyrenes having pendant ethynyl groups, and subsequently underwent curing reactions at elevated temperature to form crosslinking polystyrenes.

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